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WATER

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CHAPTER 1
WATER QUALITY GUIDELINES

Barry T. Hart

INTRODUCTION

Most countries now have water resources management policies aimed at achieving sustainable use of their water resources by protecting and enhancing their quality while maintaining economic and social development. Achieving this objective requires that the needs and wants of the community for each water resource are defined and that these resources are protected from degradation. These community needs generally are called the *environmental values* (or *beneficial uses*) of the water body and can include water for drinking, swimming, fishing, recreation, agricultural food production, and/or ecosystem protection.

Water quality guidelines (or *criteria*) are the scientific and technical information used to provide an objective means for judging the quality needed to maintain a particular environmental value. Knowledge-based management decisions made on the basis of this scientific knowledge are far more preferable than those resulting from pressure by narrowly focused lobby groups.

A number of water quality guideline compilations are now available (e.g., USEPA, 1986a; CCREM, 1991; ANZECC, 1992). With few exceptions, these are broadly similar in their approach and in the threshold values they recommend. However, the recently released Australian and New Zealand water quality guidelines mark a radical departure from the conventionally derived water quality guidelines (ANZECC/ARMCANZ, 2000a). The key elements of these new guidelines are that they are risk-based, focus on ecological issues rather than single indicators, provide information for an increased number of ecosystem types, and require more site-specific information.

This chapter seeks to define the information and knowledge required by water managers and environmental protection agencies in deciding whether a particular water body has good or bad water quality. The important role of water quality guidelines in the water resources management process is covered first. The types of water quality guidelines are then discussed, focusing first on the human uses of water (e.g., drinking, recreation, and irrigation). The main part of the chapter relates to guidelines for aquatic ecosystem protection.

USE OF GUIDELINES IN THE SUSTAINABLE MANAGEMENT OF WATER RESOURCES

The sustainable use of a water resource involves managing both the quantity and quality of the resource. This chapter will focus mainly on water quality aspects and only briefly cover other aspects of water resources management. A later section contains a short discussion of flow and habitat considerations.

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Before considering in detail the water resource management process and the role of water quality guidelines in this process, a number of important and highly relevant considerations are highlighted.

- Water environments are naturally quite variable systems, particularly in flow and ecosystem types. Therefore, any process that seeks to manage a water resource adequately must be responsive, flexible, and adaptable (Walters, 1986).
- A key objective of modern water management is to maintain the ecological integrity of the resource. However, the knowledge base and mechanisms to underpin this new ecosystem-based management approach are poorly developed (Boon et al., 1992; Sparks, 1995; Hart et al., 1999).
- It is now generally well recognized that most water bodies are closely linked to their catchment and that activities within the catchment can influence the quality of such water bodies (lake, reservoir, river, or estuary). Thus integrated catchment and waterways management is essential if the quality of particular water resources is to be maintained in the future.
- Water resource management must address community needs and wishes, and to achieve this, the community must be involved in the management process. Technical and scientific information is essential but not sufficient for the successful management of rivers.
- Water management involves difficult trade-off decisions often between incompatible objectives, such as ecosystem protection and additional water for irrigation. It is vital that the decision-making process is as transparent as possible if such decisions are to be accepted by the community.

Figure 1.1 shows the main steps involved in the water resource management process (Hart et al., 1999). These are discussed briefly below.

Knowing the system. A good scientific and technical understanding of the aquatic system is essential if it is to be managed effectively. In particular, information is needed about the condition of the catchment, the water resource itself, the present water quality and stressors* likely to degrade the quality, and uses of the water resource.

Management goals. Clearly, it is essential in any management process to decide why the system is being managed. At the highest level, the goal of managing a natural resource is to improve community well-being through sustainable use and protection of the natural environment. Effective management of a nation's water and aquatic resources is crucial to the continued viability of society.

Environmental values (or beneficial uses). Identification of the community needs and wishes for the water resource (e.g., agricultural water supply, swimming, fishing, and protection of the ecosystem) provides the first step in defining the environmental values of a particular water body. The major environmental values considered in most guideline documents are

- Ecosystem protection
- Drinking water supply
- Recreational water use
- Agricultural water use (e.g., irrigation, stock watering, aquaculture)
- Water for industry

*Stressors are the physical, chemical, or biologic factors that can cause an adverse effect on an aquatic ecosystem. Toxic stressors include heavy metals and toxic organic compounds, salinity, and pH. Nontoxic stressors include nutrients, turbidity and suspended particulate matter, organic matter, flow, and habitat.

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WATER QUALITY GUIDELINES

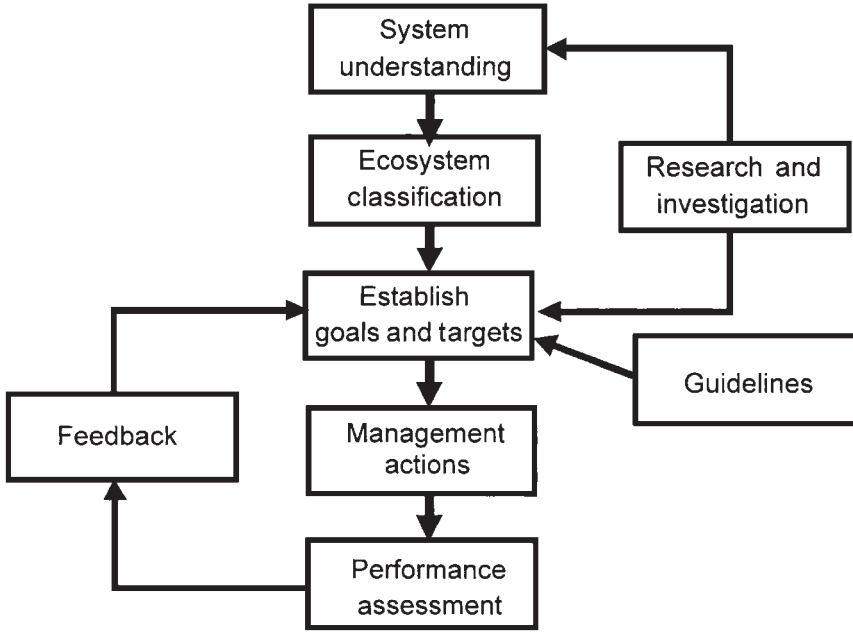

FIGURE 1.1 Water resources management framework.
(Modified from Hart et al., 1999.)

Since these uses may change with time, the water quality management process must be sufficiently adaptive to allow the goals to change in step with community values. There is no simple method for determining management goals. The process must be interactive and should involve at least the community, resource managers, and researchers.

Objectives or targets. Each environmental value requires a certain level of water quality to be maintained. The water quality to sustain environmental values may be defined by establishing water quality objectives that become the goals for management action. This is a complex process that depends on such factors as feasibility and costs of achieving the desired water quality and the lost opportunity costs to the community if these environmental goals are not reached. The objectives usually aim either

- To *protect* waterway values (e.g., those which do not allow waste discharge, no sand extraction, and those which apply restrictions on catchment activities) or
- To *restore* waterway values (e.g., works programs to prevent existing erosion of banks, stabilize beds, revegetate banks, and restore catchment buffer strips)

Key indicators of quality. These water quality objectives are established in terms of key indicators of quality that provide a means of identifying and measuring change in the environmental values. They can include physical, chemical, radiologic, microbial, or biological measures of water quality. Broadly, three types of indicators of environmental quality exist:

- Indicators that are *normally present* in the water and can be monitored usefully for a change in concentration, quantity, or quality (e.g., salinity and nutrient and heavy metal concentrations)

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- Indicators that are *not normally present* but which if detected in certain concentrations or quantities can be used to identify a change (e.g., concentrations of pesticides and other toxic organic compounds)
- Indicators that are normally present but the *absence of which* reflects a change

Guidelines. These provide an objective means for judging the quality needed to maintain a particular environmental value. Normally they are described in terms of the key indicators of quality (but see page 1.12 for a new way to define water quality guidelines).

Management actions. Water quality objectives defined by the preceding process will require actions to maintain and/or attain the desired quality and therefore achieve the environmental values identified by the community. Programs or strategies that might be developed to achieve these objectives could include control of waste discharges, water quality protection, catchment revegetation, nutrient reduction, river rehabilitation, resnagging of a river, and the provision of adequate environmental flows.

Performance assessment. There is now increased pressure on water management agencies to assess their performance and report the results publicly. This requires that an effective monitoring program is put in place and that there is an appropriate feedback mechanism to confirm that the various management goals are being met or that they need to be revised (ANZECC/ARMCANZ, 2000b). In the past, performance has been judged on the basis of whether threshold physicochemical indicator (e.g., dissolved oxygen, nutrients, pH, heavy metals) concentrations are achieved or not. In situations where protection of the ecosystem is the goal, monitoring of the biota is a more direct indicator of whether the goal has been achieved than measuring a physicochemical surrogate. For more details on indicators of ecosystem health, see Loeb and Spacie (1994), Davis and Simon (1995), Norris et al. (1995), and Wright et al. (2000).

Research. The ecological understanding of most aquatic environments is inadequate, this being particularly so for rivers and streams (Boon et al., 1992; Cullen et al., 1996; Lake, 2000). Obtaining the required information will demand sustained and focused long-term ecological research on these ecosystems. Where possible, these studies should be multidisciplinary and catchment-based and done as collaborative partnerships between researchers and managers.

WATER QUALITY GUIDELINES FOR HUMAN USES

Guidelines have been established for all the major uses of water. In this section we cover those relating to human uses: drinking water, agricultural water (including aquaculture), and water for recreational and aesthetic uses. Guidelines for ecosystem protection are covered in later Sections.

Drinking Water

Drinking water should be safe to use and aesthetically pleasing. The quality of drinking water is focused primarily on the protection of human health, and for this reason, drinking water guidelines mostly have been established by health authorities, e.g., the World Health Organization (WHO, 1984) and the Australian National Health and Medical Research Council (NH&MRC/ARMCANZ, 1996).

These authorities list guideline values for a wide range of indicators, including

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- Microorganisms (e.g., pathogenic bacteria, viruses, toxic algae)
- Inorganic chemicals (e.g., nitrates, heavy metals)
- Organic chemicals (e.g., toxic organic compounds, pesticides, disinfection by-products)
- Radioactive materials

These guideline values apply at the point of use, normally the home tap. However, the more progressive water authorities are increasingly seeking to manage the total supply system—the streams and rivers in the catchment, storage and service reservoirs, treatment and disinfection facilities, service mains, and consumer plumbing and appliances.

Agricultural Water

Guidelines generally are provided for three broad agricultural uses of water: irrigation, stock watering, and aquaculture.

Irrigation. In most developed countries of the world and in an increasing number of developing countries, irrigation uses a substantial proportion of the available water resource (UNEP, 2001). For example, approximately 70 percent (approximately 12,000 gigaliters) of Australia's developed water is used for irrigation compared with 21 percent for urban and industrial purposes and 9 percent for rural water supply (NLWA, 2001).

Guidelines for irrigation water quality generally focus on the physical, chemical, and microbiological factors that may affect crop growth or the soil environment. Trigger values or thresholds are provided for

- Microbiological indicators (e.g., human and animal pathogens, plant pathogens)
- Salinity and sodicity (these can affect both plant growth and soil structure)
- Inorganic contaminants (e.g., chloride, sodium, heavy metals)
- Organic contaminants (e.g., pesticides)

Stock Watering. Good water quality is essential for successful livestock production. Animal production and fertility can both be impaired by poor-quality water. Contaminants in water can result in residues in animal products (e.g., meat, milk, and eggs) that can create human health risks and adversely affect their salability.

Guidelines for stock water quality generally focus on the physical, chemical, and (micro)biological factors that may affect animal health. The tolerance to contaminants varies among animal species (generally decreases in the order sheep, cattle, horses, pigs, and poultry), between different stages of growth and animal condition, and between monogastric and ruminant animals (ANZECC/ARMCANZ, 2000a).

Guidelines provide threshold values for

- Microbiological indicators (e.g., cyanobacteria, pathogens, and parasites)
- Inorganic ions (e.g., calcium, magnesium, nitrate, sulfate, salinity, and heavy metals)
- Organic contaminants (e.g., pesticides)

Aquaculture. Aquaculture is a rapidly growing industry that involves production of food for human consumption, fry for recreational and natural fisheries, and ornamental fish and plants for the aquarium trade. Poor water quality can result in loss of production of culture species and also may reduce the quality of the end products.

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Few guidelines are available for aquaculture water quality; however, Australia and New Zealand have published such guidelines for the first time (ANZECC/ARMCANZ, 2000a). These focus on the physical, chemical, and microbiological factors that may affect the production or quality of the food for human consumption. Guidelines (trigger values) are provided for

- Microbiological stressors (e.g., cyanobacteria, pathogens, and parasites)
- Physicochemical stressors (e.g., dissolved oxygen, pH, salinity, and temperature)
- Inorganic and organic toxicants (e.g., heavy metals and pesticides)

Recreational Water

Water-based recreational activities are popular in many countries. Guidelines have been established to protect these waters for recreational activities, such as swimming and boating, and to preserve the aesthetic appearance of the water bodies. Guideline values are provided for the following indicators:

- Microbiological stressors (e.g., pathogens and viruses)
- Nuisance organisms (e.g., algae)
- Physical and chemical stressors (e.g., color, clarity, turbidity, pH, and toxic chemicals)

It is the microbiological stressors that normally are the main focus of recreational water quality guidelines. More information on recreational water quality guidelines can be found in USEPA (1986b), ANZECC (1992), WHO (1998, 1999), and ANZECC/ARMCANZ (2000a).

ECOSYSTEM PROTECTION

Existing Water Quality Guidelines

Water quality guidelines for ecosystem protection were first introduced in the early 1970s (Hart, 1974; NAS/NAE, 1973). These early guidelines focused primarily on physical and chemical stressors and provided threshold values for two broad water types: fresh and marine waters. These threshold values often are interpreted as indicating degradation if they are exceeded and safe conditions if not exceeded; unfortunately, they often become pseudostandards. This is so despite the fact that most of the guideline documents stress that the published values are for guidance only and that if conditions in a particular system approach or exceed the guideline value for a particular indicator, more site-specific work should be undertaken (ANZECC, 1992; Hart et al., 1999).

The ecosystem protection guidelines in use over the past 10 years are little different from these earlier guidelines in that they still focus heavily on physical and chemical stressors, although some have included biological indicators (USEPA, 1986a; CCREM, 1991; ANZECC, 1992). The physicochemical indicators can be classified into two groups:

- Those which have direct toxic effects on the biota (e.g., heavy metals, salinity, pesticides, and temperature)
- Those which affect ecosystems indirectly (e.g., nutrients, turbidity, and excess organic matter)

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The way in which these guidelines are established is discussed briefly below. Then we identify a number of limitations to these guidelines as a lead-in to discussion of the new risk-based approach recently adopted by the Australian government.

Physicochemical Indicators. Threshold values are provided for a range of physicochemical indicators, including

- Color (this can influence primary production)
- Dissolved oxygen (this can adversely affect fish and invertebrates)
- Nutrients (in excess, these can result in cyanobacterial (blue-green algae) blooms)
- pH (low pH can adversely affect aquatic biota directly and also can result in release of heavy metals from sediments)
- Salinity (high salinity can adversely affect freshwater macrophytes and other aquatic biota)
- Suspended particulate matter and turbidity (these can influence primary production)
- Temperature (both high and low temperatures can adversely affect aquatic biota)

Different threshold values normally are provided for freshwaters and marine waters. Few of the guidelines make any provision for the site differences that can occur between ecosystem types within these two broad categories.

Toxicants. Most of the trigger values for toxicants are derived using data from single-species toxicity tests on a range of test species. Readers are referred to Chapman (1995), OECD (1995), and Warne (2001) for details on toxicity testing. It would be preferable to use data from multispecies toxicity tests because these would better represent the complex interactions that occur in the field. However, few such data are available.

A number of extensive databases containing toxicity data for many inorganic and organic compounds and for many test organisms (e.g., fish, zooplankton, macroinvertebrates, and algae) now exist (USEPA, 1994; Warne et al., 1998, 1999). These generally contain a large amount of data on acute toxicity and a smaller amount on chronic toxicity.*

Guideline values for a number of types of toxicants are listed in many of the existing guideline documents (e.g., USEPA, 1986a; ANZECC, 1992):

- Inorganic compounds (e.g., ammonia, cyanide, and hydrogen sulfide)
- Heavy metals (e.g., copper, cadmium, mercury, and arsenic)
- Organic compounds (e.g., pesticides, PCBs, and dioxins)

These are derived largely from acute toxicity data using the *assessment-factor method.* This method involves dividing the lowest acute toxicity value by an arbitrary assessment factor to provide a safe level. A factor of 0.05 was used for toxicants that are nonpersistent or are not accumulated, and a factor of 0.01 was used for toxicants that are persistent. This method is far less rigorous than the statistical methods now in use and is used only as a default when insufficient data were available. Further information on the newer statistical methods is provided on page 1.23 (see also Aldenberg and Slob, 1993; Warne, 2001).

*Acute toxicity is the rapid death of organisms caused by a toxicant. It is normally specified as the concentration of the toxicant that causes death to 50 percent of the test organisms in a set time, often 96 hours—this concentration is referred to as the 96h-LC50. Chronic toxicity is the biological response to the long-term exposure to a toxicant. A chronic toxicity test generally attempts to test over several generations of the test organism and can extend from weeks to months.

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Biological Indicators. Few of the existing water quality guidelines contain information on biological indicators. The 1992 Australian water quality guidelines were the first to do so (ANZECC, 1992). These guidelines recommended that four biological indicators be considered:

- Species richness
- Species composition
- Primary production
- Ecosystem function

These guidelines did not provide specific information of what species should be considered or how the measurements should be taken. However, in requiring that these biological indicators be considered, the guidelines provided the impetus for Australian natural resource management agencies to develop the required methods (Norris et al., 1995; Schofield and Davies, 1996; Simpson and Norris, 2000).

Limitations of the Existing Water Quality Guidelines

Ecological Guidelines or Water Quality Guidelines. Water quality is only one aspect of maintaining a healthy ecosystem. Other factors also can be important, including flow regime, habitat quality, sediment quality and the condition of the riparian vegetation, barriers to fish migration, and connections between the river and its catchment and floodplain (Fig. 1.2). Ideally, all these factors should be considered when defining the water resource management program. For example, in many parts of Australia, water quality is reasonably good, but the goal of maintaining ecosystem health is not being achieved because too much water is being abstracted for irrigation or there is significant degradation of the in-stream habitat because most of the snags (large woody debris) have been removed.

The currently available water quality guidelines still focus largely on the water compartment and assume that this will protect the whole ecosystem adequately. However, there is currently considerable activity in many parts of the world aimed at establishing guidelines for these other factors that also influence ecosystem health, e.g., environmental flows and habitat quality (Cullen et al., 1996), and sediments (ANZECC/ARMCANZ, 2000a; Batley, 2000). In time, this information will be linked with available water quality guidelines to produce broader ecological guidelines for ecosystem protection.

The establishment of appropriate flow regimes to sustain the ecological values of rivers, wetlands, and estuaries is one of the most contentious issues currently facing water managers in many countries (Calow and Petts, 1992; Cullen et al., 1996; Stanford et al., 1996). Effective river flow management, where the primary objectives are conservation of native aquatic biodiversity and protection of ecosystem functions, needs to focus on achieving as close to the natural flow regime as possible, even in cases where the total annual flow has been reduced because of heavy consumptive uses. This *natural-flow paradigm* is based on the emerging evidence that the full range of natural intra- and interannual variation in the hydrologic regime is critical in sustaining the biodiversity and integrity of aquatic ecosystems (Richter et al., 1997).

Limited Use of Biological Indicators. As noted earlier, available water quality guidelines focus mainly on physicochemical stressors, with little information on biological indicators. An exception is the 1992 Australian guidelines (ANZECC, 1992). Many researchers have noted the advantages in monitoring the biota (rather than physicochemical surrogates) to provide a better indication of ecosystem health (Norris et al., 1995).

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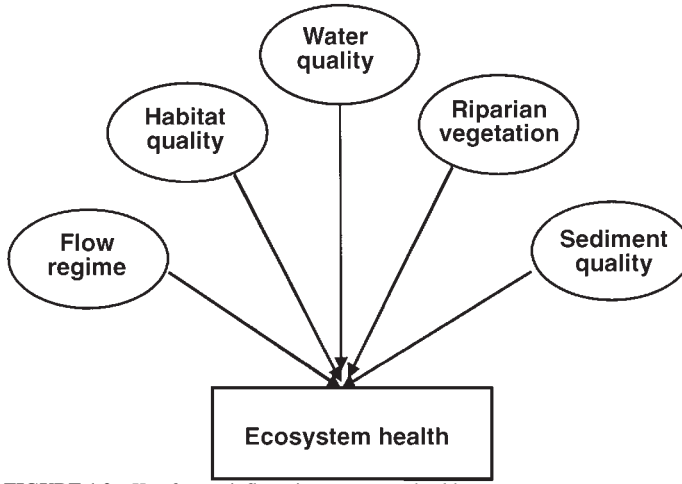

FIGURE 1.2 Key factors influencing ecosystem health.

Over the past 10 years, many countries have introduced national biological monitoring programs (Rosenberg and Resh, 1993; Schofield and Davies, 1996; Wright et al., 2000). Figure 1.3 illustrates schematically the power of a sensitive biological indicator in recording both the degradation in ecosystem quality that all to often is taking place and the subsequent improvement over time with management action. Such biomonitoring programs focus mainly on detecting changes in the patterns (e.g., abundance, richness, and species composition) of particular biological communities (e.g., macroinvertebrates, fish, and algae) compared with known reference systems. For example, Australia has a national program based on macroinvertebrates, the Australian River Assessment System (AUSRIVAS; see Simpson and Norris, 2000). As part of a recent national land and water audit, these data have been used to complete an assessment of the ecological health of the nation's rivers (Norris et al., 2001).

Bunn and Davies (2000) have shown that changes in pattern do not always equate to changes in ecological integrity. They make a case for also including measures of key ecological processes (e.g., benthic metabolism, gross primary production, respiration, nitrification, and denitrification) in programs to assess the health and integrity of ecosystems. Over the next few years we should see the development of more robust ecosystem process measures that can be incorporated into existing biological monitoring programs.

Toxicity Testing. Guidelines for toxicants are based very largely on laboratory-based single-species toxicity testing of a limited number of biological species. It is assumed that if these key organisms are protected from toxic effects, this will be sufficient to protect the whole ecosystem. It is well known that a number of modifying effects can occur in the environment, but it is quite difficult to take this into consideration. One exception is the complexation of heavy metals with carbonate and bicarbonate that generally is taken into account (Markich et al., 2001). Additionally, there are very few data relating to the testing of toxicant mixtures, the situation that exists most commonly in the real world.

Ecosystem Types. Available guidelines recommend thresholds for freshwater and marine environments. This approach neglects the quite major differences between the types of

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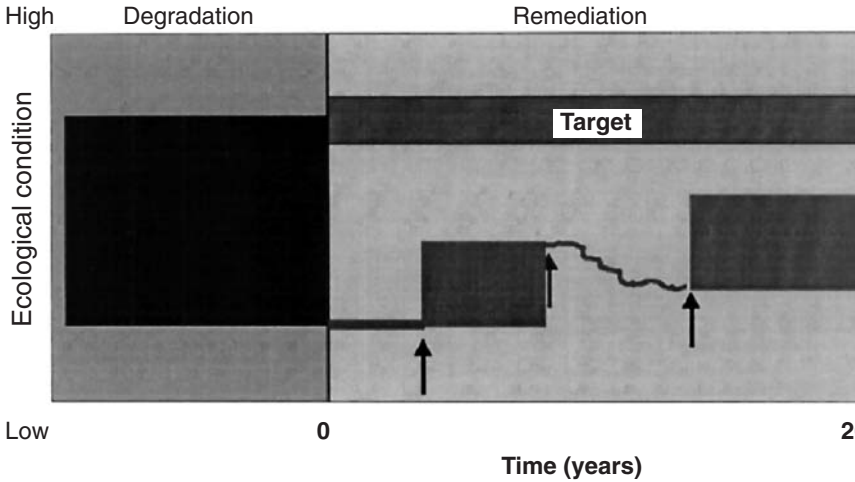

FIGURE 1.3 Schematic of the types of changes that may occur in ecosystem indicators with time and the subsequent improvement with management actions.

ecosystems that exist within these broad categories. For example, freshwater ecosystems can include permanent and ephemeral upland and lowland rivers and streams, wetlands, lakes, and reservoirs spread over temperate, tropical, and arid regions.

Modifying Factors. The current guidelines take little account of environmental factors that can modify the effect of a stressor. For example, it is well known that many heavy metals can complex with natural organic matter and suspended particles, reducing toxicity to aquatic organisms. However, there is little account for metal speciation in available water quality guidelines, which still focus on total metal concentrations and make no allowance for bioavailable forms (Markich et al., 2001).

Ecological Issues Rather Than Indicators. Most of the existing water quality guidelines provide information on indicators (or stressors) rather than on the ecological issues that need to be managed. This aspect is covered in the next section.

NEW RISK-BASED WATER QUALITY GUIDELINES

This section covers the key elements of new risk-based water quality guidelines recently introduced in Australia and New Zealand that should lead to more effective management and protection of aquatic ecosystems (ANZECC/ARMCANZ, 2000a; Hart et al., 1999; Fox, 2001; Warne, 2001; Batley, 2000; Markich et al., 2001). The essential elements of the new approach are (Fig. 1.4)

- *Ecosystem-based.* The guidelines are ecosystem-specific.
- *Issue-based.* The guidelines focus on the actual ecological issues caused by physical, chemical, and biological stressors rather than on the individual indicators or stressors.
- *A risk-based approach.* This addresses the great difficulty in deciding whether adverse biological effects will result from various stressors added to an ecosystem. The new

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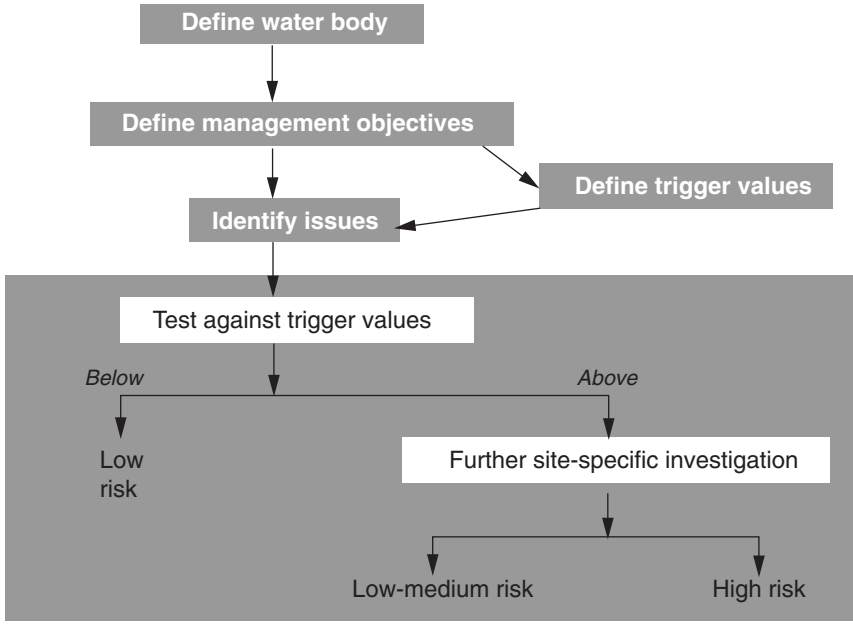

FIGURE 1.4 Risk-based approach (involving guideline packages) for assessing the risks of ecological problems occurring because of stressors.
(Modified from ANZECC/ARMCANZ, 2000.)

approach develops guideline "packages" for each issue and, where possible, for each ecosystem type. Each package consists of three parts: specified key performance indicators, trigger values for these indicators (i.e., levels that indicate the risk that adverse biological effects may occur), and for potentially high-risk situations where trigger values are exceeded, a protocol for considering the effect of ecosystem-specific factors in reducing (or enhancing) the biological effects.

Two case studies—the excessive growth of cyanobacteria (algal blooms) and heavy metal toxicity—are presented to illustrate how the new risk-based guidelines are applied.

Ecosystem-Specific Guidelines

Many different types of aquatic ecosystems exist. These often function quite differently from one another, making it desirable that ecosystem-specific management guidelines be developed where this is possible.

Aquatic ecosystems are characterized by great variability and complexity and the fact that they are now increasingly affected by human activities occurring within the catchment. Variations in the physical (e.g., light, temperature, mixing, flow, and habitat) and chemical (e.g., organic and inorganic carbon, oxygen, and nutrients) factors that control these ecosystems can occur naturally due to droughts and floods, climatic conditions, and erosion events. Changes in these variables can have important consequences for the numbers and types of biota present at any one time. Aquatic ecosystems also are characterized by a large number of quite complex interactions (Harris, 1994), the details of which are often known on the broad scale but are less well known on a smaller scale.

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Additionally, a wide range of human-related stressors can have an impact on aquatic ecosystems and modify their health. These include pollution from industrial, urban, agricultural, and mining sources; regulation of rivers through the construction of dams and weirs; salinization; siltation and sedimentation from land clearance, forestry, and road building; clearance of stream bank vegetation; overexploitation of fisheries resources; introduction of alien plant and animal species; and removal and destruction of habitat, to name but a few.

All too often the presently available guidelines simply lump ecosystems into two categories: freshwater and marine (USEPA, 1986a: ANZECC, 1992). This is insufficient to discriminate between the ecosystem types that exist in many countries. Obviously, the biotic communities and the ecosystem functioning within this wide range of ecosystem types will differ, sometimes markedly. Thus it is difficult to see how effective management can occur without some further discrimination between ecosystem types than the simple freshwater and marine categories.

The new Australian and New Zealand guidelines recommend six ecosystem types: upland rivers, lowland rivers, lakes and reservoirs, wetlands, estuaries, and marine (ANZECC/ARMCANZ, 2000a). However, even with this admittedly limited number of ecosystem types, there is often a lack of knowledge on what lives in them and in particular how they function. This lack of knowledge has precluded a further segmentation of these ecosystem types on the basis of geography (e.g., tropical versus temperate, coastal versus inland), although, hopefully, this will come in the near future.

Management Objectives (or Targets)

An important part of any water quality or ecosystem management plan is a clear statement of the objectives or targets to be achieved. Typically, the objective for the protection of aquatic ecosystems is "*…to protect biological diversity (biodiversity) and maintain ecological processes and systems*" (ANZECC, 1992).

Ideally, the targets or objectives specifically aimed at protecting an ecosystem should be set in terms of ecosystem-specific indicators. At present, in those cases where this is done, it is largely restricted to changes in the patterns of biological communities (e.g., reduction in biodiversity and/or abundance caused by toxicants or changes in species composition and/or abundance caused by excessive nutrients). With time, targets related to measures of ecosystem functioning (e.g., gross primary production and community respiration) also will be included (Bunn and Davies, 2000).

Before ecosystem management targets can be established, the type of ecosystem desired must be decided on. This generally means deciding what level of protection is required for the ecosystem. Of the many levels of ecosystem protection that could be defined, the new Australian and New Zealand guidelines recommend three:

- *High conservation/ecological value systems.* These are effectively unmodified or other highly valued ecosystems. Typically, they occur in national parks, conservation reserves, or remote and/or inaccessible locations.
- *Slightly to moderately disturbed systems.* Ecosystems in which aquatic biological diversity may have been changed to a relatively small but measurable degree by human activities. The biological communities remain in healthy condition, and ecosystem integrity is largely retained.
- *Disturbed systems.* These are measurably degraded ecosystems of lower ecological value. Most urban streams receiving road and storm water runoff would be disturbed systems.

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The provision of the highest level of protection for pristine or near-pristine ecosystems in a national park is obvious. However, for a significantly modified urban creek, it is unlikely even with the best will in the world (and an appropriate bank account) that this could be rehabilitated to a near-pristine system. In particular, the flow regimes in most urban systems have been changed permanently. To ensure that there is some balance and practicality in the targets set, it is therefore essential that decisions on the level of protection and the targets to achieve this level are negotiated among the stakeholders, who may include the community, management agencies, and dischargers.

Measurement of acceptable ecological change is difficult (Mapstone, 1995). In very few situations is our scientific knowledge sufficient for us to gauge with any certainty what change from the target condition will cause an adverse ecological effect. Both the time and duration of the change and the absolute level of change can be important. For example, an increase in toxicant concentration over a very short time period can cause a significant reduction in the biological diversity, whereas the deposition of particulate matter or silt on the bottom of a small stream to levels that cause problems may occur over a considerable time period. For these reasons, there are very few examples where the level of change from some prescribed target condition has been specified in a water quality management plan.

It is quite possible, of course, to define a particular level of change in statistical terms given an adequate data set (Mapstone, 1995; Quinn and Keough, 2001). However, a defined statistical change in a physicochemical or biological indicator does not necessarily equate to any particular ecological change.

As described earlier, the new Australian and New Zealand guidelines use comparison with an appropriate reference ecosystem as the basis for judging whether the test ecosystem is being protected adequately. This referential approach is also being adopted widely for interpreting the results of macroinvertebrate monitoring [e.g., the AUSRIVAS approach in Australia (Simpson and Norris, 2000) and the RIVPACS approach in the United Kingdom (Wright, 1995; Wright et al., 2000)].

Focus on Issues

Existing water quality guidelines focus almost exclusively on the individual stressors, e.g., on nutrients, turbidity, or particular toxicants such as copper. However, it is generally the ecological issues caused by physical, chemical, and/or biological stressors that need to be tackled by management agencies, and these are rarely caused by only one stressor. Most ecological issues are multistressor problems. Therefore, it more appropriate to focus on the issues rather than on single indicators or stressors. Such an issue-based focus requires that the guidelines be organized in terms of "packages" of information provided on the stressors (and modifying factors) that relate to each particular issue.

Ecosystem management issues for which guideline packages have been developed in the new Australia and New Zealand guidelines include (ANZECC/ARMCANZ, 2000a)

- Effects due to toxicants (e.g., heavy metals, toxic organic compounds) in the water column (changes in biological diversity, fish kills)
- Effects due to toxicants in sediments (changes in biological diversity)
- Nuisance growths of aquatic plants (eutrophication)
- Lack of dissolved oxygen (asphyxiation of respiring organisms)
- Excess suspended particulate matter (smothering of benthic organisms, inhibition of primary production)
- Unnatural change in salinity (change in biological diversity)

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- Unnatural change in temperature (change in biological diversity)
- Unnatural change in pH (change in biological diversity)
- Poor optical properties of water bodies (reduction in photosynthesis, change in predator-prey relationships)

Risk-Based Approach

The effect of a particular stressor on the biological diversity and abundance* depends on three major factors:

- The type of ecosystem and hence the biological communities
- The types of stressors and the issues (or problems) these cause
- The influence of environmental factors (which also may be stressors) that may modify the effect of the stressor

As noted earlier, many of the existing water quality guideline documents do not adequately address either the *variability and complexity* known to characterize all aquatic ecosystems. This variability and complexity make effective management of aquatic ecosystems extremely difficult. Additionally, the influence of *environmental factors* in modifying the ecological effects of key stressors is rarely considered in existing guidelines.

The new Australian and New Zealand guidelines have adopted a risk-based approach, which by implicitly accounting for the variability and complexity should provide a more realistic and effective means of protecting the biodiversity or ecological integrity of aquatic ecosystems (ANZECC/ARMCANZ, 2000a). This risk-based approach is based on the ecological risk assessment (ERA) methodology, a process for determining the level of risk posed by stressors (e.g., chemicals and nutrients) to the survival and health of aquatic ecosystems.

The ERA process has evolved because of difficulties in assessing the impact of multiple stressors on complex ecosystems (Suter, 1993; USEPA, 1995). Initially, most ERAs focused on the risks associated with the effects of toxic chemicals. There is now a growing realization that degradation of catchments and waterways is also related to physical and biological stressors (e.g., nutrients, environmental flows, habitat, sediments, and exotic species) in addition to chemical stressors and that the ERA process must be expanded to address these broader issues (Burgman et al., 1993; Hart et al., 2001). Risk assessment involving aquatic ecosystems is particularly challenging because of the large number of different species involved and the difficulties in deciding what end points or targets are to be used to assess whether adverse effects have occurred.

Risk is defined as the *probability* of a hazard occurring times the *consequence* if the hazard does occur, and ecological risk is defined as the *likelihood* of an ecological effect times the *consequence* of that effect. Thus ecological risk assessment includes a consideration of both the severity (consequence) and frequency (likelihood) of the issue. For example, a situation where an extremely toxic chemical (e.g., mercury) is effectively contained so that there is no exposure to the ecosystem represents a low risk. On the other hand, a less hazardous material (e.g., orthophosphate) that is released in large quantities into the environment can result in a high-risk situation if toxic cyanobacterial blooms occur.

*Broadly, the effects on the biologic diversity and abundance are (1) *reduction in biodiversity and/or abundance* due to toxicants such as heavy metals, pesticides, or salinity and (2) *changes in species composition and/or abundance,* particularly toward nuisance populations caused by excess nutrients or a lack of light (e.g., caused by increased turbidity).

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In commenting on the application of ERA to river management, Hart et al. (2001) identified two aspects of the risk-based approach that need to be developed further. The first is to develop explicit conceptual models that link the key stressors (or drivers) with the ecological consequences for the system being managed. It should then be possible to quantify these linkages (e.g., via stochastic models or decision trees) and to develop more helpful and predictive decision support tools. The second aspect identified by Hart et al. (2001) was to invest additional time and effort to undertake more *quantitative* risk analyses. These should provide elements of transparency, internal consistency, and freedom from ambiguity that are difficult or impossible to obtain in subjective risk assessments. There is now a worldwide push to develop more quantitative (model-based) risk assessment methods that include the use of fault and event trees, interval arithmetic, probability arithmetic, bayesian statistical inference methods, Monte Carlo simulations, confusion matrices and receiver operating characteristic (ROC) curves, and quantitative ecological modeling (Burgman et al., 1993; Swets et al., 2000; Hart et al., 2001).

Defining Low-Risk Trigger Values

Low-risk trigger values are the concentrations of the key performance indicators for the ecosystem type being managed below which there is a low risk that adverse biological effects will occur. They are not designed to be used as "magic numbers" or threshold values at which an environmental problem is inferred if they are exceeded. Rather, they are designed to provide an initial assessment of the state of a water body regarding the ecological issue in question. They can trigger two possible responses (see Fig. 1.4):

- If the test-site value is less than the trigger value, a low-risk situation exists. The management response would be to continue monitoring.
- If the test-site value is greater than the trigger value, a possible high-risk situation exists. The management response here would be either to introduce some remedial actions or to undertake further site-specific investigations. The aim of the site-specific investigations would be to determine whether or not a problem exists.

Two methods are commonly used to derive low-risk trigger values for the designated performance indicators. These are biological effects data and data from a reference ecosystem. Additionally, professional judgment may be needed for cases where it is not possible to obtain appropriate data for a reference ecosystem either because no appropriate reference system exists or because insufficient study has been undertaken to provide an adequate database. This professional judgment should be backed by appropriate scientific information (Hart, 1974, 1982; USEPA, 1986a; CCREM, 1991; ANZECC, 1992).

Biological Effects Data (Bioassays). These data are obtained either from biological effects testing (known as *bioassays* or *toxicity tests*) using local biota and local waters, if possible, or from the scientific literature. This method is most appropriate for toxicants (e.g., heavy metals, toxic organic compounds, salinity, and ammonia) but also can be used for naturally occurring stressors such as nutrients (e.g., nutrient addition bioassays). Information on biological testing procedures can be found in Chapman (1995), OECD (1995), and Warne (2001). There are a number of very good compilations of biological effects data (e.g., USEPA, 1994; Warne et al., 1998, 1999).

Reference System Data. The use of reference-site data to judge acceptability or otherwise of a particular test ecosystem is a key feature of the new Australian and New Zealand guidelines. These reference data are obtained either from the same (undisturbed) ecosystem (i.e.,

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from upstream of possible impacts), from a local but different system, or from regional reference ecosystems. This approach is particularly useful for aquatic ecosystems where the management target is to maintain or restore the system in an essentially natural or unmodified condition and where there are sufficient resources available to obtain the required information on the reference ecosystem (Reynoldson et al., 1997; Bailey et al., 1998). This method takes account of the natural variability of the key indicators in the reference system.

The new Australian and New Zealand guidelines define low-risk trigger values for slightly or moderately disturbed ecosystems in terms of the 80th and/or 20th percentile values obtained from an appropriate reference system (ANZECC/ARMCANZ, 2000a). For stressors where high concentrations cause problems (e.g., nutrients, turbidity, BOD, and salinity), the low-risk trigger level is taken as the 80th percentile of the reference distribution. For stressors where low concentrations cause problems (e.g., low-temperature water releases from reservoirs, low salinity in estuaries, low dissolved oxygen in waterbodies), the 20th percentile of the reference distribution is taken as the low-risk trigger level. For stressors where both high and low levels can result in problems (e.g., temperature, salinity, and pH), the desired range is defined by the 20th and 80th percentiles of the reference distribution.

The choice of the 80th and 20th percentile cutoffs to represent a well-functioning, unmodified ecosystem is arbitrary. There is currently no consensus on how best to define the influence of variations of physical and chemical stressors on the ecological functioning of an aquatic system.

Guidelines as Packages of Information

For each issue, the Australian and New Zealand guidelines provide a guideline package rather than threshold values for single indicators. Each guideline package consists of two components (see Fig. 1.4 and Table 1.1):

- *Key performance indicators.* These are used to make an initial decision on the risk (high or low) that an adverse biological effect will occur in the particular ecosystem type. Table 1.1 lists the performance indicators specified for each of the ecological issues. The low-risk trigger values for these key performance indicators were established as outlined on page 1.17.
- *A protocol for further investigating the risk when the trigger value is exceeded.* For potentially high-risk situations, ecosystem-specific modifying factors that may alter the biological effect of the key stressor need to be considered before the final risk can be decided. The two case studies below illustrate how these modifying factors can be taken into consideration.

Sediment Quality

Sediments often contain high concentrations of toxicants. They can act as both a sink and a source of toxicants and can be detrimental to aquatic organisms living in or using bottom sediments. Additionally, under certain conditions (e.g., anaerobic conditions), heavy metals may be released back into the water column and cause toxic problems. There has been considerable research over the recent years on developing methods for assessing the toxicity of sediments (Burton, 1992).

The new Australian and New Zealand guidelines provide for the first guidance on low-risk concentrations of toxicants in sediments in any guideline document (Batley, 2000; ANZECC/ARMCANZ, 2000a). The recommended guidelines draw heavily on the large North American effects database because of a lack of local data. This database defines the

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TABLE 1.1 Summary of the Condition Indicators and Performance Indicators for Each Ecological Issue

Issue	Condition indicator/target	Performance indicator	Method for obtaining trigger values	Use ecosystem-specific modifiers
Toxicity	Species composition/ abundance	Toxicant concentration	Reference data	Yes
Nuisance aquatic plants	Species composition Cell numbers Chlorophyll a concentration	Total phosphorus concentration Total nitrogen concentration Chlorophyll a concentration	Reference data	Yes
Lack of dissolved oxygen (DO)	Reduced DO concentration Species composition/ abundance	DO concentration	Reference data	Yes
Excess of Suspended particulate matter (SPM)	Species composition/ abundance	SPM concentration Turbidity	Reference data	Yes
Change in salinity	Species composition/ abundance	Electrical Conductivity (salinity)	Reference data	No
Change in temperature	Species composition/ abundance	Temperature	Reference data	No
Change in pH	Species composition/ abundance	pH	Reference data	No
Poor optical properties	Species composition/ abundance	Turbidity Light regime	Reference data	No

10th and 50th percentile concentrations for a range of toxicants. The 10th percentile concentrations have been adopted as the interim trigger values. It is assumed that below these values there will be a low probability of adverse effects on benthic biota. The median values provide an indicative higher concentration above which there is a high probability of that biota will be affected. A selection of interim trigger values is given in Table 1.2.

It should be noted that the 10th percentile value is not equivalent to the protection of 90 percent of the species in the same sense that the water quality guidelines for toxicants have adopted. The latter were derived from toxicity tests on a large range of species, whereas the sediment toxicity data are usually from one test organism (a burrowing amphipod) and occasionally include two other tests on species whose ecological relevance is questionable. The uncertainties in the derived trigger values are larger than the water quality values, and this should be recognized in their application.

Case Study 1: Nuisance Aquatic Plant Growth

Issue. The ecosystem issue considered in this case study is the excessive growth of nuisance algal species, an increasingly important problem in many countries including Australia (SoE, 1996). High concentrations of nutrients, particularly phosphorus (P) and

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nitrogen (N), can result in excessive growth of aquatic plants, such as phytoplankton, cyanobacteria, macrophytes, sea grasses, and filamentous and attached algae, in most ecosystems. These excessive growths can lead to problems such as toxic effects, particularly due to cyanobacteria in fresh and brackish waters and dinoflagellates in marine waters; reduction in dissolved oxygen concentrations when the plants die and are decomposed; reduction in recreational amenity (phytoplankton blooms and macrophytes in wetlands and lakes, sea grasses in estuaries and coastal lagoons); blocking of waterways and standing waterbodies (macrophytes); and changes in biodiversity as the species composition is changed.

Targets. For this issue, the targets could be set in terms of chlorophyll a concentration, cell numbers (particularly of cyanobacteria), or species composition. The key stressors are assumed to be the nutrients P and N, and the potential ecosystem factors that could modify the biological effects of these nutrients would include hydraulic retention time (flows and water body volume), mixing regimes, light regime, turbidity, temperature, suspended solids (nutrient sorption), estimates of grazing rates, and type of substrate (Harris, 1994). Nutrients also may become available as a result of remobilization from sediments, where nutrient release is influenced by the composition of the sediments (particularly bioavailable organic matter, Fe, S, N, and P), temperature, mixing regime of the water body, and oxygen transfer rates (Bostrom et al., 1988; Harper, 2001).

Trigger Values. If sufficient information is available, the low-risk trigger concentrations for the three key performance indicators (chlorophyll a, total P, and total N) should be determined from an appropriate reference system. In cases where this is not possible, the new Australian guidelines provide default trigger values. Table 1.3 contains the default trigger values for nutrients for six ecosystem types within southeast Australia. The trigger values were derived either from the nutrient distributions for unmodified ecosystems (80th percentile) or using professional judgment.

Use of the Guideline Package. Figure 1.4 shows the recommended approach for determining the risk of nuisance aquatic plant growth occurring in a particular ecosystem. The approach involves three steps:

1. Test the three performance indicators (chlorophyll a, total P, and total N concentrations) for the particular ecosystem against the appropriate low-risk trigger values for that ecosystem type. Compare the trigger value with the median (50th percentile) concentration for the test system measure under low-flow or high-growth conditions. Fox (2001) explains the basis for comparison of the 50th percentile from the test system with the 80th percentile from the reference system (P_{50}-P_{80} comparison).

TABLE 1.2 Interim Sediment Quality Trigger Values for Five Contaminants

Contaminant	Interim trigger value (mg/kg)	Interim high-risk value (mg/kg)
Zinc	200	410
Lead	50	220
Copper	65	270
Mercury	0.15	1
Arsenic	20	70

Note: Also listed are the interim high-risk values (Batley, 2001).

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TABLE 1.3 Default Trigger Values for Stressors Causing Algal Problems in Slightly Disturbed Ecosystems in Southeast Australia.

Ecosystem type	Chl a (μg/liter)	TP (μg/liter)	FRP (μg/liter)	TN (μg/liter)	NO_x (μg/liter)	NH_4^+ (μg/liter)
Upland river	na	20	15	250	15	13
Lowland river	5	50	20	500	40	20
Freshwater lakes and reservoirs	5	10	5	350	10	10
Wetlands	nd	nd	nd	nd	nd	nd
Estuaries	4	30	5	300	15	15
Marine	1	25	10	120	5	15

Note: na = not applicable; nd = no data; Chl a = chlorophyll a; TP = total phosphorus; FRP = filterable reactive phosphorus; TN = total nitrogen; NO_x = oxides of nitrogen (mainly nitrate); NH_4^+ = ammonium. Trigger values derived from data supplied by state agencies. Where possible, trigger values were the 80th percentiles of data distributions from unmodified ecosystems (ANZECC/ARMCANZ, 2000).

2. If test values are less than trigger values, there is low risk of adverse biological effects, and no further action is required, except for regular monitoring of the key performance and condition indicators.
3. However, if the test values are higher than the trigger values, there is an increased risk that adverse biological effects will occur, and either management action or further ecosystem-specific investigation is required.

Decision Tree. Figure 1.5 is an example of a simple decision tree for assessing the risk of cyanobacterial blooms occurring in a lowland river due to nutrients added by irrigation drains (Hart et al., 1998). This decision tree is based on a simple conceptual model where it is assumed that cyanobacterial growth in lowland rivers is controlled by three major factors:

- The concentrations of the nutrients P and N
- The light climate (turbidity used as a surrogate because of a lack of data on light)
- The flow conditions in the river when cyanobacterial growth can occur

The guideline package in this case includes values for the key stressors (chlorophyll a, total P, total N) and values for turbidity and flow as the modifiers. The values provided in the decision boxes for total P and turbidity should be taken as indicative only because they will depend on the particular ecosystem being considered. The decision box for flow was based on the need for a sufficient period of low flow to allow cyanobacterial numbers to increase to an alert level of 5000 cells/ml. A period of 6 to 10 days was estimated based on a cyanobacterial doubling time of 2 days and an initial cyanobacterial concentration of 10 to 100 cells/ml. A *growth event* was then defined as a period consisting of at least 6 consecutive days when the flow was less than the 25th percentile flow obtained from the long-term flow record for the system.

For the system described in Fig. 1.5, a high-risk situation is indicated if the total P concentration is greater than 15 μg/liter, the turbidity is less than 30 NTU, and there is more than one growth event of more than 6 days' duration per year. In this case, further investigation and appropriate management actions would be warranted.

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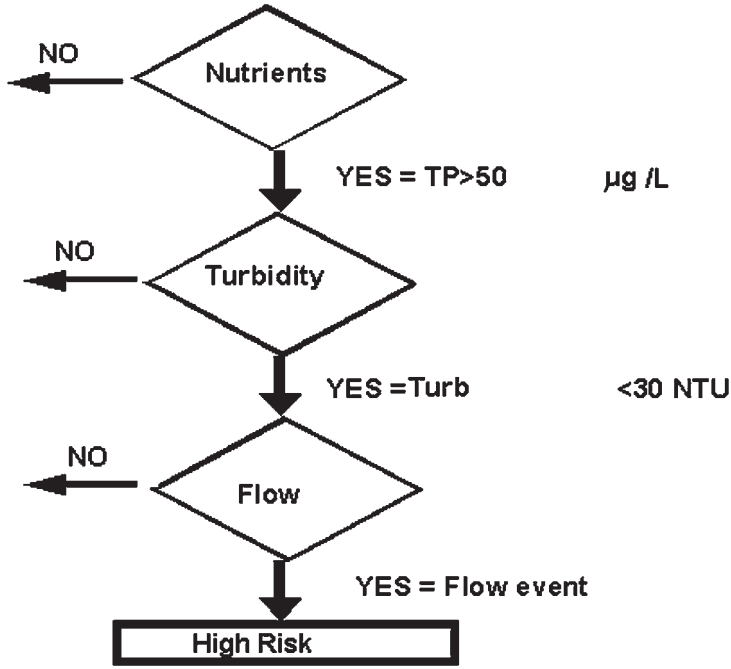

FIGURE 1.5 Decision tree for assessing risk of cyanobacterial blooms in a lowland river. *(Modified from Hart et al., 1999.)*

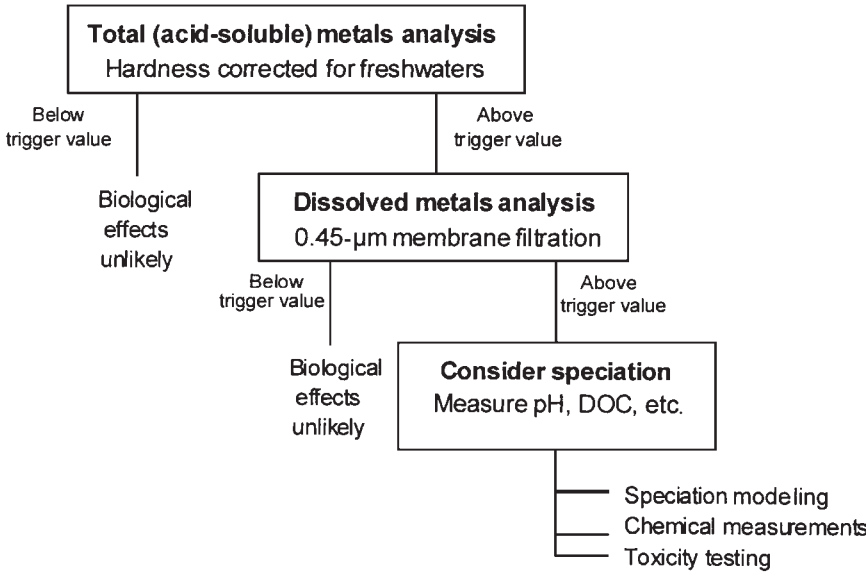

FIGURE 1.6 Decision tree for assessing risk of toxic effects from copper in a lowland river. *(Modified from Batley, 2001.)*

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Case Study 2: Toxicants

Issue. The ecosystem issue considered in this case study is the toxicity to aquatic organisms cause by excessive concentrations of copper. Copper is known to be toxic to a wide range of aquatic animals and plants (CCREM, 1991; ANZECC/ARMCANZ, 2000a).

Targets. Targets could be set in terms either of water column copper concentration or biological species composition or abundance (see Table 1.1). The key stressors are assumed to be copper, and the potential ecosystem factors that could modify the biological effects of this toxicant are hardness/alkalinity, suspended and dissolved organic matter, pH, temperature, and salinity (Markich et al., 2001).

Trigger Values. In the new Australian and New Zealand guidelines, trigger values for heavy metals and organic toxicants were derived mainly using the *statistical-distribution method.* The assessment-factor method, discussed earlier, was used as a default to obtain interim trigger values for toxicants where insufficient toxicity data exist. The statistical method uses the distribution of all toxicity data and determines the toxicant concentration that will protect an agreed percentage of species. The Australian guidelines use an adaptation of the Aldenberg and Slob (1993) approach. The objective is to determine the toxicant concentration required to protect some high percentage (typically 95 percent) of the aquatic biota. An extra statistical dimension is introduced by specifying a level of confidence to the stated concentration. For example, for slightly to moderately degraded ecosystems, the new Australian guidelines adopt 95:50 as the basis for setting trigger values; i.e., 95 percent of the species are protected with 50 percent confidence. Fox (2001) provides further explanation of the statistical basis of this method.

Table 1.4 records the trigger values derived for some common heavy metals in freshwater ecosystems. Note that these are affected by the level of protection required.

Use of the Guideline Package. The recommended approach for determining the risk that toxic effects will occur in a particular ecosystem is shown in Fig. 1.4. Three steps are involved:

1. Test the performance indicators (total toxicant concentrations) for the particular ecosystem against the appropriate low-risk trigger values for that ecosystem type. Compare the trigger value with the median (50th percentile) concentration for the test system.
2. If test values are less than trigger values, there is low risk of adverse biological effects, and no further action is required, except for regular monitoring of the key performance and condition indicators.

TABLE 1.4 Trigger Values for Different Levels of Protection in Freshwater (Calculated for a Hardness of 30 mg/liter $CaCO_3$)

	Trigger value (μg/liter)		
Toxicant	99%	95%	90%
Cadmium	0.06	0.2	0.4
Lead	1.0	3.4	5.6
Zinc	2.4	8	15
Silver	0.02	0.06	0.11

Note: The 99%, 95%, and 90% refer to the percent of species protected by the indicated trigger value.

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3. However, if the test values are higher than the trigger values, there is an increased risk that adverse biological effects will occur, and either management action or further ecosystem-specific investigation is required.

Decision Tree. Figure 1.6 shows a typical decision tree that can be used to assess the ecological risk from heavy metals in freshwater ecosystems (Batley, 2000). Thus, to assess the ecological risk from copper in a river system, the following steps would be involved:

- *Initial measurement of total copper concentration.* Assume that the trigger value for copper (modified for the hardness of the river) is 2.6 μg/liter and that an initial measurement of total copper in an unfiltered water sample was 15 μg/liter. Then, because the test measure is higher than the trigger value, the decision would be to do further analyses.
- *Filterable copper concentration.* If the sample was filtered through a 0.45-μm filter, acidified and the filterable copper concentration measured at 6.4 μg/liter (still above the trigger value), still further work would be required.
- *Bioavailable copper concentration.* Suppose now that speciation modeling showed that dissolved inorganic copper was 1.8 μg/liter, that this result was confirmed by chemical measurements of labile copper using anodic stripping voltammetry (2.0 μg/liter), and that the test water was shown in a toxicity test to be nontoxic to sensitive algal species. Since the bioavailable copper concentrations was below the trigger value (2.6 μg/liter), it would be reasonable to assume that the water quality is acceptable.

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CHAPTER 2
DESIGN OF WATER QUALITY MONITORING PROGRAMS

William A. Maher and Graeme Batley

INTRODUCTION

Water quality monitoring programs are undertaken to provide information to answer questions relating to the management of water bodies and their catchments. They may be a single exercise to examine a particular issue, or they may be ongoing monitoring programs to ensure that acceptable water quality is maintained. Both single investigations and ongoing monitoring programs require careful planning if they are to give value for money.

Good monitoring programs obtain information and are not just data-collection exercises (Table 2.1). Such programs should be cost-effective yet provide information and knowledge to inform those commissioning the data collection

When planning a monitoring program, it is essential before field work is commenced to have clear objectives and documented methods that will be used to analyze data. There are many examples of studies where insufficient thought has gone into planning and the wrong parameters have been measured, often at inappropriate scales and time intervals.

Monitoring programs require the systematic collection of physical, chemical, and biologic information and the interpretation of those measurements. Decisions have to be made as to

- The information that is required
- Specific data requirements
- Where, when, and how data are to be collected
- Occupational health and safety issues
- How the data are to be analyzed and interpreted
- How the quality of data is to be assessed
- What procedures are needed to ensure that data are of a defined standard
- How data are to be managed, i.e., checked and stored
- How information is to be presented and communicated to those who need it

A framework for addressing these questions is given in Fig. 2.1. Each of the elements in Fig. 2.1 is expanded in the text. Since designing monitoring programs is an iterative process, each of the elements will need to be refined as other elements are considered.

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TABLE 2.1 Distinction between data and information

Data, measurements	Information, interpretation/knowledge
Total Phosphorus, filterable reactive Phosphorus, trace metals,	Spatial patterns
E. coli, algal counts	Trends Effects Differences Risks Feedback on management initiatives

SETTING MONITORING PROGRAM OBJECTIVES

A number of questions need be considered when designing monitoring programs. These can be thought as "how" questions, i.e., how to collect, what to collect, when to collect, where to collect, and how to store and analyze samples. These are unanswerable without a clear specification of the information required. Without knowing the answer to the "why" question, it hardly matters how we answer the "how" questions.

Defining the Issue

A preferred approach initially will consist of identifying and articulating the issue (Ellis and Lacy, 1980). This is an interactive process between the designer of the monitoring program and the user(s) of the information.

Issues normally fall into four categories:

- Establishment of environmental (ecosystem/use) values and long-term management, protection, and restoration of aquatic ecosystems
- Identification of contaminant sources and cycling in aquatic ecosystems and assessment of the magnitude of problems and measures that need to be taken to protect ecosystem values
- Evaluation of the performance of management strategies
- Compliance with legislative or administrative standards

How an issue is defined will be a function of values, previous knowledge, and experience. The initial statement of the issue may be the most crucial single step in determining the information required from a monitoring program (Miller et al., 1960; Bardwell, 1991). Being able to redefine or reframe an issue and to explore the issue may change the perspective on the information to be obtained.

The Need for a Conceptual Process Model

Once the issue has been defined, the aquatic ecosystem under consideration needs to be defined in general terms; i.e., the key processes that define how the system works must be identified. The system may be a river, lake, estuary, or coastal zone, and it will have unique key processes.

Conceptual process models may be no more than simple box diagrams. They should, however, be made explicit to illustrate the components and linkages in the system to be

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DESIGN OF WATER QUALITY MONITORING PROGRAMS

Setting program objectives:
- Has the issue been defined?
- Has the identity of all the information users been ascertained so that all information required is obtained?
- Has a shared conceptual process model of the system been developed and made explicit?
- Has an analysis been undertaken to identify the essential water quality information required?
- Have the specific objectives been stated?

Study design, data analysis techniques, and specific data requirements:
- Have the study location and spatial boundaries been defined?
- Has the scale of measurements been considered?
- Has the duration of the study been defined?
- Has the study type been made explicit and agreed on?
- Have the parameters to be measured been chosen?
- Have appropriate data presentation format and summary statistics been selected?
- Have appropriate techniques been selected to allow inferences, testing of hypotheses, or changes over time to be assessed?
- Have specific data requirements been clearly stated?

Sampling:
- Has a reconnaissance or literature study been undertaken to characterize spatial and temporal variability of variables?
- Is spatial and temporal (frequency and timing) replication adequate to obtain information required?
- Are sampling sites safe and accessible under adverse weather conditions?
- Have the smallest differences or changes to be detected been specified?
- Have appropriate sampling equipment, storage containers, and preservation procedures been identified?
- Is a quality assurance/control program in place to identify, measure, and control sampling errors?
- Have all the reasonable steps been taken to protect health and safety of employees?
- Has the cost-effectiveness of the sampling program been assessed?

Laboratory analysis:
- Have the analytes to be analyzed been clearly stated?
- Will the analytes be processed within the sample's storage life?
- Is an appropriate analysis technique being used?
- Does the laboratory have the equipment, expertise, and experience to undertake the planned analyses?
- Is a quality assurance/control plan in place to identify, measure, and control errors?
- Have all the reasonable steps been taken to protect health and safety of employees?

Data management and analysis:
- Has a data management system been established?
- Are the data analysis techniques selected to allow inferences, testing of hypotheses, or changes over time available and competent staff available to use them?

Reporting:
- Has the identity of all information users been ascertained and the level of understanding of each user been established?
- Has the time frame in which each information user requires information been established?
- Has the appropriate form of information presentation that will best convey information been decided?
- Have the available forms of information transmission been ascertained and what form of transmission is most appropriate for each information user?

FIGURE 2.1 Framework for designing monitoring programs.

monitored. These components present the factors that are perceived to be driving the changes in the system and the consequences of those changes. Models can be based on mass transport or flux, equilibrium considerations or kinetics (Fig. 2.2). The illustrations of important processes in Fig. 2.2 are highly simplified. In nature, key processes can interact in more complex ways.

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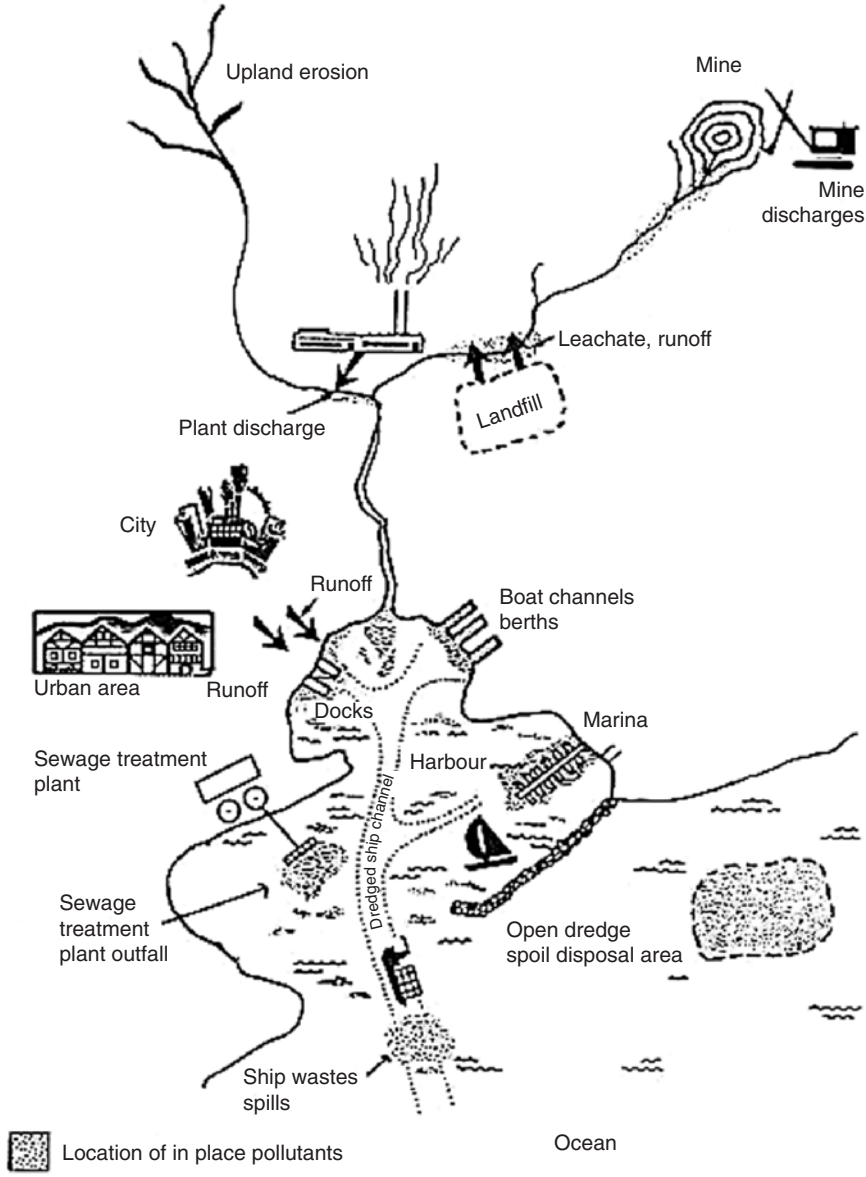

(*a*)

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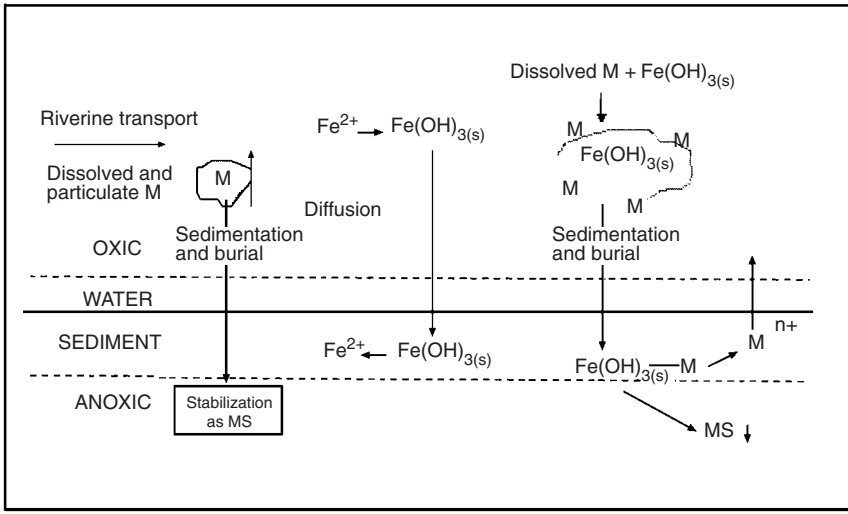

(*b*)

Water column:

Precipitation reactions: $Cu^{2+} \rightarrow Cu(OH)_2$ (mins) $\rightarrow$ tenorite (?) (hours-days)

Reaction with dissolved organics: $Cu^{2+} + L \rightarrow Cu\text{-}L \rightarrow$ (minutes)

Reactions with metal organic complexes: $Cu^{2+} + ML \rightarrow Cu\text{-}L + M^{2+}$ (days-months)

Mobilisation from suspended sediments: Cu- Sed + L $\rightarrow$ CuL + Sed

(hours)facilitated by dissolved organics

Release of copper from antifouling paints: Polymer-CuSCN $\rightarrow$ Cu^{2+} months

Sediment:

Oxidation of copper sulfides: CuS $\rightarrow$ $Cu^{2+} + SO_4^{2-}$ (days-months)

Oxidation of iron sulfides: FeS $\rightarrow$ $Fe^{3+} + SO_4^{2-}$ (hours)

(*c*)

FIGURE 2.2 Types of conceptual process models for movement and reactions of copper in aquatic environments: (*a*) mass transport; (*b*) equilibrium; (*c*) rate.

Conceptual process models assist in defining the "why" questions. The models enable us to illustrate our knowledge of an aquatic system in an explicit manner; especially our assumptions of how a system functions and what we believe to be the important processes. It is best if such models articulate the collective wisdom, experience, and perspectives of more than one individual.

Conceptual process models can be used to help define

- What the important components of the system are and what the important linkages are likely to be

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- The important questions to be assessed
- The key processes and cause-effect relationships
- The spatial boundaries
- The temporal and seasonal considerations
- The scales at which measurements are to be made
- Site selection
- What the valid measurement parameters are for the processes of concern

Conceptual process models can be a powerful tool when we argue about them and come to a shared understanding of the system that is the basis for the study. It is desirable for the parties involved in planning the monitoring program to develop their own concept of the system and then to share and integrate these conceptual models. Differences in the models can be important in clarifying the real issues and setting monitoring objectives. When this process is not undertaken, the different concepts of the system held by individuals can lead to disagreements about operational decisions and the importance of various types of data. Ultimately, this can lead to samples and data being collected that are not needed or used. Once an appropriate process model of the system has been made explicit and agreed on, then many of the design questions become more obvious. However, all process models are simplifications of reality and involve personal judgments. They do not need to be so comprehensive as to embrace all components of the system, but they do need to be sufficient for the issue being investigated.

It is important to be aware that the conceptual process model being used might be wrong. Data that seem inconsistent can be important, leading to significant scientific breakthroughs when new conceptual process models evolve.

Often the models will be based on accumulated wisdom as opposed to hard data. The assumptions underlying the process model need to be articulated, and the gaps in information supporting these assumptions need to be identified. These assumptions also must be reviewed critically because incorrect assumptions may lead to incorrect conclusions being drawn as to information needs. One objective of the monitoring program then will be to collect data to validate these assumptions. As information is collected and reviewed, the assumptions underlying the model should be validated and, if necessary, the model changed to reflect any changed perspectives.

Identifying the Water Quality Information Required

It is necessary to become aware of other studies that have been undertaken (or currently in progress) on the system of concern or on any similar system. Existing data need to be collected, checked, and put into a common form. These data will include water quality measurements; stream-flow, tidal, or current records; and any biologic data that might be available. Some of these studies may have been published; others may be in the departmental records of various agencies or in local university departments. Once existing data are reviewed, gaps and other information needs will become more apparent.

Articulating Specific Program Objectives

The setting of specific monitoring program objectives commonly will go beyond scientific issues to address management issues. This means that the resource manager needs to be involved in this negotiation. The resource manager often will have only a limited range of intervention options available and will seek to specify objectives that improve the capacity

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to make an appropriate choice between them. The resource manager needs to be clear about how the information to be collected will be used in the decision-making process.

Clear objectives make it possible to design a sampling program to obtain the information required. Developing useful objectives requires practice and experience. Table 2.2 presents a list of some criteria that may be used as a checklist for writing objectives so as to get beyond data to information.

Study Design, Data Analysis Techniques, and Specific Data Requirements

The study design stage is fundamental for ensuring a cost-effective sampling and analysis program. Based on the monitoring program objectives and the agreed-on conceptual process model, general decisions must be made on

- Spatial boundaries
- Measurement scales
- Study duration
- Study type
- Measurement parameters
- Presentation and interpretation of data

This information is used to specify the data requirements to satisfy the monitoring program objectives.

Defining Spatial Boundaries, Measurement Scales, and Study Duration

Once the conceptual process model is agreed on, the spatial boundaries of the system being investigated can be set and questions of measurement scale considered. These considerations are important because inappropriate boundaries may focus the study away from important driving factors. The investigation of disturbances in rivers and estuaries, for example, normally will require the spatial boundaries to be those of the catchment. The pertinent point here is that the people designing the study need to explain the logic for their decisions with respect to the spatial boundaries chosen.

The measurement scales of the monitoring program need to be determined. *Scale* refers to the units of space or time at which the system is observed. What is the level of resolution appropriate to address the issue of concern? Different processes operate at different scales (Table 2.3).

These measurement scale decisions should be made after considering the measurement opportunities at the various possible scales and the likelihood that reliable and valid mea-

TABLE 2.2 Criteria for writing good objectives

Good	Bad
Specific, precise	General, vague
Measurable	Nonmeasurable
Result orientated	Activity orientated
Realistic, obtainable	Unrealistic, unattainable
Meaningful	Trivial
Concise and clear	Elaborate, complex
Understandable	Obscure

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TABLE 2.3. Processes operating within a catchment or water body and scale

Process	Spatial or Temporal Scale
Hydrological (Rainfall-runoff response)	
Urban	Minutes-Hours
Rural	Days
Physical	
Particle settling silt/rocks/clays	Meter/h
Molecular diffusion of oxygen—no mixing	Meter/day
Oxygen diffusion (oxidized sediment microlayer)	One cm/day
Chemical	
Iron oxidation	Minutes
Manganese oxidation	Days
Biological	
Bacterial growth	Hours
Algal growth	Days
Macroinvertebrate community establishment	Months
Mass transport	
Nonpoint sources	Catchment wide
Point sources (mixing zones)	Meters to kilometers

surements can be made. The costs of data collection at the various measurement scales need to be considered. The uniformity over space of the parameters of interest also must be considered. The larger the spatial extent of data collection, the greater will be the heterogeneity or the patchiness of the measures, and the greater will be the number of replicate samples needed to achieve the same confidence in the results. It is essential to choose a measurement scale that is appropriate for the parameter under consideration and then sample at that scale.

Similar problems exist with the decision on the duration required to obtain the information required. For example, given the natural rainfall and hence stream-flow variability, what might be required to get an appropriate understanding of the remobilization, transport, and effects of contaminants in an estuary? The system will need to be sampled in both dry and wet conditions to get some idea of how the system functions. In addition, variables such as the influence of tides and long-term climatic changes also may need to be considered. Contaminants may only be causing sublethal effects, and changes in biota abundance and diversity may only occur over a long period.

The appropriate duration of the monitoring program is an important issue that is often ignored. Few hydrologists are expected to make definitive statements on the quantity of water resources with data sets for as little as 2 or 3 years, yet in water quality studies, such expectations are common.

Study Type

It is necessary to decide if the monitoring program is to have a descriptive focus (i.e., describing the state of a system or some change that has occurred) or whether it is to focus on understanding system processes. This decision will have a major influence on the sampling regime chosen and the path subsequent data analyses take. Study types and their application are summarized in Table 2.4.

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Descriptive studies are concerned with gathering data and conducting analyses to describe the state of a system or predict its state at a future time or under different circumstances. We might wish to determine the current concentration of a particular contaminant and compare it with guideline values or across localities, or we might wish to monitor trends in concentration through time. We also might wish to quantify the relationships between several variables and develop models for the prediction of one or more variables from measurements of the others. These descriptive models can enable us to make informed predictions on the numerical values of unmeasured variables *within the bounds* of the data we have collected.

In studies designed to increase our understanding of processes, we are often interested in establishing causality. Understanding causal relationships among the variables operating in an aquatic system allows us to make informed predictions about the behavior of the system *outside the bounds* of our data and experience. If the monitoring program is to establish causal relationships, the sampling program must be designed to this end from the start. This is often taken to imply controlled manipulation of the system and measurement of the

TABLE 2.4 Study purpose, design, and application

Study Purpose	Design	Application
Reporting of status and trends	Spatial and temporal studies of parameters to obtain summary statistics and trends	Documentation of the state of the system, or predicting state at a future time or under changed circumstances
Measurement of change due to a disturbance	1. BACI (before/after, control/impact) designs in which multiple samples are taken before and after a disturbance from both control locations and the affected site	Detection of environmental change from an activity suspected to cause a disturbance
	2. Inference from change over time in which samples are taken from one or more sites before and after disturbance	
	3. Inference from spatial changes in which no samples can be collected before the disturbance. Other sites are sampled and used for comparison, e.g., upstream of a disturbed site or from similar aquatic ecosystems	
Prediction	Quantify relationships between variables to develop a predictive model relating variables	Development of models for predicting one or more variables from measurements of other variables. Often used to compare reference and test sites to establish if a disturbance has occurred

After Green 1979; Stewart-Oaten, Murdoch and Parker 1986; Welsh and Stewart 1989; Keough and Mapstone 1995,1997; Underwood 1991, 1992, 1994, 1996

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response of the system to that manipulation. Intervention followed by a reproducible outcome, with all other confounding variables held constant, is taken as sound evidence of cause and effect. Manipulative experiments that are conducted in the field can be expensive, and the prerequisite control over all confounding variables may be impossible to achieve.

Another approach is to propose a conceptual process model of the system that links cause and effect and then make observations or measurements that refute or support the model. If our process model predictions fail, we must accommodate the failure by modifying our model. The sampling design should allow the process model to be refuted or supported. This approach is important when we wish to demonstrate that a particular human activity or management intervention will cause a specified effect on the system under consideration.

Whatever the approach, any statistical analysis typically will focus on detecting a difference between observed or measured and predicted events, and sampling must be adequate to provide a rigorous test of predictions.

Selection of Measurement Parameters

There are decisions to be made as to whether driving or causal factors should be measured or whether consequential or resulting factors are more appropriate to address the issue of concern. Or do you need to measure both? If so, why? For example, the result may be excessive algal biomass (indicated by chlorophyll), and the cause may be enrichment with phosphorus or nitrogen.

When selecting parameters to be measured, the following considerations should be borne in mind:

- *Relevance.* Do measurement parameters directly reflect the issue of concern? In our example, the issue of concern is the consequences of an algal bloom, not the concentration of phosphorus in water.
- *Validity.* Do parameters respond to changes in the environment and have some explanatory power?
- *Diagnostic value.* The parameter must be able to detect changes in conditions that occur over the duration of the monitoring program. Do the parameters detect changes early enough to enable a management response, and will they reflect changes due to the manipulation by management?
- *Reliability.* The parameters should be measurable in a reliable and cost-effective way.

Many monitoring programs include measurements of parameters that do not relate to the conceptual process model of the system and therefore have no predictive power. The inclusion of these measurements needs to be justified. Table 2.5 gives a summary of some parameters and the reasons they might be chosen to be measured.

Presentation and Interpretation of Data

To present and convey essential information contained in a data set, data reduction is desirable using summary statistics presented in tables (e.g., means, medians, frequencies, distributions, standard deviations, percentiles, etc.) and graphs (e.g., histograms, box plots, scatterplots, time series, etc.). Decisions on what sort of data set is required for this purpose need to be made before data are collected so that they are adequate for the appropriate analyses to be performed and unwanted data are not collected.

Most interpretations of data are based on statistical analyses designed to infer some characteristic about the population from samples drawn from that population. There are two

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TABLE 2.5 Some measurement parameters and their use

Parameter	Use
Conductivity	Salinity
Algal counts	Algal growth
Chlorophyll	Algal growth
Turbidity	Suspended solids
Coliforms (e.g., E. coli)	Bacteria, viruses, protozoa
Biochemical oxygen demand	Biodegradable organic carbon
pH	Acidity
Trace metals	Potential exposure to organisms and possible toxicity
Pesticides	Potential exposure to organisms and possible toxicity
Macroinvertebrate community structure	Ecosystem health
Fish community structure	Ecosystem health
Stream community metabolism	Ecosystem health

main categories of inferential statistics: estimation and hypotheses testing. *Estimation* is where a value or a range of values is given that approximates the true value (e.g., confidence limits). *Hypothesis testing* is making a judgment about a spatial or temporal difference or cause and effect (e.g., null-hypothesis tests) (Sokal and Rohlf, 1981). All statistical procedures have specific data requirements and assumptions that need to be satisfied. Thus decisions on how data are to be analyzed have to be made before data are collected.

Articulating Specific Data Requirements

Once decisions on the preceding issues have been made, a summary of the specific data requirements needs to be created. Specific data requirements would include location, spatial boundaries, measurement scales, study duration, type of study, parameters to be measured, and techniques to be used for data presentation and interpretation. This summary serves as the concrete instructions for decisions to be made as to the appropriate sampling and analysis program.

Sampling

Sampling involves the collection from a defined population of a portion that represents the population as a whole with respect to some measurement parameter. Sampling can involve the physical collection and removal of a subset of the system for later analysis or the taking an in situ measurement at a selected place and time. The major problem of sampling is representativeness. Errors in accurately representing a water body or population by a subsample can far exceed errors in analyses (Gy, 1986). The aim of a sampling program is to collect useful data that result in information that satisfies the monitoring program objectives with the least cost. Data are not information (see Table 2.1), so if the samples cannot provide the information required, they are not worth the time and expense of collection and analysis.

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Sampling-Site Selection

While preliminary selection of sites may be undertaken from maps and aerial photographs, it is important to undertake a field reconnaissance to check each proposed site. Safe access under all weather and flow conditions should be verified. It is important to test that the water at the site is reasonably well mixed and that a sample does represent the flow in the river or the tidal stretch of the estuary. It is not reasonable to assume that any water body is uniformly mixed. Even fast-flowing mountain streams have been observed flowing "uphill" in eddies next to the bank. The issue of edge sampling versus a transect across a water body also needs consideration. It is important to ensure that weirs, perhaps installed for flow gauging, will not alter the water quality and that samples can be collected above any such structures in free-flowing waters.

It is important to select sites that provide appropriate spatial information. The issue being addressed largely will determine the location of sampling sites.

Characterization of Spatial and Temporal Variability

Obtaining representative samples is difficult because of environmental heterogeneity, both spatial and temporal (Eberhardt, 1978; Kerekes and Freedman, 1989). Such variability will determine the number of sites, number of replicates, and the frequency of collection. High environmental variability and logistical and financial constraints on sample collection and analysis often result in data that are too variable to detect a disturbance or trend.

Types of variability include

- Spatial variability of parameters because of environmental heterogeneity
- Time dependency and temporal and seasonal effects
- Disruptive processes (e.g., floods, droughts, and global warming)
- Dispersal of pollutants

Normally, the design of an ongoing monitoring program will require a short period of intensive monitoring as a reconnaissance study to determine the spatial and temporal variability characteristics of the system. The necessary sampling regime and frequency necessary to provide a representative profile of the system then can be determined for each parameter. Estimating the variability of the system will allow an appropriate number of replicate samples to be taken that will provide the precision required for the data interpretation and analysis.

Three types of sampling regimes are used to account for spatial and temporal variability:

- *Systematic sampling.* Samples are collected at regular intervals in space or time. Sampling sites are selected by personal judgment to best cover the area and may be biased. For example, contaminants in sediments may not be distributed uniformly but may be high near sources and low elsewhere. Sampling would be intensive around these sources. If systematic sampling is chosen, any assumptions need to be stated and validated to prevent criticisms.
- *Random sampling.* This is a requirement of many statistical tests, and there are clear procedures that are not based on haphazard sampling for achieving this (Cochran, 1977; Elliot, 1977). Normally, samples within a site are collected randomly, such that each sample has an equal chance of representing the whole. An equal chance of being selected during sampling is a precondition for valid statistical conclusions. There should be no conscious or unconscious selection of samples. Samples selected in a casual or haphaz-

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ard way are not random. Random number tables or grids with random orientation of axes can be used as a means of selecting random sites. Because of the inherent variability in natural systems, random sampling will require the greatest replication.

- *Stratified random sampling.* A substantial reduction in variability often can be achieved by using this in place of random sampling. The system to be sampled is divided into parts (strata), each as uniform in the parameter of interest as possible. Strata do not need to be of equal size, and the number of samples is usually in proportion to the variance of the strata. For example, for water sampling to obtain nutrient, chlorophyll, and algal measurements, a lake can be divided into two strata (i.e., epilimnion and hypolimnion) and estuaries via salinity gradients. If we are collecting fish in a lake to look at the accumulation of contaminants, such concentrations often increase with fish age. Fish also may be mobile. Fish age (size) becomes the sampling unit, not geographic location.

Stratified sampling is judgmental in that prior information is used to choose strata, but this is probably the best compromise between random and systematic sampling because it is relatively free of personal judgment and reduces replication needs. Sampling precision is improved because uncertainty arises from variations within strata, not differences between strata.

There may be spatial variation *within* a site that needs to be quantified in the monitoring program because otherwise the estimates of the chosen measurement parameters may be imprecise or even inaccurate. For example, in thermally stratified waters, the depth of sampling is important because the concentrations of many measurement parameters (e.g., hydrogen ions, dissolved oxygen, nitrate, hydrogen sulfide, and plankton) can vary greatly between the top and bottom layers. In rivers, samples taken from the edge rather than from midstream are likely to contain quite different amounts of suspended material and therefore different amounts of various compounds bound to the particulate matter. In benthic sampling for biota or for sediments, the habitats or sediment types may vary at a site depending on the behavior of the overlying waters. In formal terms, these different habitats or water types within a site are called *strata.*

There are three options for dealing with such strata:

1. *Sample a particular stratum.* For example, if sandy sediments dominate the substrate at all the study sites, it may be sensible to confine sampling to sandy substrates. However, the inferences drawn are limited to *sandy* substrates within the sites and cannot be generalized to the strata that were not sampled.
2. *Sample each stratum.* For example, at each site in a reservoir or lake we may take water samples from the epilimnion and the hypolimnion (i.e., two strata) but keep these strata separate in the analysis because we are interested in reporting on chemical components in each of these strata.
3. *Divide the sampling effort among the strata.* Here, the goal is to estimate the value of the measurement parameter for each site as a whole rather than for an individual stratum.

Frequency and Timing of Sampling

Timing of sampling might range from intermittent to continuous. The consideration of timing depends on the process under investigation (see Table 2.3). In an algal bloom development, the numbers of algal cells may double every 2 to 3 days. If the question relates to suspended sediments, i.e., nutrient or heavy metal loads, then sampling needs to reflect flow events that transport them into and through the aquatic system.

Some parameters give snapshots of existing condition; some are integrating measures that reflect conditions over the past (x) months. These decisions on time scale need to consider

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- The purpose of the data collection.
- The characteristics of the response of interest. For example, weekly measurements of algal cells might be appropriate during the development of an algal bloom but would be inappropriate for investigating fish. The generation time of the organism might be the critical determinant of time scales.
- The statistical or other tools that will be used to interpret the data. For instance, time-series analysis may require a set sampling interval, and the critical decision is what the interval should be.
- Anything that takes longer to happen than the period over which measurements are made cannot be detected.

Some phenomena, such as the mass transport of substances, are best sampled on a hydrologic rather than a calendar basis. In many water bodies, the greatest input of contaminants can occur during a small number of storm events. Events transport particulate matter, nutrients, heavy metals, pesticides, and other organic compounds into streams and estuaries (Maher et al., 1995). Higher flows resuspend material that has settled out. There also may be seasonal variations relating to grass cover and agricultural land management in the catchment that affect the quantity and quality of the runoff. For these measurements, it is important to sample during high-flow events because a large number of measurements taken during low flow may be relatively unimportant. Event-based sampling is best undertaken using automatic sample collection equipment that is activated by changes in stream height. Decisions have to be made as to whether to use continuous data collection or discrete sampling.

Biological sampling also must take into account the time dependency of an organism's behavior. For example, Magman (1991) reexamined a published study on *Phoxinus eos* and *Phoxinus neogaeus* in which the densities of both fish were reported to be at their highest at or near the shore, the reported conclusion being that both species exploited the same microhabitat. Fish were sampled by trapping over a 16- to 18-h period beginning at 1600 to 1900 h. The initial study failed to recognize that *P. eos* has a diurnal pattern of inshore-offshore migratory behavior. The fish swim in shoals in the inshore zone ($<$0.5 m depth) during the day and migrate to the offshore zone ($>$2 m depth) at sunset when shoals break up into single fish and then go back to inshore zone at sunrise. A shorter interval of sampling (3–4 h) was required to observe this movement. The density of fish offshore seemed to be lower because the fish shoals had broken up. Subsequent studies revealed that the diet of *P. eos* was zooplankton rather than green algal diatoms, indicating that the fish's main food source was offshore and not inshore.

Mathematical formulas are available to calculate the sampling frequency required for a particular study (Sharp, 1971; Montgomery and Hart, 1974); however, these are not in widespread use.

Precision and Replication

It is important to decide on the smallest differences or changes that must be detected because this determines the number of replicates and the precision needed (Norris and Georges, 1986). If a copper guideline concentration is 5 μg/liter, is it important to be able to identify 5.01, 5.1, or 5.5 μg/liter? Note that this is a decision about the ecological or socioeconomic importance of the difference or change that needs to be detected. This is not the same as statistical significance (see Mapstone, 1995).

Once the difficult questions about the size of the differences or magnitude of the trends that must be detected have been answered, then the statistical question of how many replicates are required can be answered by performing the appropriate calculations (see Green,

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1989, 1994; Cohen, 1988; Norris et al., 1992; Sokal and Rohlf, 1995; Keough and Mapstone, 1995, 1997; McBride and Smith, 1997). Most sampling programs will require subsampling within sites and within time periods to improve the precision of measurements.

We need to be clear about what constitutes true replication in a monitoring program because pseudoreplication occurs often (Hurlbert, 1984; Stewart-Oaten et al., 1986; Eberhardt and Thomas, 1991) when it is believed that samples are being replicated when in fact they are not. For example, taking multiple subsamples in a river above and below the site of a disturbance to determine an effect is pseudoreplication. True replication would require sampling at a number of times.

Field Measurements

Some measurements need to be taken directly in the field, such as pH and temperature, because they may alter during transport and storage. Field measurements consist of

- Data measured by field sensors
- Remote sensing
- Field observations
- Real-time measurement by automatic means

It is important to ensure that appropriate calibration of instruments is undertaken. Each measurement should be given a reality check in the form of the question, "Does this seem reasonable in terms of the water body?"

Field measurements of parameters allow cost-effective, real-time investigation of spatial distribution of contaminants. Unfortunately, the precision of such measurements is usually poor because of the low detection limits required for most contaminants, so they are best used as screening tools. Successful in situ monitoring of nutrients has been used, however.

Sample Collection

Decisions have to be made about the most appropriate ways to actually collect data from each site. Some of the choices include

- Collection of a sample by hand for later analysis
- Collection by automatic sampler

If samples are to be collected for later analysis, the sampling device to be used will need to be tested for its efficiency to collect a representative sample. Sample contamination must be avoided when ultratrace contaminants are to be measured.

Green (1979) in his 10 principles of sampling stated the need to "verify that the sampling device is sampling the population you think it is sampling with equal or adequate efficiency over the entire range." This requires specification of what population is to be sampled and what is the likely spatial and temporal variability. The ability of the collecting device to collect an undisturbed and representative sample might need to be tested. Device-related sampling errors cannot be accounted for by statistical methods or replication, and in many cases, they will be undetectable unless specific tests have been undertaken. For example, in rivers, discharge can change by two orders of magnitude, and the effectiveness of sampling devices may change over this velocity range.

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The sampling device should not significantly disturb the environment being sampled or alter the samples taken. The problems in sediment sampling illustrate these difficulties (Blomqvist, 1991). Grab samplers often do not enter sediments perpendicularly, and mixing of sediment layers occurs on closing. Most grabs have jaws that close semicircularly, and sediment layers below the initial penetration are sampled only semiquantitatively. Coring devices must be designed to ensure that easily resuspended surficial material is not washed away (Mudroch and Azcue, 1995).

Quantitative biologic sampling also presents a challenge. If trawling is used to catch fish, the question arises as to whether you are capturing a representative sample of fish. Fish may be avoiding the nets, and only specific species and sizes of fish may be caught by the trawl. Devries and Stein (1991) in their comparison of the efficiency of three devices (i.e., tube sampler, vertical tow net, and Schindler-Patlalas trap) for collecting zooplankton found that there was no best method. Zooplankton consist of a mixture of copepods, cladocerans, and rotifers. Generally, copepods and cladocerans were best collected using the tube sampler, whereas rotifers were best collected using the Schindler-Patalas trap. However, some species were best collected using the vertical tow net. Decisions need to be made as to what organisms need to be collected and the appropriate equipment and procedures to be used. It may be that several devices will need to be used to ensure quantitative sampling of all the required organisms.

Sampling devices should be tested under controlled conditions to determine if they quantitatively collect the sample of interest. In lieu of this, studies that have compared the efficiency of sampling devices and document the limitations of various alternatives should be consulted (e.g., water samplers: Harris and Keffer, 1974; sediments: Blomqvist, 1991; Schneider and Wyllie, 1991; Mudroch and Azcue, 1995; biota: Devries and Stein, 1991). Using this information, a choice of sampling device can be made based on the matrix to be sampled and the unique conditions at the chosen sampling site. Checks should be made that sampling devices are not made of materials that will contaminate samples (Batley, 1989).

Note that sampling errors may occur by the device being in contact with media other than the sample of interest. For example, when collecting subsurface water samples for hydrocarbon analysis, the sample collection device should be closed as it enters the water, or it may pick up hydrocarbons from the surface microlayer.

Sample Preservation and Storage

In most cases, samples need to be stored prior to analysis. In all cases, clear and distinctive sample labeling is important. Precautions must be taken to ensure that samples do not become contaminated or change after collection before being analyzed. Once the samples have been collected, it usually will be necessary to preserve them to retard physical, chemical, and biological changes. Protocols must specify the appropriate sample container and preservation technique. Preservation choices will vary depending on the analyte to be measured. Some possible changes and preservation/storage procedures are listed in Table 2.6.

Considerations for preservation and storage include selection and decontamination of sample containers, selection of a preservation technique, and the acceptable time interval between sample collection and analysis. Choices will vary depending on the parameter to be measured. Standards exist to provide guidance in this area (e.g., AS/NZS, 1998).

The composition of the sample container may affect the stability of the sample through adsorption and reactions of constituents with container walls. For example, adsorption of phosphorus and trace metals from water samples occurs with glass and plastic bottles, whereas gases may diffuse through plastic bottles (Batley, 1989; Maher and Woo, 1999).

Contamination of samples may occur from contaminants leached from containers, e.g., trace metals from glass or organics from plastics (Ahlers et al., 1990). Bacteria on

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TABLE 2.6 Changes and preservation/storage procedures for physical, chemical, and biological samples.

Change	Preservation Techniques
Physical	
Adsorption/absorption losses	Inorganic: acidify Organic: add solvent
Volatilization losses	No head space
Diffusion losses	Choose correct container type and cap liners
Chemical	
Photochemical decomposition	Use dark containers
Precipitation	Lower pH, avoid use of chemicals which cause precipitation (e.g., sulfates)
Biological	
Microbiological	Reduce pH, add bactericide e.g., for sulfide add zinc acetate Freeze
Cell degradation	Freezing, add fixing agent e.g., formaldehyde, ethanol

After, Maher, Cullen, and Norris 1994.

container walls may use nutrients from the solution. The caps of containers often contain inserts (e.g., cardboard, cork, or rubber) that may cause contamination, and these should be removed. Containers need to be cleaned rigorously to remove possible contaminants and should be stored in a manner to prevent contamination. Containers should be chosen such that contamination of the sample is avoided. For example, if pesticide analyses are to be undertaken, plastic bottles and caps should not be used because of the presence of plasticizers, which even after container cleaning may be leached by the sample.

Normally, to prevent chemical and biologic changes, samples are frozen or a chemical is added. Freezing ($-10°C$) reduces but does not eliminate biologic activity in samples. All biologic activity is eliminated effectively only at $-40°C$. Chemicals such as chloroform and mercuric acetate also have been used to prevent biologic activity. Acid often is added to prevent adsorption of metals to containers (and precipitation of insoluble salts; Batley, 1989), whereas solvents (e.g., hexane) are added to prevent losses of organic compounds such as polycyclic aromatic hydrocarbons.

Chemical preservatives should be avoided, if possible, because they may contaminate samples or interfere in chemical or biologic analysis. For example, mercury can interfere in the colorimetric determination of phosphate (Maher and Woo, 1999). If preservatives are used, their contribution to the measured parameters also should be taken into account.

Even if a sample is frozen or a preservative is added, samples can only be stored for a finite time. In some cases this period may be years (e.g., phosphorus in seawater) but in other cases may be much shorter (e.g., 6 h for *E. coli*). This needs to be determined before samples are collected, and protocols must be designed to ensure that samples are analyzed before a significant change in composition occurs.

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Quality Assurance in Sampling

If samples are to be the basis for later legal proceedings, the following areas are likely to be under challenge:

- Exactly where was the sample taken from?
- Was the person taking the sample competent to do so?
- How was the sample labeled to ensure that no possibility of mixup or substitution occurred?
- Was there any possibility of contamination of the sample during collection?
- Did the sample deteriorate after collection?
- Was sample storage adequate to avoid losses?

Once sampling sites have been determined, their locations must be specified accurately, preferably using a geographic positioning system. Where transects are sampled, the location range should be specified if this is within the precision of the positioning instrument. The exact location of sampling sites and any subsites must be recorded in the sampling protocol. Field notebooks must contain an accurate description of where samples were collected to allow cross-checking with those specified in the sampling protocol. Taking note of the time when samples were taken (standard or daylight savings time) is an obvious but frequently overlooked requirement of rigorous sample definition. Where automatic sampling devices are used, their timing mechanism must be calibrated to ensure that samples are acquired at the specified intervals. This is especially critical where hydrologic or other conditions result in significant short-term concentration variations.

Transfer of results to a database should be automated where possible, with checking of the printout against the field and analysis register. Validation of entries can be achieved by electronic screening against expected range, other analytes for the same site, and sampling date and field measurements.

Chain-of-custody documentation is the formal means of recording the people who have been in contact with a sample from collection to analysis (Table 2.7). This is mandatory in legal cases.

A field-sampling sheet is mandatory if parameters are to be measured in the field. All field data are recorded on this sheet, as well as instrument calibration data. All field records must be completed before a sampling site is left. Any observations or information on the conditions at the time of sampling that may assist in interpretation of data should be entered on the field-sampling sheet or in a field notebook. This information may explain unusual data, which may have been attributed to problems in sampling or analysis.

All equipment and field instruments should be kept clean and in good working order, with records kept of calibrations and preventative maintenance. Records should be kept of all repairs to equipment and instruments and of any incidents that may affect the reliability of equipment.

Quality Control in Sampling

The objective of a field quality control program is to control sampling errors to acceptable levels. Thus procedures are designed to prevent, detect, and correct problems in the sampling process and to statistically characterize errors through quality control samples.

Major errors to be avoided are faulty sampling device operation, incorrect sample collection and labeling, and sample changes before measurement (e.g., contamination or chemical/biological changes).

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TABLE 2.7 Chain-of-Custody documentation

Process step	Quality Assurance Procedure
Field sampling	Field register of sample number, site, type/technique, time, date, technician, field data sheet
Sample storage and transport	Field register of transport container number and sample numbers, time, date
Laboratory receipt of samples	Laboratory register of transport container number and sample numbers, time, date
Laboratory storage of samples	Laboratory register of storage location, type, temperature, time, date
Sample preparation	Analysis register of sample (laboratory) number, pretreatment, date, technician
Sample analysis	Analysis register of instrument, calibration, technician, standard method, date, result

Sampling Protocols

Sampling errors can be minimized by ensuring that correct procedures have been followed during field sampling, transport, and storage. Sampling protocols (procedures to be followed in the collection, labeling, transport, and storage of samples and ancillary field data required) need be written and adhered to. Protocols will be matrix- and constituent-specific and will determine the sample collection device, type of storage container used, and preservation procedures.

The protocol also will specify the types and numbers of quality control samples to be taken. This will require consideration of the nature of errors to be assessed (both systematic and random) and the accuracy desired. Sources of error include reaction with sample or sample container, contamination (sampling device and containers), chemical and physical instability, and biologic changes.

Training of the sampler to use sampling equipment is also specified within the protocol. Attention should be given to anticipating problems in the field. Sample containers may be lost, and sample volumes may be low. Do we include foreign objects? What criteria do we set for rejecting foreign matter? What do we do if sites cannot be sampled? Adherence to chain-of-custody procedures, whether or not required externally, is necessary if sample integrity is to be defensible.

Before a sampler is permitted to do reportable work, competence in sampling and taking field measurements should be demonstrated. At a minimum this would include a demonstration of adherence to protocols and evidence of not contaminating samples and the ability to calibrate field instruments and make field observations.

Prevention of Sample Contamination

One of the major challenges of sampling is the prevention of contamination. Basic precautions to avoid contamination that must be included in protocols include

- Field measurements should be made on a separate subsample of water.

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- Sample containers must be cleaned.
- Only the sample bottles recommended for each analyte should be used.
- Container lids should be checked for liners that may cause contamination.
- Containers used for other purposes should be discarded.
- The insides of containers and lids should not come in contact with hands or objects.
- Sample containers and filter units should be kept in a clean environment away from dust, dirt, fumes, etc.
- Preservatives should be tested for contamination.
- Attention should be paid to not cross-contaminating samples when adding preservatives.
- Sample containers used for collecting samples for microbiological analyses must be sterilized.
- Sample collectors should keep their hands clean.

Where the possibility exists of the introduction of contamination into the sampling process, a blank should be devised to detect and measure the contaminant (Lewis, 1988). There are various types of blanks:

Container blanks. Prior to sampling, containers of each type to be used for sampling (about 1 in 10) are selected at random and filled with high-purity deionized water or seawater and preserved in the same manner as field samples. Analysis of these blanks is used to detect contamination during container preparation.

Equipment blanks. Water/solvent is used to rinse the sampling equipment between samples, and this is analyzed to determine contamination introduced through contact with sampling equipment and or sampler.

Trip blanks. These are samples that are similar to the sample collected (e.g., high-purity water or seawater) in which the analyte of interest is at background or low levels. They are used to assess gross cross-contamination of samples during transportation and storage.

Field blanks. One in every 10 samples should be a blank prepared by filling sampling containers in the field with high-purity deionized or seawater and, if necessary, adding preservative. This allows estimation of contamination from the environment in which sample containers are being filled.

Field filter blanks. Blanks should be prepared by passing a sample of high-purity deionized or seawater through a precleaned filter. A preservative may have to be added to the deionized or seawater sample in the field. This allows estimation of contamination by filtration in the field.

Often we are not able to avoid contamination but rather seek contamination levels that are stable. Contamination outside our acceptable limits indicates new sources of contamination.

Reproducibility and Accuracy

Three procedures are commonly used to ensure reproducible and accurate sampling:

Duplicate samples (splits). Duplicate samples are obtained by dividing one sample into two or more subsamples. This allows the magnitude of errors (contamination, random, and systematic) occurring from sampling to sample analysis to be determined.

Replicate samples. Two or more samples are collected simultaneously to establish the reproducibility of sampling.

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Recovery of known additions. Spiking of subsamples in the field with a known amount of the analyte of interest and subsequent measurement will allow the detection of change.

Quality assurance/control is a partly reactive process. If changes in samples are detected by spikes and blanks, a specified procedure is required to determine and rectify the problem and resample if necessary.

Field Occupational Health and Safety

Hazards and risks involved in field sampling need to be identified and documented on a preliminary site visit. The major issues could include

- Access. Can samplers reach the site in safety?
- Can a sample be taken safely? Is the water fast-flowing? Is a boat to be used? Is there safe boat access? Is the site prone to flash floods? Is the bank stable? Are tidal changes likely?
- Will samplers be exposed to toxic or other hazardous substances?
- Will samplers be exposed to any pathogens, e.g., Ross River virus, malaria, etc.?
- Will any potentially dangerous fauna be encountered, e.g., spiders, ticks, snakes, leaches, crocodiles, sharks, pigs, etc.?
- Are weather conditions likely to endanger personnel? In alpine areas especially, weather patterns are extremely variable.

Personnel who are to conduct sampling should be physically and mentally able to carry out field work. For example, if problems do occur (such as falling into a water body), sampling personnel must be physically fit enough to survive without assistance (although samplers should never work alone in the field). It is necessary that samplers working near water be able to swim. They also may need to be able to climb up river banks. Proper professional practice requires that risks be reduced as much as possible and that samplers not be required to operate in conditions where they are unsafe.

All staff must be appropriately trained as part of the formal risk-minimization strategy. Training will include

- Familiarization with environmental hazards that may be encountered
- Familiarization with sampling protocols (e.g., sampling procedures, chain-of-custody considerations, etc.)
- Use of sampling equipment
- Qualification to drive appropriate vehicles (e.g., off-road four-wheel-drive vehicles, bikes, tractors, or boats)
- Familiarization with safety procedures
- Qualification in advanced first aid

Actions to reduce risks include

- *Choose safe sites with safe access.* Potential sites should be visited and checked after tentative selection from map surveys. They should have reasonable access; be free of dangerous animals or prickly or poisonous plants; have no steep, slippery, or unstable banks; and should not be prone to rapid flooding or tidewater rise without warning.

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- *Wear appropriate clothing.* Weather forecasts for an area to be sampled need to be obtained. Staff should be prepared, for example, to wear raincoats if there is likelihood of rain, warm clothing if it is cold, hats and sunscreen at all times, and footwear with a good grip on wet rocks (do not go barefoot, risking injury from sticks or broken glass), and extra clothes and a towel should be taken in case someone falls into the water.
- *Take appropriate safety gear and a first aid kit.* Lifejackets should be worn when sampling near deep water with poor footing or from a boat. Rubber gloves are essential when handling chemicals or polluted water for anyone who has an open or bandaged wound or if the water quality at the site is unknown. A fully stocked first aid kit should be taken to the monitoring site, and ideally, someone in the monitoring party should have first aid training.
- *Maintain contact with help, and never sample alone.* Work with at least two others, and stay in contact with someone who can raise an alarm. Carry a mobile telephone, if available, or at least keep coins or a phone card to be able to make a telephone call. In remote areas, carry maps, compass, mirror, and matches, and inform a responsible person of intended movements. Written procedures must be in place indicating how emergency services are to be accessed.
- *Never go into deep water.* If sampling has to be done in deep water, use of an appropriate boat with the necessary safety equipment (e.g., life jackets, flares, etc.), if required. Sample from a bridge or use a cableway if installed at the site.
- *Avoid contact with contaminated water.* Carry drinking water; do not drink from the source being monitored. Always wear gloves when water quality at the site is unknown and in particular when collecting samples where the presence of algae, pathogenic organisms and/or toxins can be expected (blue green algae can cause skin and eye irritations). Wash hands after monitoring and before eating. Treat all bacterial cultures as pathogenic.

Cost-Effectiveness of the Sampling Program

It is desirable that the cost of sampling programs be as low as possible to meet the stated monitoring objectives. Cost-effectiveness considerations involve trade-offs between the data required for statistical analyses and the cost of data acquisition. It is necessary to determine all the resources and associated costs required, thereby ensuring that the study can be carried out. Costs of data acquisition are determined by the number of sampling sites, the number of sampling occasions, replication, cost of sample collection (e.g., staff, transport, and consumables), cost of analyses, and the cost of data handling and interpretation.

There is extensive information available concerning the optimization of sampling programs with regard to precision and cost (Ebehart, 1976; Montgomery and Hart, 1974; Ellis and Lacy, 1980; 1985; Lettenmaier et al., 1984.

LABORATORY ANALYSIS

Choosing an Analytical Technique

Appropriate chemical and biologic analysis procedures can be determined via reference to accepted published procedures such as *Standard Methods for the Examination of Water and Wastewater* (APHA, 1998) or U. S. Environmental Protection Agency (EPA) sampling

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and analysis methods (Keith, 1991). The choice of an appropriate analytical method is based on three considerations:

1. *The range of concentrations of the analyte that need to be determined.* Detection limits are method-specific, and the lowest concentration of interest will need to be specified.
2. *The accuracy and precision required.* All results are only estimates of the true value, and the greater the accuracy and precision required, the greater are the analytical complexity and cost.
3. *The maximum period between sampling and analysis.* Real-time analysis may be required given the use the data have to be put to.

Before analysis is undertaken, data users should check that the laboratory has the appropriate equipment, expertise, and experience to undertake the analysis chosen. In addition, an adequate quality assurance program is needed.

Quality Assurance in Analysis

The objective of a laboratory quality assurance program is to control subsampling and analytical measurement errors and produce data for the user that are acceptable. Thus procedures are designed to prevent, detect, and correct problems in the measurement process and to statistically characterize errors through quality control samples.

Traceability of Results

The record system needs to provide a traceable pathway covering all activities from receipt of samples to disposal and allow retrieval, for a period of at least 3 years, of all original test data within the terms of registration. Therefore, for all analyses, the following are required:

- Unique sample identification
- Identification of analyst
- Identification of equipment used
- Original data and calculations
- Identification of manual data transfers
- Documentation of standards preparation
- Calibration solutions used
- Certified reference materials used

When samples are delivered to the laboratory for analysis, it is essential that the samples are signed into the laboratory and given a unique identification code. This ensures the integrity of the sample from collection to final analysis. Where possible, data should be transferred automatically from the instruments to a database to prevent any transcription errors.

Laboratory Facilities, Human Resources, and Protocols

The laboratory environment must be clean and checked regularly for airborne contamination that can enter through air-conditioning systems or be generated by users of the labora-

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tory. Deionized water is the most extensively used reagent in the laboratory and must be maintained to an appropriate standard. The conductivity of the deionized water should be monitored regularly, and the absence of contaminants should be confirmed on a regular basis. To prevent contamination, deionized water should not be stored.

All equipment should be kept clean and in good working order, with records of calibrations, preventative maintenance, all repairs, and any incidents that may affect equipment reliability.

All staff undertaking analyses must be technically competent and skilled in the particular techniques being used and should have a professional attitude toward their work. Staff will need to be trained in all aspects of the analyses being undertaken.

Laboratories undertaking analyses need to fully document the methods used. The methods must be described in sufficient detail that an experienced analyst, unfamiliar with a particular method, can follow the procedure and obtain acceptable results

The importance of strict adherence to analytical protocols and an appreciation of the need for rigorous quality assurance and control in the laboratory are far more thoroughly appreciated than in the field. Proper laboratory practice is codified in the requirements of registration authorities. Accredited laboratories will be familiar with the effort required to ensure a credibly performing facility.

Before analysts are permitted to do reportable work, their competence to undertake laboratory measurements must be demonstrated. At a minimum, this would include demonstrating adherence to a written protocol and evidence of not contaminating samples, ability to work safely in the laboratory, and producing data that are of acceptable accuracy and precision.

Quality Control in Analysis

All laboratories must have a formal system of periodically reviewing the technical suitability of analytical methods. If standard methods are used, it is not enough to quote the standard method. Any variation of the standard method must be technically justified and supported by a documented study on the effects of the changes.

The principal indicators of data quality are their bias and precision. *Bias* is a measurement of systematic error and can be attributed to either the method or the laboratory's use of the method. *Precision* is the nearness with which measurements of a given sample agree with each other. When combined, bias and precision are expressed as *accuracy,* i.e., the nearness of the mean of a set of measurements to the true value. Data can be referred to as being accurate when both the bias is low and the precision is high. Techniques used to ensure the quality of measurement processes in terms of accuracy and precision and to detect contamination are given below.

Analysis of Certified Reference Materials

Certified reference materials are materials of a known concentration with a similar matrix to the sample being analyzed that have been analyzed comprehensively such that their composition can be certified reliably. The accuracy of laboratory methods and procedures can be established by comparison of results with the certified values. Results within the confidence limits specified for the certified reference material are deemed acceptable. The National Institute of Science and Technology (United States), the National Research Council (Canada), the International Atomic Energy Agency (Europe), the Institute for Reference Materials and Measurements (Belgium), and the National Institute of Environmental Standards (Japan) provide a comprehensive range of certified reference materials.

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Independent Methods Comparison

Analytical inaccuracies can be determined by the analysis of samples by two or more independent methods. For the methods to be independent, they must be based on different measurement principles. For example, the determination of iron in water can be ascertained by atomic absorption spectrometry or molecular absorption of a colored iron complex. Bias in methods (i.e., interference or insensitivity to chemical species) can result in different concentrations being obtained by different methods.

Recovery of Known Additions

By spiking a sample with a known amount of analyte, it's possible to estimate the recovery and hence the accuracy of the method used. It is assumed that any interference or other effects biasing the method will affect the spike in a similar way to the analyte in the unspiked sample. Note that single-point standard addition assumes a linear concentration dependence and should be avoided. Multiple standards are required to confirm this linearity. Hence good recoveries of the spike indicate accurate methods. This approach may be invalid if

- The chemical species added are different from the native chemical species in the sample. An example is the spiking of marine biological samples with AsO_3^- when arsenic is present as arsenobetaine ($(CH_3)_3As^+CH_2COO^-$).
- An interfering species is dependent on the relative concentration of the analyte and the interferent, but addition of a spike changes this dependency.
- An interference is constant regardless of the analyte concentration. Recoveries can be quantitative, but analysis of the original analyte in the sample may have large errors.

Calibration Check Standards

The linearity of calibration plots must be verified initially by the use of multiple standards. Standard curves can then be verified daily by analyzing at least one standard within the linear range. This will ensure that the instrument is giving the correct response and reduce the likelihood of concentrations in samples being under- or overestimated.

Blanks

Blanks should be incorporated at every step of sample processing and analysis. However, only those blanks which have been exposed to the complete sequence of steps within the laboratory usually will be analyzed unless contamination is detected in these fully integrative blanks; i.e., blanks incorporated at intermediate steps are retained for diagnostic purposes only and should be analyzed when problems occur so as to identify the specific source of contamination. In principle, only field blanks need to be analyzed in the first instance because they record the integrated effects of all steps. However, a laboratory normally will wish to test the quality of its internal procedures independently of those in the field, so laboratory procedural blanks usually will be included in a suite for analysis in addition to field blanks.

Blanks cannot be used to detect analyte loss. They are useful only to detect contamination. They are particularly useful in detecting minor contamination, where the superimposition of a small additional signal on a sample of known concentration may not be evident in the statistical evaluation of analytical data; i.e., blanks are more sensitive to contamination.

If any blank measurement is greater than 3 standard deviations of the mean, or if two of the three successive blanks measurements are greater than 2 standard deviations of the mean, discontinue analyses and correct the problem.

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Replicate Analyses

Duplicate analyses of samples are used for assessing precision. At least 5 percent of samples should be analyzed in duplicate.

Quality Assessment of Analyses

Quality assessment is the process using internal and external measures to determine the accuracy and precision of the analytical data being produced. Techniques used to assess the quality of measurement in terms of accuracy and precision and detect contamination are given below.

Internal Evaluation Samples

These are samples with a known analyte concentration prepared in the laboratory but independent of the analyst or obtained from an outside source (e.g., certified reference materials). The acceptable range of measurement (recovery and precision) needs to be established, and the analyst is expected to be within this range on all samples tested.

Proficiency Testing Programs (Interlaboratory Comparisons)

Interlaboratory comparison of unknown samples is useful for testing instrument calibration, performance, and operator skills, and accreditation authorities frequently sponsor these programs. Generally, only a modest degree of sample preparation is required, probably to restrict the range of sources of variance between laboratories.

An individual laboratory will compare its results with the consensus values generated by all the laboratories participating in the program to assess the accuracy of its results and hence its procedures. However, it should be noted that the consensus values can be wrong. There should be a known result from the authority conducting the proficiency program.

Results within the confidence limits specified for the unknown samples are deemed acceptable.

Performance Audits

Performance audits are unscheduled checks in which deviations from standard operating procedures and protocols are identified and corrective action taken.

Laboratory Occupational Health and Safety

Occupational health and safety requirements for analytical laboratories are provided in the relevant standards. In Australia, Australian Standard AS 2243-1982 sets out the requirements and recommended procedures for safe working practices in laboratories.

Practical guidance on safety procedures and information needed to perform practical scientific work and practices in the laboratory are available in *Laboratory Safety Manual: An Essential Reference for Every Laboratory* (Haski et al., 1997).

The hazards and risks associated with laboratory work need to be identified and documented. The major issue is, Will staff be exposed to toxic or other hazardous substances or be placed in a position of potential physical danger?

All staff must be appropriately trained as part of the formal risk-minimization strategy. Training will include familiarization with protocols (analysis procedures, safe handling procedures, disposal procedures, chain-of-custody considerations, etc.), use of laboratory equipment, familiarization with safety procedures, and qualifications in advanced first aid.

Proper professional practice requires that risks be reduced as much as possible and that staff not be required to operate in conditions where they are unsafe. Actions to reduce risks include

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- Wearing appropriate clothing. Staff should wear appropriate clothing and footwear to protect against accidental chemical spills.
- An appropriate first aid kit should be in close proximity to where analyses are being undertaken.
- Training of laboratory staff in first aid procedures.
- Maintaining contacts with help and never working alone. Work with at least two others, and stay in contact with someone who can raise an alarm. Written procedures must be in place indicating how emergency services are to be accessed.

Data Analysis and Management

Decisions about specific data requirements and data presentation and interpretation are made as part of the general study design. It is essential that appropriate statistical tools are available and that the person(s) undertaking the analysis of data has sufficient training to do so. There are many pitfalls in data analysis, and an awareness of the assumptions underlying statistical procedures and the limitations of the statistical package being used is required.

Data Management

Need for a Data Management and Reporting System. In view of the substantial investment in data collection, it is important that data are archived in a systematic and easily accessible manner. The sheer magnitude of data accumulated after just a few years of monitoring dictates the adoption of computer-based data management systems as the basis for data storage and retrieval.

Types of Data Management Systems. A number of databases have been developed, often associated with the operational systems of particular authorities (e.g., water supply, wastewater management, and storage management). The difficulty with these systems has been the cost of updating them to use new computer technologies and their incompatibility with other databases, resulting in difficulties of transferring data.

There has been substantial growth in electronic transfer and online access to data in recent years, requiring standardization of databases. There are a number of commercially available databases, e.g., dB4, dB5, ACCESS, and FoxPro. The wide industry adoption of these databases and the suppliers' commitment to their periodic upgrading to exploit new computer technologies and software developments ensure their ongoing relevance and utility. The choice of a particular database depends on the types and intended use of the data and the types and compatibility of the computer hardware and software.

System Design Considerations. The needs of the user are the most important feature in the design of a water quality database. A data management system should have

- Reliable procedures for recording results of analyses or field observations
- Procedures for systematic screening and validation of entered data
- Secure storage of information
- A simple retrieval system
- A simple means of analyzing data
- Flexibility in terms of accommodating additional information, e.g., analytes and sites

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The following attributes need to be considered at the design stage:

- *Scope of data to be stored.* Sources, sample numbers, sample types, sites, time/date, field, descriptive notes, analytes, number of records.
- *Multiple sources of data.* Validation and standardization procedures, transfer formats, and harmonization.
- *Quality assurance, quality control, and quality assessment.* Validation procedures and chain-of-custody documentation.
- *Documentation.* Laboratory standard methods and validation procedures.
- *Access to data.* Online real-time and online retrieval.
- *Analysis.* Descriptive, trends, regression, and multivariate statistics.

The record system needs to provide a traceable pathway covering all activities from receipt of samples to disposal to ensure the integrity of the sample from collection to final analysis with respect to the variables of interest. All data need a unique identification code. Data entry protocols need to be developed to ensure that the entry of data is accurate. Data from instruments should be transferred automatically to the database where possible to prevent transcription errors. Storage of chain-of-custody documentation ensures that these questions can be answered.

The *harmonization* of data refers to the ability to compare or use two or more data sets concurrently. For example, if nutrient loads are to be calculated, nutrient concentrations and flow data must be collected at the same location at the same time.

Reporting and Information Dissemination

Monitoring programs should clearly identify the end users' needs and their information requirements. A reporting system is required that efficiently and accurately transmits this information.

Monitoring programs normally provide information to a number of different clients. These clients may want data in different forms and on different time scales. It is important to identify the various users and work with them to articulate their data needs. Water users may be concerned with failure of particular measurements to be within safe operating limits and will seek urgent advice when numbers depart from this range. Water managers' needs are similar to those of users, but water managers also will seek diagnostic information to identify where and when interventions may be needed to rectify situations. Environmental managers may be concerned with providing a report on the state of a water body that summarizes conditions over one or more years and identifies trends. Resource managers may be interested in the effects of activities in catchments or remedial works on water quality. Community groups may wish to provide feedback on the state of the waters to help communities understand their land and water resources.

User(s) will request information over different time frames depending on the use and application of the information. In a monitoring program supplying information on the quality of drinking water, information will need to be transmitted rapidly to the user because of the obvious ramifications. Often information used for long-term planning will not be required as urgently as this, but it will still be required within a certain time frame. In both short- and long-term monitoring programs, a realistic time frame in which to report the information must be developed. Factors that need to be considered include the duration of the study, legal requirements of the study, sampling frequency, and laboratory turnaround time and data entry and verification.

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The scope and format of reports will be a function of the client or community groups to which they are targeted. Types of reports include scientific journals, conference papers, technical reports, guidelines, and manuals. Avenues for dissemination include the Internet, compact discs, videos, industry and professional association seminars and workshops, abstracting services, community group presentations, and media articles.

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CHAPTER 3
IN SITU MEASUREMENT OF PHYSICOCHEMICAL WATER QUALITY PARAMETERS

Ian D. McKelvie

INTRODUCTION

A number of physicochemical measurements can be made on site when collecting samples for other analyses of nutrients, metals, organic, or major ions. These in situ measurements may include pH, electrical conductivity, temperature, dissolved oxygen concentration, redox potential, and turbidity or irradiance. While the choice of these parameters is to some extent an artifact of the relative ease of their measurement, each of these parameters provides vital information on the state and/or behavior of a water body. As such, they often may be used as gross measures of water quality or to provide an early warning of an excursion from normal conditions because of contamination, illicit discharge, or some measurable ecological or biological change. However, a single or even several different in situ parameters seldom would provide sufficient information about the sorts of changes described earlier and would be used in conjunction with sampling and analysis of other more specific chemical or biological parameters.

The advantages of in situ measurements are that they obviate the need to collect, transport, and store samples pending analysis and that they provide an instantaneous indicator of the prevailing physicochemical conditions. For this reason, increasing use is made of on-site instrumental techniques for monitoring simple water quality parameters, and there is active research and development into new sensors and techniques.

pH

Significance Many processes in natural waters are either dependent on or alternately are manifest by some change in the hydronium ion (H_3O^+ or H^+) concentration. For example, the surface charge of colloids in natural waters and hence their ability to coagulate or sorb ions will depend on the hydronium ion concentration, as will the solubility and speciation of dissolved ions, such as dissolved carbonates. The hydronium ion concentration commonly is expressed as the pH value:

$$\mathrm{pH} = -\log_{10}[\mathrm{H}^+]$$

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However, in all but dilute solutions (total ionic strength < 0.1; total ionic strength $I = 1/2C_I z_i^2$, where C is concentration in mol/liter and z is the ionic charge), the hydronium ion concentration should be replaced by the *activity* $a_{H}{}^{+}$, and it is this quantity that is measured experimentally. Thus

$$\text{pH} = -\log a_{H}{}^{+}$$

The logarithmic pH scale is defined by the ionization constant for water, $K_w = 1 \times 10^{-14}$ at 25°C, such that

$$(-\log a_{H}{}^{+}) + (-\log a_{OH}{}^{-}) = -\log K_w = 14$$

At 25°C, a pH value of 7 is considered neutral, whereas values higher than 7 are basic and those lower than 7 are acidic, respectively.

The pH value of a natural water sample reflects the natural buffering by dissolved carbonates that originate either from the dissolution of atmospheric carbon dioxide or from the weathering of calcareous rocks in the stream catchment. In most natural waters the pH typically ranges between 6.5 and 7.5, whereas in marine waters the presence of borates may extend this range to approximately 8.3.

Thus a measured pH change provides a very useful indication that some biogeochemical effect has caused the buffer capacity of a water body to be exceeded. Possible causes of a decrease in the measured pH include the intentional or accidental release of strongly acidic waste into a stream; the influence of acid rain, bacterial nitrification, or sulfate reduction; and the release of acid mine drainage water. Increases in pH may be caused by accelerated algal growth, such as that which may occur during an algal bloom (when pH can exceed 10) and denitrification (Table 3.1).

TABLE 3.1 Effects of Some Biogeochemical Processes on pH and Alkalinity in Closed Systems

Process (forward reaction)	Alkalinity	pH change
Photosynthesis and respiration:		
$CO_2 + H_2O \rightarrow$ "CH_2O" $+ O_2$	None	None
$106CO_2 + 16NO_3{}^- + HPO_4{}^{2-} + 122H_2O + 18H^+ \rightarrow C_{106}H_{263}O_{110}N_{16}P + 138O_2$	Increase	Increase
Algal protoplasm:		
$106CO_2 + 16NH_4{}^+ + HPO_4{}^{2-} + 108H_2O \rightarrow C_{106}H_{263}O_{110}N_{16}P + 107O_2 + 14H^+$	Decrease	Decrease
Nitrification:		
$NH_4{}^+ + 2O_2 \rightarrow NO_3{}^- + H_2O + 2H^+$	Decrease	Decrease
Denitrification:	Increase	pH < 6.3, pH increases; pH > 6.3, pH decreases slightly
$5CH_2O + 4\,NO_3{}^- + 2H^+ \rightarrow 5CO_2 + 2N_2 + 7H_2O$		
Sulfate reduction:	Increase	pH < 6.3, pH increases; 7.0 $>$ pH > 6.3, pH constant; pH > 7, pH decreases
$SO_4{}^{2-} + 2CH_2O + 2H+ \rightarrow H_2S + 2H_2O + 2CO_2$		
Sulfide oxidation:	Decrease	Increase
$HS^- + 2O_2 \rightarrow SO_4{}^{2-} + H^+$		

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Measurement. The pH of natural waters is measured most commonly by potentiometry using a glass electrode and a suitable reference electrode. The glass electrode consists of a thin glass envelope filled with HCl and containing a reference electrode (Ag/AgCl or calomel). For convenience, the glass and reference electrodes are commonly manufactured as a combination electrode, i.e., in the same electrode probe body. The potential difference of the two electrodes is measured using a high-input-impedance voltmeter or potentiometer calibrated in pH units. The potential difference between the reference and glass electrodes is a function of the hydrogen ion concentration and is related by the Nernst equation; that is,

$$\mathrm{pH}_S = \mathrm{pH}_B \pm \frac{F\,(E_S - E_B)}{2.303RT}$$

where pH_S is the measured sample pH, pH_B is the pH of a calibration buffer, F is the Faraday's constant (96,487 $\mathrm{J \cdot V^{-1} \cdot mol^{-1}}$), E_S is the measured sample emf (V), E_B is the calibration buffer emf (V), R is the gas constant (8.3143 $\mathrm{J \cdot K^{-1} \cdot mol^{-1}}$), and T is the temperature (K). The expression $F/(2.303RT)$ is called the *Nernstian slope* and varies according to the temperature, as shown in Fig. 3.1*b*.

Calibration of a pH electrode and meter always should be performed prior to measurement of pH in the field and involves

1. Using a buffer of standard pH to set the *intercept* control (also called *asymmetry, standardize,* or *set buffer*) such that the response curve is shifted so that at pH 7 the cell emf is 0 mV (see Fig. 3.1(*a*).
2. Adjusting the *slope* control (also called *temperature* or *offset*) with a second buffer (e.g., pH 4) by rotating the slope of the response curve about the isopotential point so that the influence of temperature is compensated.

Calibration buffers should be chosen so that they span the range of likely sample pH values. Some suitable primary standards for buffer solutions are listed in Table 3.2. Buffers should be prepared from analytical-grade reagents, but for maximum accuracy, certified buffer materials from the National Institute of Standards and Technology (NIST) should be used.

The glass electrode is highly selective toward the hydronium ion activity, and the only major interference is from higher concentrations of sodium ions (the so-called sodium

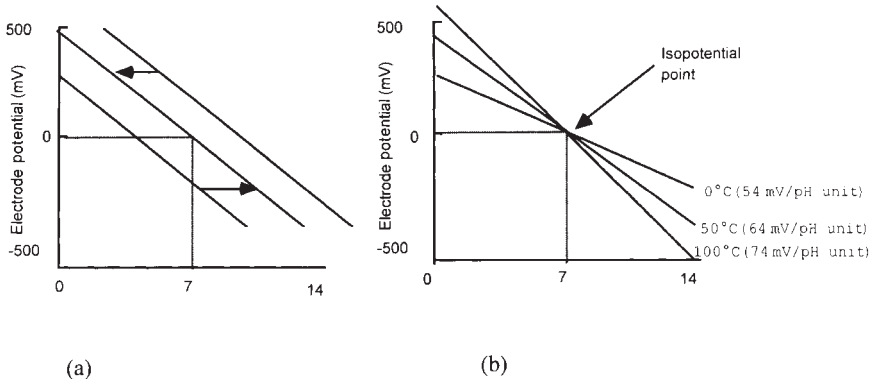

FIGURE 3.1 Relationship between intercept and slope controls in pH measurement. (*a*) lateral adjustment of the electrode potential using the intercept control; (*b*) effect of temperature on pH electrode response. *(Modified from APHA/AWWA/WEF, 1998.)*

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TABLE 3.2 Some Standard Buffer Solutions Suitable for pH Calibration

Buffer solution	pH (°C)
Saturated potassium hydrogen tartrate	3.557
0.05 *M* potassium dihydrogen citrate	3.776
0.05 *M* potassium hydrogen phthalate	4.004
0.025 *M* potassium dihydrogen phosphate and 0.025 *M* disodium hydrogen phosphate	6.863
0.008695 *M* potassium dihydrogen phosphate and 0.03043 *M* disodium hydrogen phosphate	7.415
0.01 *M* sodium tetraborate decahydrate	9.183
0.025 *M* sodium bicarbonate and 0.025 *M* sodium carbonate	10.014

Source: Modified from APHA/AWWA/WEF, 1998.

error) that occurs at pH > 10. Specially manufactured low-sodium-error combination electrodes are available if this effect is likely to be problematic.

When not in use, combination pH electrodes should be stored in saturated KCl. The response of combination pH electrodes may deteriorate because of the porous liquid junction of the reference electrode or because of fouling of the glass electrode surface. The glass electrode surface may be cleaned by alternately immersing the membrane in 0.1 *M* HCl followed by 0.1 *M* NaOH three times. A 30-s rinse in KF solution also may be employed for more intractable cases. Following this treatment, the electrode should be rinsed and then allowed to soak overnight in pH 7 buffer (APHA/AWWA/WEF, 1998).

Short-term measurements of pH in the field can be made accurately and reproducibly using a calibrated combination electrode. However, for longer-term in situ measurements, potentiometric measurements may be less effective because of problems such as electrode drift, clogging of the reference electrode, or biofouling of both electrodes. Thus, for extended in situ measurement of pH (e.g., in seawater during an oceanographic cruise), pH may better be determined by spectrophotometry using an indicator solution (Dickson, 1993). Bellerby et al. (1995) have described a flow injection system used for this purpose, whereas Tapp et al. (2000) have more recently described a continuous-flow spectrophotometric system for pH measurement. Both these spectrophotometric devices are capable of high-precision pH measurements.

Electrical Conductivity (EC)

Significance. *Conductivity K* or *specific conductance* is a measure of the electric current-carrying ability of water and is related to the concentration of dissolved ions present. In situ measurement of electrical conductivity in freshwaters provides an instantaneous estimate of the dissolved solids concentration, whereas in marine waters it is used commonly to measure the salinity *S*. In situ conductivity measurements can be used as a simple and effective means of monitoring temporal or spatial changes in salt concentrations (Fig. 3.2) such as those that occur in catchments undergoing salinization. Short-term temporal changes in conductivity may be detected in streams during flooding or as a result of illicit or accidental discharges or in estuaries as part of their normal tidal cycles.

Conductivity may be used as a means of assessing and classifying the potability of water, as shown in Table 3.3.

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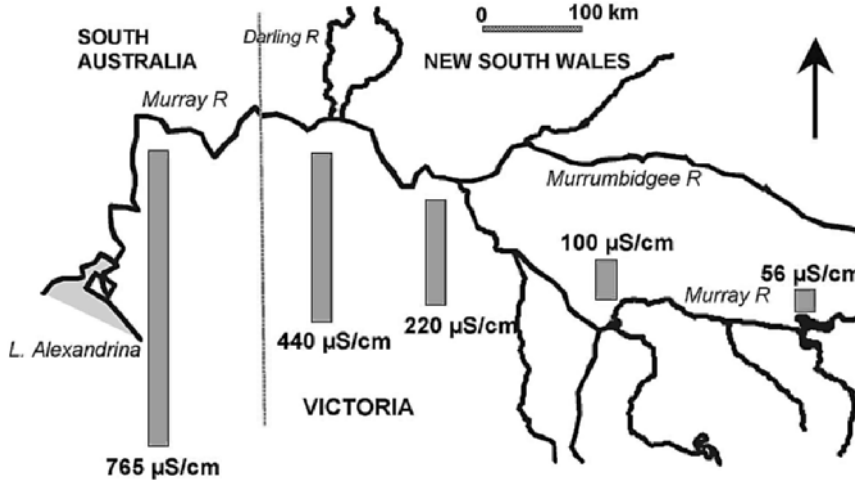

FIGURE 3.2 Electrical conductivity measurements on the Murray-Darling River system showing the effect of progressively increasing salt load.

TABLE 3.3 Classification of Potability Based on Electrical Conductivity (MDBC, 2001)

Potability classification	Range of conductivity ($\mu S \cdot cm^{-1}$)	Beneficial use
Fresh	<325	Potable water
Marginal	>325 but <975	At the limit of potable water, suitable for watering of livestock, irrigation, and other general uses
Brackish	>975 but <3250	Suitable for selective irrigation and watering of almost all livestock
Saline	>3250	Suitable for a diminishing range of salt-tolerant livestock up to about 9750 $\mu S \cdot cm^{-1}$ Suitable for coarse industrial processes up to about 32,500 $\mu S \cdot cm^{-1}$

Measurement: Electrical Conductivity. The *conductance* G (Ω^{-1} or Siemen S) of a water sample is the reciprocal of the electrical resistance R measured in a conductance cell comprising two electrodes of surface area A (cm^2) at a distance l cm apart and is related by

$$G = \frac{1}{R} = K\frac{A}{1}$$

where the constant of proportionality K is the *conductivity* in siemens per centimeter. Hence

$$K = \frac{1}{A}G = kG$$

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The conductance electrode is usually constructed of either carbon or platinum that has been coated with platinum black (APHA/AWWA/WEF, 1998) such that the cell constant k (cm^{-1}) is unity. In practice, it is difficult to construct a cell with these exact dimensions, and the cell constant must be determined using solutions of known conductivity as part of the instrument calibration. Most conductivity instruments produced for water quality monitoring provide a direct readout of K in millisiemens or microsiemens per centimeter (some manufacturers persist with the unit micromhos per centimeter) but the cell constant must be obtained first to enable direct conversion of G to K.

The cell constant calibration is performed by measuring G for a solution of known conductance (usually 0.0100 M KCl) at a given temperature. The temperature-corrected value of conductivity for this solution is given by

$$K_{calc} = 1412\,[1 + 0.0191\,(t - 25)]$$

where K_{calc} is the expected conductivity ($\mu S \cdot cm^{-1}$), and t is the observed temperature (°C). (APHA/AWWA/WEF, 1998). Hence

$$k = \frac{K_{calc}}{G} \qquad (units: cm^{-1})$$

This k value is thus stored or set on the meter, enabling conductivity K to be read directly. Both K and G are temperature-dependent and should be reported at a standard temperature (usually 25°C, although 18°C also has been used historically by limnologists) (Wentzel and Likens, 1991). Many commercially produced conductivity probes include a temperature sensor, and the conductivity is corrected automatically to 25°C, but for those instruments which do not have this facility, the following correction should be applied:

$$K_{25} = \frac{K_{\text{measured}}}{1 + 0.0191\,(t - 25)}$$

where K_{measured} is the measured conductivity in microsiemens per centimeter at t°C.

Conductivity meters and probes should be checked prior to use in the field by measuring the conductivity of a standard potassium chloride solution whose conductivity is known (Table 3.4).

Conductivity: TDS Relationship. Electrical conductivity is used commonly to conveniently estimate the total dissolved solids (TDS) concentration in freshwaters. Examples of

TABLE 3.4 Conductivity K of Standard Potassium Chloride Solutions at 25°C (APHA/AWWA/WEF, 1998)

KCl concentration (M)	Conductivity K ($\mu S \cdot cm^{-1}$)
0.0001	14.9
0.0005	73.9
0.0010	146.9
0.0050	717.5
0.0100	1,412
0.0500	6,667
0.1000	12,890
0.5000	58,670
1.0000	111,900

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typical K = TDS relationships are shown below and are based on the assumption that pH lies between 4 and 9. At pH values outside this range, the conductivity of H^+ or OH^- becomes significant. These relationships are empirical and quite specific to regions or even catchments and should be used on this basis. Depending on whether waters are dominated by chloride or sulfate, the relationship typically might range from TDS (mg/liter) = $0.64K$ ($\mu S \cdot cm^{-1}$; chloride-dominated waters) to TDS (mg/liter) = $0.765K$ ($\mu S \cdot cm^{-1}$; sulfate-dominated waters) (Evangelou and Sobek, 1988).

Conductivity: Salinity Relationship. Because the major ion composition of seawater is quite constant, *salinity* S may be determined accurately from K measurements, and most field conductivity meters designed for water quality measurement provide the option to display salinity directly. Whereas salinity was defined previously by the salinity-chlorinity relationship $S\% = 1.80655\text{Cl}\%$, where Cl% is the chlorinity in grams per kilogram obtained from argentometric titration (Riley and Chester, 1971), the Practical Salinity Scale 1978 is set relative to the conductivity of a potassium chloride solution of known concentration. By definition, seawater with Practical Salinity $S = 35$ has the same conductivity (or resistivity = 1/conductivity) as a 32.4356 g/kg KCl solution at 15°C. Salinity-resistivity equations with temperature corrections are listed in standard methods (APHA/AWWA/WEF, 1998).

Dissolved Oxygen Concentration (DO)

Significance. Natural waters in equilibrium with the atmosphere will contain dissolved oxygen concentrations ranging from about 14.5 to 5 mg O_2 per liter depending on the water temperature, salinity, and altitude. The dissolved oxygen concentration present in water reflects atmospheric dissolution, as well as autotropic and heterotropic processes that, respectively, produce and consume oxygen (Fig. 3.3). Thus, in rivers and streams, dissolved oxygen concentrations might be expected to vary with time because of the changing influence of photosynthesis, respiration, and temperature throughout the day and night.

In lakes, the dissolved oxygen concentration may decrease with depth, especially in a stratified lake, where the bottom hypolimnetic waters become oxygen-depleted because of bacterial respiration and there is no reoxygenation through atmospheric contact (Fig. 3.4*a*). In streams that receive point-source inputs of high-oxygen-demand sewage or industrial wastes, the dissolved oxygen concentration downstream of the discharge point decreases rapidly (the so-called oxygen sag effect) because of increased microbial respiration. With time and distance, the stream may become reoxygenated through direct contact with the atmosphere, hydromechanical agitation, and increasing photosynthesis (see Fig. 3.4*b*).

Analysis of dissolved oxygen is extremely important in determining water quality. The dissolved oxygen concentration provides information on the biological and biochemical reactions occurring in a water body and therefore is an important indicator of stream metabolism (Wetzel and Likens, 1991). In situ measurements of this parameter can be used as a primary indicator of water quality, and regulatory and advisory agencies often will recommend a minimum dissolved oxygen requirement for maintenance of fish populations [e.g., "dissolved oxygen should not be permitted to fall below 6 mg/liter or 80 to 90 percent saturation, this being determined over at least one diurnal cycle" (ANZECC, 1992)].

Measurement: Electrometric Method. DO usually is measured in the field using an electrometric technique based on a galvanic or voltametric membrane sensor (the Clark electrode). This consists of a platinum disk cathode held at a potential of approximately −0.6 V with respect to the annular silver anode surrounding it. A thin (approximately 20 μm) gas permeable membrane (e.g., PTFE or polyethylene) is held in tension across the end of

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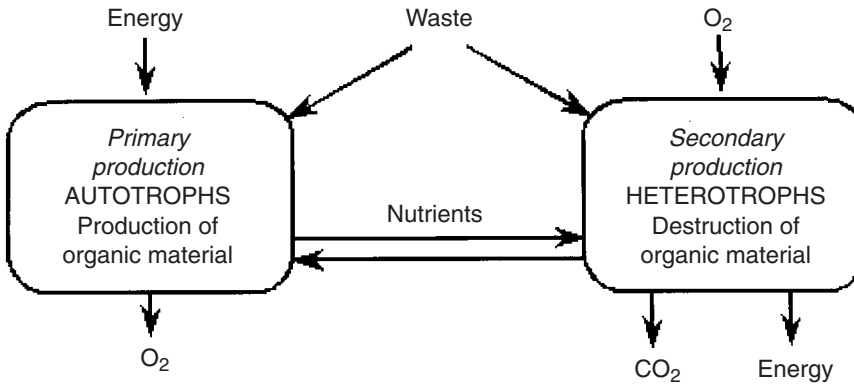

FIGURE 3.3 Energy relationships in streams showing production and consumption of dissolved oxygen. *(Adapted from Stumm and Morgan, 1996.)*

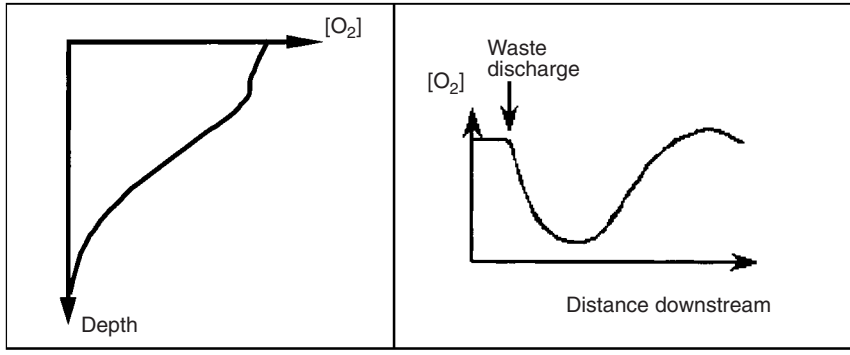

FIGURE 3.4 Spatial variation in dissolved oxygen concentration in (*a*) a stratified lake and (*b*) a stream receiving a point-source discharge of waste with a high biologic oxygen demand. *(Adapted from Stumm and Morgan, 1996.)*

this assemblage such that there is a thin film (approximately 10 μm) between the membrane and the anode and cathode (Fig. 3.5) immersed in a buffered KCl electrolyte solution. When the sensor is immersed in water containing dissolved oxygen, molecular oxygen diffuses through the membrane and the internal electrolyte film, and the following electrode processes occur:

Cathode reaction:

$$O_2 + 4H^+ + 4e \rightleftarrows 2H_2O$$

Anode reaction:

$$Ag + Cl^- \rightarrow AgCl(s) + e$$

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The diffusion current that flows between the electrodes is proportional to the oxygen concentration and, by calibration, can be set to read directly in milligrams of O_2 per liter. The galvanic electrode is similar in construction and operation, except that the electrode reaction occurs spontaneously.

Because the sensor response is highly temperature-dependent, temperature compensation must be performed, and many sensors have a thermistor incorporated in the probe body that permits automatic compensation.

The sensitivity of DO sensors is also strongly dependent on salinity or ionic strength, whereby greater amounts of oxygen diffuse through the gas permeable membrane. This effect must be taken into account when measuring DO concentrations in waters of widely varying salinity such as may be encountered in an estuary. Most modern DO instruments include an adjustment control that allows compensation for this salinity effect.

For reliable and accurate results, the DO sensor and probe should be calibrated regularly, certainly on a daily basis and more frequently if measurement is made at a range of altitudes. A single-point calibration usually is performed using water-saturated air at a measured temperature or, alternately, with water having a known oxygen concentration measured by the Winkler titration (see next section). A zero DO sample may be prepared by adding saturated sodium sulfite. Where possible, water with the same salinity as the samples should be used for calibration purposes, except in the case of wastewaters, where deionized water or unpolluted seawater should be used in order to avoid membrane contamination.

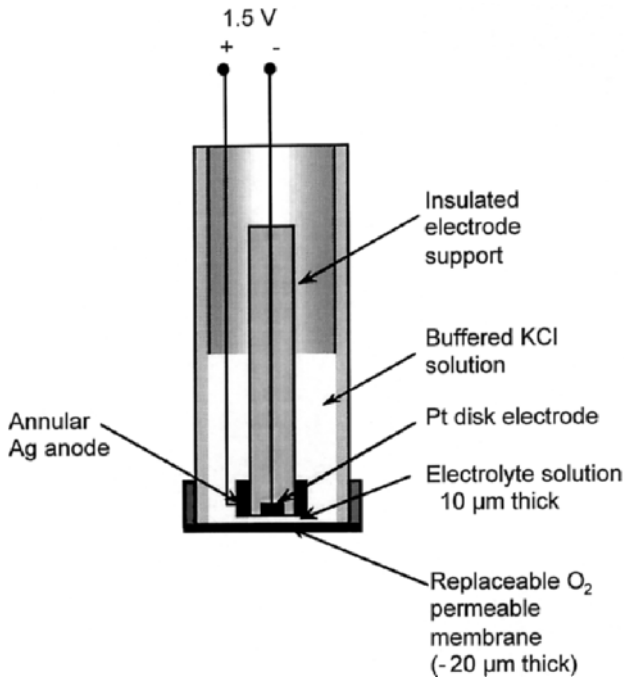

FIGURE 3.5 Voltametric oxygen electrode (Clark-type).
(Adapted from Skoog et al., 1998.)

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Because both galvanic and voltametric DO sensors involve electrode reactions that consume O_2, samples should be actively transported across the membrane surface continually to avoid fluctuating or drifting electrode response. This may be achieved by the use of a mechanical stirring paddle attached to the probe or by agitation of the probe while measurements are being made.

With regular maintenance (changing the membrane and replenishing the electrolyte) and calibration, DO membrane electrodes should be capable of measurements with an accuracy of ± 0.1 mg O_2 per liter and a precision of 0.05 mg O_2 per liter (APHA/AWWA/WEF, 1998), although most commercially available electrodes are unreliable in the concentration region of 0 to 1 mg O_2 per liter (Wetzel and Likens, 1991).

Recent developments in electrode technology have seen the commercial introduction of solid-state or microelectrode-array sensors for oxygen. These electrodes tend to have similar sensistivity and better stability and may not require agitation to achieve a steady signal.

Measurement: Titrimetric Method. The alternative method for DO determination is the Winkler method. While this method lacks the convenience of the electrometric DO methods, it does provide results with the greatest accuracy and precision. In this method, a manganous hydroxide floc is formed in the water sample by the addition of NaOH/NaI reagent to manganous sulfate (3.1). The manganous hydroxide is readily oxidized by dissolved oxygen to manganic hydroxide (3.2), and at this stage the DO is fixed and the sample can be transported back to the laboratory for analysis or, alternately, titrated in the field. When sulfuric acid is added, manganic hydroxide is solubilized, and the manganese is reduced from Mn(IV) to Mn(II) (3.3), whereas the iodide present is oxidized to free iodine (3.4). The free iodine is then titrated with sodium thiosulfate solution (3.5) to a starch end point (Wetzel and Likens, 1991).

$$\text{Mn (II) } SO_4 + 2NaOH \rightarrow \text{Mn (II) } (OH)_2 + Na_2SO_4 \tag{3.1}$$

$$2\text{Mn (II) } (OH)_2 + O_2 + 2H_2O \rightarrow 2\text{Mn (IV) } (OH)_4 \tag{3.2}$$

$$2\text{Mn (IV) } (OH)_4 + 4H_2SO_4 \rightarrow 2\text{Mn (IV) } (SO_4)_2 + 8H_2O \tag{3.3}$$

$$2\text{Mn (IV) } (SO_4)_2 + 4NaI \rightarrow 2\text{Mn (II) } SO_4 + 2Na_2SO_4 + 2I_2 \tag{3.4}$$

$$4Na_2S_2O_3 + 2I_2 \rightarrow 2Na_2S_4O_6 + 4NaI \tag{3.5}$$

The Winkler titration of DO suffers from a number of interferences, the most common being caused by nitrite, which reacts with iodides as follows:

$$2NO_2^- + 2I^- + 4H^+ \rightarrow I_2 + N_2O_2 + 2H_2O$$

$$N_2O_2 + 1/2O_2 + H_2O \rightarrow 2NO_2^- + 2H^+$$

As the reaction proceeds, more nitrite is formed, followed by the formation of free iodine (I_2). Thus a cyclic reaction occurs, making it impossible to titrate a permanent end point. This is overcome by the sodium azide, or the Alsterberg modification of the Winkler method, which involves the removal of interfering nitrites by reducing them to nitrous oxide and nitrogen, that is,

$$2NaN_3 + H_2SO_4 \rightarrow 2HN_3 + Na_2SO_4$$

$$HNO_2 + HN_3 \rightarrow N_2O + N_2 + H_2O$$

The Winkler method also depends on the pH of the water sample, and enough acid must be added to bring the pH below 1.7. Other interferences may occur when there are high con-

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centrations of Fe(III), such as that found in acid mine drainage or in waters containing activated sludge with high O_2 demand. Techniques for suppressing these interferences may be found in standard methods (APHA/AWWA/WEF, 1998).

From the stoichiometric relationships in Eqs. (3.2) to (3.5), it can be shown that

$$\text{mg}O_2/\text{liter} = \frac{1}{4} \times \frac{T\,(\text{ml})}{1000} \times [S_2O_3^{2-}]\,(\text{mol/liter}) \times \frac{1000}{V\,(\text{ml})} \times 32{,}000\ \text{mg/mol}$$

where T is the titration volume and V is the volume of sample titrated. If $[S_2O_3^{2-}]$ is 0.0250 M and a sample volume of 200 ml is used, then the titration gives the dissolved oxygen concentration directly; i.e., mg O_2/liter = titer (ml).

Relative (Percentage) Saturation. Comparisons of DO concentrations from the same stream or lake over time or at different locations or between different water bodies largely will be meaningless because DO depends on temperature, salinity, and altitude. For this reason, relative or percentage saturation often is reported, where

$$\%\text{Saturation} = \frac{[\text{DO}]_{\text{observed}}}{[\text{DO}]_{\text{saturated}}} \times 100$$

Algorithms for calculation of the saturation concentration of DO over a range of temperature and salinity values can be found in standard methods (APHA/AWWA/WEF, 1998), and these have been used to calculate the saturation values shown in Table 3.5. Most commercial DO instruments have a *%Saturation* option for data readout.

TABLE 3.5 Calculated Oxygen Saturation Values at Different Salinity and Temperature Conditions

Temperature (°C)	Salinity (S)							
	0	5	10	15	20	25	30	35
0.0	14.62	14.12	13.63	13.16	12.71	12.28	11.85	11.45
1.0	14.22	13.73	13.26	12.81	12.38	11.96	11.55	11.15
2.0	13.83	13.36	12.91	12.48	12.06	11.65	11.26	10.88
3.0	13.46	13.01	12.58	12.16	11.75	11.36	10.98	10.61
4.0	13.11	12.67	12.25	11.85	11.46	11.08	10.71	10.35
5.0	12.77	12.35	11.95	11.55	11.17	10.81	10.45	10.11
6.0	12.45	12.04	11.65	11.27	10.90	10.55	10.21	9.87
7.0	12.14	11.75	11.37	11.00	10.65	10.30	9.97	9.65
8.0	11.84	11.46	11.10	10.74	10.40	10.07	9.74	9.43
9.0	11.56	11.19	10.84	10.49	10.16	9.84	9.53	9.22
10.0	11.29	10.93	10.59	10.26	9.93	9.62	9.32	9.02
11.0	11.03	10.68	10.35	10.03	9.71	9.41	9.12	8.83
12.0	10.78	10.44	10.12	9.81	9.50	9.21	8.92	8.65
13.0	10.54	10.21	9.90	9.60	9.30	9.02	8.74	8.47
14.0	10.31	9.99	9.69	9.39	9.11	8.83	8.56	8.30
15.0	10.08	9.78	9.48	9.20	8.92	8.65	8.39	8.14
16.0	9.87	9.57	9.29	9.01	8.74	8.48	8.22	7.98
17.0	9.66	9.38	9.10	8.83	8.57	8.31	8.06	7.82
18.0	9.47	9.19	8.92	8.65	8.40	8.15	7.91	7.68
19.0	9.28	9.00	8.74	8.48	8.24	8.00	7.76	7.53

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TABLE 3.5 Calculated Oxygen Saturation Values at Different Salinity and Temperature Conditions (*Continued*)

Temperature (°C)	Salinity (*S*)							
	0	5	10	15	20	25	30	35
20.0	9.09	8.83	8.57	8.32	8.08	7.85	7.62	7.40
21.0	8.92	8.66	8.41	8.17	7.93	7.70	7.48	7.26
22.0	8.74	8.49	8.25	8.01	7.78	7.56	7.34	7.13
23.0	8.58	8.33	8.10	7.87	7.64	7.43	7.22	7.01
24.0	8.42	8.18	7.95	7.73	7.51	7.30	7.09	6.89
25.0	8.26	8.03	7.81	7.59	7.38	7.17	6.97	6.77
26.0	8.11	7.89	7.67	7.45	7.25	7.05	6.85	6.66
27.0	7.97	7.75	7.53	7.33	7.12	6.93	6.73	6.55
28.0	7.83	7.61	7.40	7.20	7.00	6.81	6.62	6.44
29.0	7.69	7.48	7.28	7.08	6.89	6.70	6.52	6.34
30.0	7.56	7.35	7.15	6.96	6.77	6.59	6.41	6.24
31.0	7.43	7.23	7.04	6.85	6.66	6.48	6.31	6.14
32.0	7.30	7.11	6.92	6.73	6.55	6.38	6.21	6.04
33.0	7.18	6.99	6.81	6.63	6.45	6.28	6.11	5.95
34.0	7.06	6.88	6.70	6.52	6.35	6.18	6.02	5.86
35.0	6.95	6.77	6.59	6.42	6.25	6.08	5.92	5.77
36.0	6.84	6.66	6.48	6.32	6.15	5.99	5.83	5.68
37.0	6.73	6.55	6.38	6.22	6.06	5.90	5.75	5.60
38.0	6.62	6.45	6.28	6.12	5.96	5.81	5.66	5.51
39.0	6.52	6.35	6.19	6.03	5.87	5.72	5.58	5.43
40.0	6.41	6.25	6.09	5.93	5.78	5.64	5.49	5.35
41.0	6.31	6.15	6.00	5.84	5.70	5.55	5.41	5.27
42.0	6.21	6.06	5.91	5.76	5.61	5.47	5.33	5.20
43.0	6.12	5.97	5.82	5.67	5.53	5.39	5.25	5.12
44.0	6.02	5.87	5.73	5.58	5.45	5.31	5.18	5.05
45.0	5.93	5.78	5.64	5.50	5.37	5.23	5.10	4.98
46.0	5.84	5.70	5.56	5.42	5.29	5.16	5.03	4.90
47.0	5.75	5.61	5.47	5.34	5.21	5.08	4.96	4.83
48.0	5.66	5.53	5.39	5.26	5.13	5.01	4.88	4.76
49.0	5.58	5.44	5.31	5.18	5.06	4.93	4.81	4.70
50.0	5.49	5.36	5.23	5.11	4.98	4.86	4.74	4.63

Note: These values are calculated for sea-level barometric pressure of 1 atm (760 torr). At higher altitudes, the solubility values should be corrected; thus $S_P = S\,(P/760)$, where S_P is solubility at pressure P, S is solubility at 760 torr, and P is atmospheric pressure in torrs

Source: Adapted from APHA/AWWA/WEF, 1998.

Optical Measurements: Turbidity and Quantum Irradiance

Significance. Small particles and colloidal material in suspension affect the clarity of water. This material may originate from erosion and consist of clay colloids and silt particles, or it may be biological in origin and consist of phytoplankton and other aquatic organisms. Turbidity is a measure of the clarity of water and is determined by the amount of light scattering caused by suspended particulate and colloidal material. It is often used as an indicator of the effectiveness of water and wastewater treatment and clarification processes and often may be specified as a wastewater discharge consent condition.

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Quantum irradiance, on the other hand, measures the *intensity* of photosynthetically active radiation (PAR), i.e., light that occurs in the wavelength range of 350 to 700 nm and which is a limiting factor in photosynthesis by plants and phytoplankton. Penetration of PAR into the water column is controlled by the optical properties of the water body, namely, absorption by the water, dissolved organic matter, particles, and phytoplankton, and by scattering by particles and phytoplankton. These absorption and scattering effects are all included in the *vertical attenuation coefficient* K_d, which is determined by measuring the quantum irradiance at specified depths below the surface.

Measurement: Turbidity. The turbidity of a sample is determined by a light scattering technique (nephelometry) by measuring the amount of scattered light at 90 degrees from an incident beam with a photocell or photodiode in the wavelength range of 400 to 600 nm, although International Standards Organization (ISO) standard 7027 specifies a detection wavelength of 860 nm (Siouffi, 2000). A primary standard is prepared by mixing hydrazine sulfate with hexamethylenetetramine to produce a formazin polymer that has a turbidity of 4000 nephelometric turbidity units (NTUs) (APHA/AWWA/WEF, 1998), and after suitable dilution with 0.1-μm filtered water, this can be used for calibrating the turbidimeter or nephelometer at appropriate levels of turbidity. Instrument manufacturers also may provide secondary standards prepared from suspensions of styrene-divinylbenzene copolymer or latex.

Portable turbidimeters are common, and although they may not be as sensitive as their laboratory counterparts, they can be used successfully in the field, provided that they are maintained and calibrated properly. Care should be taken to ensure that there is a gentle flow of sample through the detection cell to avoid sedimentation of fine particulate material and to ensure the displacement of any stray bubbles present in the sample. When measuring turbidity in streams, the probe should be immersed completely in the stream water in the flow but not in areas where there is sufficient agitation and aeration to form fine bubbles that also will cause light scattering. Routine maintenance of field turbidimeters should involve cleaning of the light source and detector windows of the turbidity cell with a soft brush or cloth to remove any accumulated particulate material or biofilm. This is especially important where field turbidimeters are deployed in situ for extended periods.

Measurement: Quantum Irradiance. Quantum irradiance is measured using a light meter that detects the radiant flux per unit area of PAR (in microeinsteins per second per square meter). Irradiance probes consist of either a submersible *planar* sensor that is used to measure the irradiance in the upward or downward direction or a *scalar* sensor that integrates light intensity almost over a whole sphere. By determining the quantum irradiance values $E_d(z_1)$ and $E_d(z_2)$ at two individual depths z_1 and z_2, the vertical attenuation coefficient K_d can be obtained for that depth segment of water; i.e.,

$$K_d = \frac{1}{z_2 - z_1} \ln \frac{E_d(z_1)}{E_d(z_2)}$$

The euphotic depth z_{eu} can be determined from the attenuation coefficient. It is defined as the depth of river or lake water at which the quantum irradiance is reduced to 1 percent of the surface value. The euphotic depth is assumed to define the depth of water that receives sufficient light to support photosynthesis (Fig. 3.6). Manipulation of the preceding K_d expression gives

$$z_{eu} = \frac{4.6}{K_d}$$

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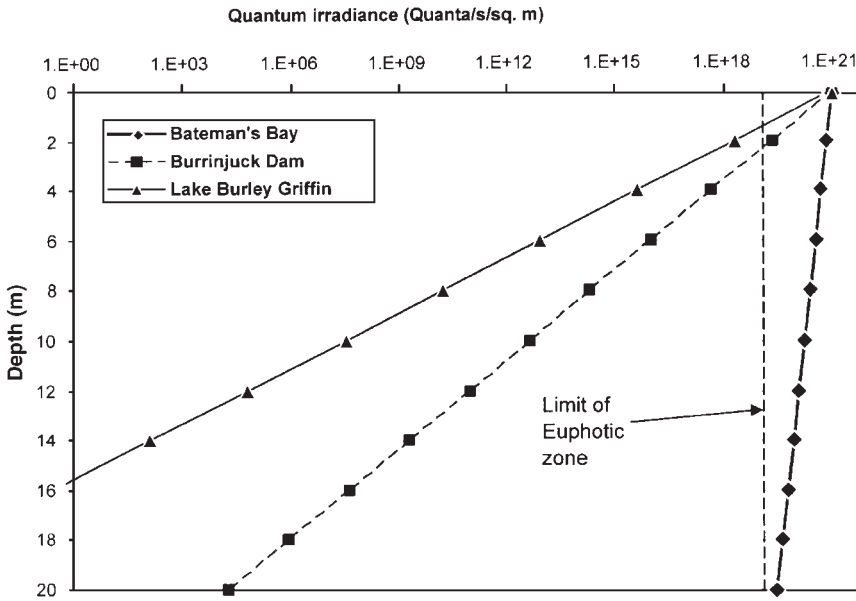

FIGURE 3.6 Quantum irradiance data illustrating the low attenuation of marine water (Bateman's Bay) compared with more turbid inland waters (Burrinjuck Dam and Lake Burley Griffin). The "Limit of Euphotic Zone" line corresponds to the depth at which the surface quantum irradiance has been reduced by 99 percent. *(Adapted from Kirk, 1983.)*

A major source of error in the measurement of quantum irradiance is in measurement of the surface or near surface irradiance value. This is may fluctuate widely and rapidly because it is affected by varying clouds, wave action, and shading from the sampling vessel. Ideally, the incident irradiance value should be integrated over a period of several minutes, and this facility is offered in some commercial light meters.

An approximate but cheap, convenient, and widely used technique for estimating the K_d value that has been used since the nineteenth century is that involving the Secchi disk. This is a metal disk 20 cm in diameter painted with alternating black and white quadrants. It is lowered into the water, and the depth at which it can no longer be seen is recorded as the Secchi depth; this depth corresponds to a reduction of between 99 and 85 percent light intensity depending on the nature of the water (Wetzel and Likens, 1991). Secchi disk transparencies can vary from a few centimeters in turbid river waters to many meters in pristine lake waters.

Redox Potential

Significance. Redox reactions play a crucial role in the behavior of many so-called inorganic and biochemical processes in aquatic systems. The biogeochemical cycles of important elements such as sulfur, nitrogen, iron, oxygen, and carbon and numerous metals in aquatic systems are all influenced strongly by redox processes, and the speciation and behavior of such elements will depend largely on the prevailing pH and oxidation-reduction potential (*Eh,* also abbreviated as ORP). *Eh* is the oxidation-reduction potential of the system in volts with respect to the standard hydrogen electrode potential.

For a given redox couple, such as $Fe^{3+} + e \rightarrow Fe^{2+}$, the theoretical E_h can be related to the activities of the individual chemical species by the thermodynamic Nernst relationship:

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$$E_h = E^0 + \frac{RT}{nF} \ln \frac{a_{Fe}{}^{3+}}{a_{Fe}{}^{2+}}$$

and at 298K, this can be written as

$$E_h = E^0 + \frac{0.0592}{n} \log \frac{a_{Fe}{}^{3+}}{a_{Fe}{}^{2+}}$$

where E^0 is the standard reduction potential (volts), R is the gas constant (8.3143 $J \cdot K^{-1} \cdot mol^{-1}$), n is the number electrons transferred in the reaction (=1 in this case), F is Faraday's constant (96,487 $J \cdot V^{-1} \cdot mol^{-1}$), and T is the temperature in kelvins.

In some disciplines (e.g., biochemistry, geochemistry, and aquatic chemistry), E_h may be expressed in terms of the electron activity or redox intensity *pe*. For the preceding example, the corresponding *pe* expression would be

$$pe = pe^0 + \frac{1}{n} \log \frac{a_{Fe}{}^{3+}}{a_{Fe}{}^{2+}}$$

where pe^0 is the standard or equilibrium electron intensity, which is related to the equilibrium constant and E^0; thus

$$pe^0 = \frac{1}{n} \log K_{eq}$$

and since

$$K_{eq} = e^{-\Delta G^0/RT} = e^{-nFE^0/RT}$$

it can be shown that

$$E^0 = \frac{2.303RT}{nF} pe^0$$

and, similarly, that

$$E_h = \frac{2.303RT}{nF\, pe}$$

However, these are thermodynamic predictions for reversible reactions with fast electrode kinetics.

The practical measurement of E_h involves determining the potential difference of a platinum electrode coupled to either an Ag/AgCl or calomel reference electrode. The *Pt* electrode acts as either an electron donor or acceptor of electrons from the electroactive species in solution, and the measured E_h can provide an indication of whether the system is in an oxidizing or reducing state. However, measured or apparent *Eh* values seldom correspond with those calculated based on thermodynamic theory. This is so because many different redox couples exist in natural water, some of which may undergo irreversible reactions, whereas others might poison the electrode surface. Furthermore, the *Pt* electrode does not respond to many important redox couples that are present in aquatic and wastewater systems, including O_2/H_2O, $SO_4{}^{2-}/H_2S$, CO_2/CH_4, $NO_3{}^-/N_2$, and $N_2/NH_4{}^+$.

The principal value of measured or apparent *Eh* values is that they can be used to assess whether a water or sediment system is in an oxidizing or reducing environment. In aquatic systems, measured E_h values vary from greater than 500 mV in well-oxygenated waters to less than −100 mV in anaerobic sediments. In general, any water with $E_h > 100$ to 200 mV is considered to be oxidizing (Golterman et al., 1978).

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Measurement. E_h is measured using a pH-millivoltmeter with a *Pt* indicator electrode and either an Ag/AgCl or calomel reference electrode. Gold or wax-impregnated graphite also may be used as indicator electrode materials. The electrode-meter assembly may be calibrated against a standard that is both chemically stable and provides a specified electrode potential for a particular indicator–reference electrode combination. The most commonly used standard is Zobell's solution, which consists of a mixture of 3 m*M* potassium ferricyanide and 3 m*M* potassium ferrocyanide in 0.1*M* KCl. For the *Pt* Ag/AgCl electrode combination, the E_h of Zobell's solution is given by

$$E_h = 0.428 - 0.0022\,(T - 25)$$

where T is the sample temperature in the range 8 to 85°C (APHA/AWWA/WEF, 1998).

To measure the E_h of a sample, the cell potential should be measured for both sample and Zobell's solution. The apparent E_h for the sample can then be calculated from

$$E_{h\,\text{sample}} = E_{h\,\text{measured}} + E_{h\,\text{Zobell theoretical}} - E_{h\,\text{Zobell measured}}$$

where $E_{h\,\text{measured}}$ is the measured cell potential for the sample relative to the reference electrode, $E_{h\,\text{Zobell theoretical}}$ is determined from the preceding equation, and $E_{h\,\text{Zobell measured}}$ is the measured E_h for the Zobell's solution standard relative to the reference electrode.

E_h preferably should be measured in situ because sediment-water redox chemistry is inherently unstable and is susceptible to even small environmental changes. For example, waters from the anoxic hypolimnion of a lake will contain higher amounts of $Fe^{(II)}$, and this will oxidize to Fe(III) within a minute of being brought in contact with air. Where in situ measurement is not feasible, closed sampling devices should be used that permit electrode potential measurement without exposure of the sample to air or at least allow sample measurement in a glove bag filled with an inert gas such as argon.

Most experimental difficulties in the measurement of E_h are associated with poisoning or contamination of the electrodes. This may be due to sorption of contaminants such as sulfide, bromide, dissolved organic matter, or biofilms on the electrode surface. For this reason, the indicator electrodes should be cleaned regularly by soaking in strong acid (e.g., aqua regia or chromic acid) or hydrogen peroxide or polished with jeweler's rouge (Langmuir, 1971; APHA/AWWA/WEF, 1998). For reference electrodes, the most common maintenance requirement is replacement of the electrolyte solution in the salt bridge.

Repeated E_h measurements on the same sample should be within ± 10 mV if the electrode and meter combination are functioning properly.

Multiparameter Instruments and Portable Analysis Systems

A number of instrument manufacturers offer multiparameter instruments that include all or some of DO, pH, EC, turbidity, and temperature as a standard instrument configuration (e.g., Horiba, YSI, and WTW*). While the initial purchase cost of these multiparameter instruments may be large, this is still probably more cost-effective than purchasing individual instruments. From the perspective of portability and ease of application, multiparameter instruments are highly advantageous. Most multiparameter instruments have the option of either data storage or data logging and data transport capability (radio, cellular telephone, or satellite), and a number offer a much wider range of parameters than those just discussed. One manufacturer offers a system capable of in situ measurement of up to 17 parameters. In addition to pH, DO, EC, T, E_h, and turbidity, the system has the facility

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to determine depth, chlorophyll by fluorescence measurement, and ammonia, nitrate, and chloride by potentiometry. However, "fitness for purpose" should be a guiding principle in selecting such instruments. For example, a multiparameter system that uses ion-selective electrodes for ammonia and nitrate determination may be suitable for measurements in waste and receiving waters but insufficiently sensitive for determinations in pristine waters, where the concentrations of these parameters may be in the range of 10 μg/liter or less.

The same care should be exercised in the application of portable photometric analysis kits that have been developed specifically for the water industry. While these systems are based on established, robust detection chemistries and are very satisfactory for wastewater analysis, the achievable sensitivity and accuracy may not be suitable for analysis of uncontaminated waters.

Flow (Discharge) Measurement

In addition to the measurement of concentrations of water quality parameters such as nutrients, metals, and pesticides, most of which are determined in the laboratory, there is often a need to determine the *chemical load L* of these species in a stream. Calculation of chemical load requires a knowledge of the flow or discharge; that is,

$$L = CQ$$

where L is the load (grams per second), C is the concentration (grams per cubic meter), and Q is the flow (cubic meters per second).

Thus, in addition to collection of water quality samples and measurement of in situ parameters, sampling personnel also may be required to measure the discharge. Detailed description of flow measurement techniques may be found elsewhere (Wetzel and Likens, 1991; Gordon et al., 1992). These can be summarized as follows:

Velocity-Area Techniques. The velocity or current of the stream is measured with a calibrated electromechanical current meter at measured distances across the stream. In shallow streams the average velocity is measured at 40 percent of the depth above the bottom, whereas in deeper channels the average may be determined from measurements made at 20 and 80 percent of the depth; that is, 0.4 of total depth from bottom for shallow streams (<0.5 m depth):

$$\bar{v} = v_{0.4}$$

0.2 and 0.8 of total depth from bottom:

$$\bar{v} = \frac{v_{0.2} + v_{0.8}}{2}$$

From these data, the flow is computed for each segment of the stream, and summation yields the total flow $Q = \Sigma$ (segment discharges):

$$Q = \Sigma\,(w_1 D_1\,\bar{v}_1 + w_2 D_2\,\bar{v}_2 + \cdots + w_n D_n\,v_n)$$

where w is the width and D is the depth of each segment. This method is suitable for streams with moderately uniform channel shape.

Dilution gauging. For smaller streams with less uniform bed shape, dilution gauging can be used. This involves discharge of a concentrated nonreactive tracer solution into the stream. The concentration of this tracer is monitored downstream either by a direct-reading

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instrument such as a conductivity meter (e.g., where NaCl is used as the tracer) or by collection of samples for later laboratory analysis (e.g., bromide as tracer). Two types of tracer discharge may be performed:

Constant-discharge injection. This is where a known concentration of tracer C_i is allowed to flow or is pumped into the stream at a constant rate q (Fig. 3.7*a,* and the equilibrium concentration C_d reached downstream is measured. If the background stream concentration of tracer is C_b, then the stream discharge Q can be calculated from

$$Q = q\,C_i - \frac{C_d}{C_d - C_b}$$

Slug injection. This is a known volume V of tracer of concentration C_i is discharged (tipped from a bucket) into the stream, and concentration C is recorded at regular intervals as the slug of tracer that passes the downstream measurement point (Fig. 3.7*b*). In this case, Q is calculated by integrating the area under the concentration-time peak; that is,

$$Q = \frac{VC_i}{\int (C - C_b)\,dt}$$

Gauging Structures. Where water quality measurements are made regularly at the same location in a stream, discharge may be determined using a gauging structure such as a weir or flume. A weir consists of a retaining wall containing a rigid plate of stainless steel with a V-shaped or rectangular notch through which water may flow (Fig. 3.8). The height of water H above the bottom of the V measured by a staff gauge or hydrostatic head sensor can be related to the discharge by an appropriate equation; e.g., for a 90-degree V-notched weir:

$$Q = 1.38H^{2.5}$$

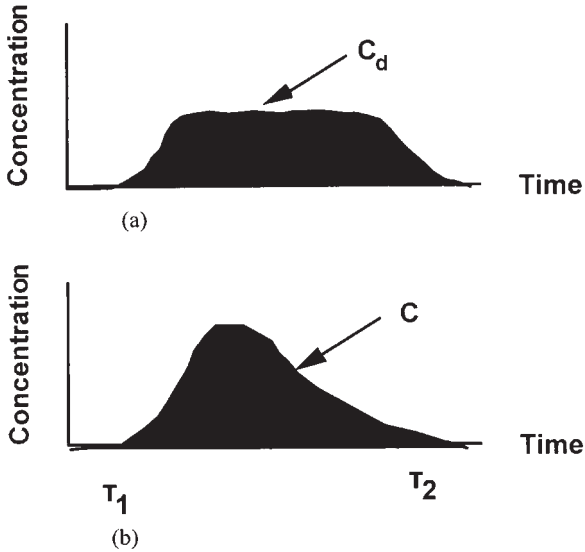

FIGURE 3.7 Concentration-time responses observed for (*a*) constant discharge and (*b*) slug injection techniques of dilution gauging.

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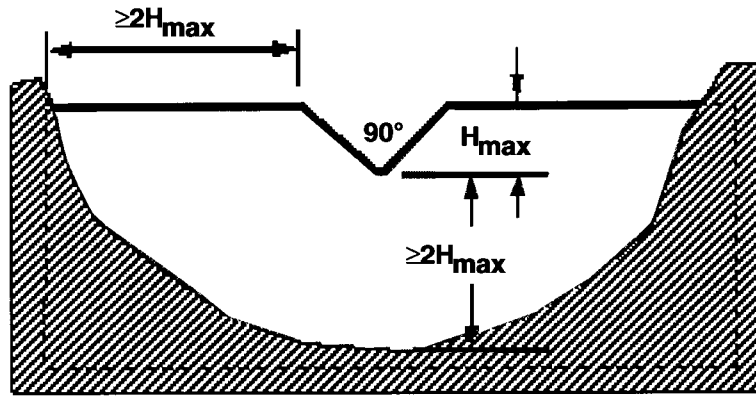
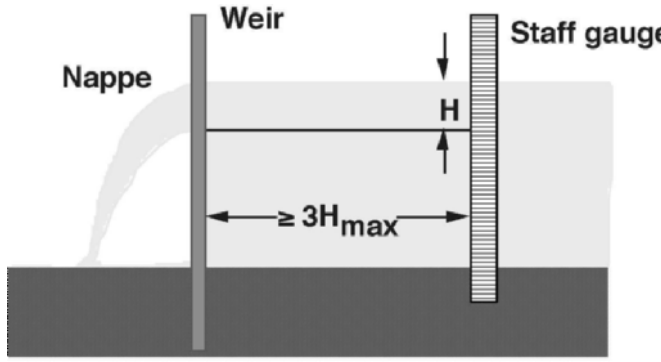


(a)



(b)

FIGURE 3.8 Front (*a*) and side (*b*) elevations of a typical V-notch weir setup for measuring discharge.

where Q is in cubic meters per second, and H is in meters. A range of equations is available for determining discharge from weirs with different shaped notches, e.g., rectangular, stepped, 120-degree, and compound.

These structures can be either temporary or permanent and constructed of metal, wood, concrete, or perpex (the V notch should be made from stainless steel). A disadvantage of weirs is that they tend to accumulate sediment over time and periodically need cleaning. An alternative to the weir for gauging is the use of a flume. This is a rectangular-shaped channel that has a step or projection in the center over which the water must pass to exit. In a similar manner to that for weirs, the height of water passing over the stepped section can be related to the discharge by the appropriate calibration equation.

A similar principle is involved in the use of stage-discharge relationships to determine flow, except that the natural river channel is used as the gauging structure. For a regularly

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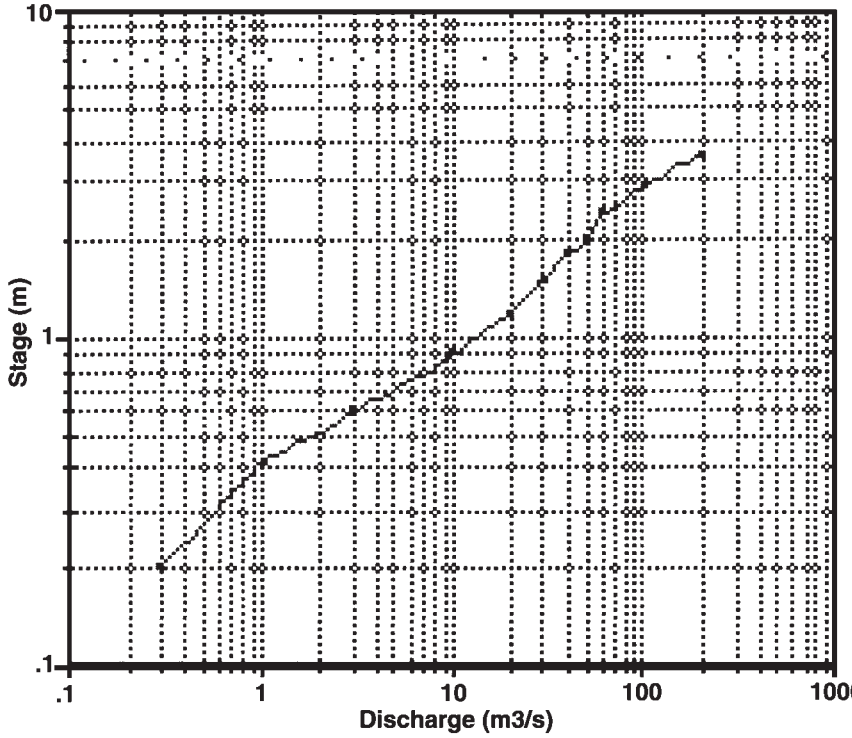

FIGURE 3.9 Stage-height relationship for determining discharge of a river or stream.

visited site, a stage (height) versus discharge relationship can be obtained by recording the water height and at the same time measuring the discharge by velocity-depth or dilution gauging. When sufficient data are collected, a stage-discharge relationship can be determined (Fig. 3.9) and thereafter used to determine discharge simply on the basis of water level. Stage-height relationships typically are of the form

$$Q = a\,(h - z)^b$$

where Q is discharge (m^3/s), h is gauge height (m), z is zero-flow gauge height (m), and a and b are coefficients. Such arrangements can be telemetered or logged to provide frequent or remote measurements of discharge. However, allowance needs to be made for changes in stream morphology with season or flooding.

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CHAPTER 4
WATER QUALITY ASSESSMENT BY ALGAL MONITORING

Martyn Kelly

INTRODUCTION

The term *algae* refers to a highly diverse group of organisms that can be found in almost all habitats on earth (terrestrial as well as aquatic). There are, at a conservative estimate, 35,000 species of algae distributed throughout freshwater, marine, and terrestrial ecosystems worldwide (Anderson, 1992). Which species are found in any particular sample will depend on the interaction between environmental factors and physiological processes operating at a variety of different scales. Several of these factors can be modified by human activities, and as knowledge of the impact of these activities has increased over the past century or so, so it has become possible to make inferences and predictions about environmental conditions based solely on the algae found at a site.

Proposals for using algae in this way extend back to the introduction of the saprobian system (Kolkwitz and Marsson, 1908, 1909), but the practical application of such systems is much more recent. In the first half of the twentieth century, this largely reflects the absence of the raîson d'être that strong, enforceable environmental legislation creates, but more recently, algal-based methods were overshadowed by more practically oriented invertebrate-based methods. Only in the last two decades of the twentieth century have algal-based methods taken a prominent role in the toolkits of regulatory organizations in the developed world.

The literature on algal-based methods is very broad, and this review, necessarily, is selective. It concentrates on the role of algae in monitoring rivers—reflecting my own interests—but the role of algae in monitoring other environments also will be highlighted where appropriate. This review also concentrates on community-level approaches—which infer water quality from the known tolerances of the organisms present—rather than single-organism approaches such as tissue analysis or bioassays. These latter techniques were reviewed by Whitton and Kelly (1995).

The decision about whether or not use of algae is appropriate in a monitoring program is essentially about determining the value of the information provided by algae over that provided by chemical analyses or analyses of other biological elements that are present. This is well illustrated by the case of eutrophication (pollution by inorganic nutrients), which is one of the main areas where algae are used as environmental monitors. Although the chemical factors responsible for eutrophication (phosphorus and nitrogen) are measured relatively

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easily in an analytical laboratory, both show considerable spatial and temporal variation. Moreover, the deleterious effects of eutrophication are not caused directly by the chemicals themselves but by the response of aquatic organisms (particularly algae) to these chemicals. Although it is possible theoretically to use almost any taxonomic group for monitoring eutrophication, it is the primary producers (algae and higher plants) that have the most direct response because it is these which assimilate the nutrients (Kelly and Whitton, 1998). The extent to which such effects are transmitted to higher trophic levels (if at all) depends on a number of ecological and hydrological factors (see Biggs et al., 1998; Stevenson, 1997a, 1997b). Algal-based monitoring therefore is justified in studies of eutrophication.

Another example of a situation where algae are the preferred organisms for biological monitoring is the Artois-Picardie Region of northern France, where many of the rivers are deep, turbid, canalized, and often highly polluted. Under circumstances such as these, invertebrate-based monitoring techniques are limited by habitat and sampling techniques. By contrast, the diversity of diatoms (a common group of algae) was not limited by habitat in the same way, and as a result, pollution indices based on diatoms were able to differentiate between sites and provide valuable information for water quality managers (Prygiel, 1991).

By contrast, biologists with the United Kingdom Environment Agency routinely collect invertebrate samples following intermittent pollution incidents. These samples are used to locate the source of the pollution and can be used as supporting evidence in subsequent prosecutions under the 1991 Water Resources Act. There is no a priori reason why algal samples should not be collected at the same time; however, it is arguable that the extra effort would not be justified because invertebrate samples alone can provide sufficient biological evidence of the pollution event, and their use in a prosecution in the United Kingdom is supported by case law.

PRACTICAL ISSUES

Experimental Design: The Importance of Temporal Scale

Until relatively recently, most algal-based monitoring took the form of broad surveys of water quality with the objective of providing managers and planners with an overview of conditions in a particular geographic area. Although the objectives of biological monitoring are widely accepted, most legislation is still cast in terms of measurable chemical variables, and the role of biological monitoring therefore is usually subsidiary to that of chemical monitoring. This situation is changing gradually with the European Union beginning to frame water quality objectives in ecological rather than chemical terms (e.g., European Community, 1991, 1992). Undoubtedly, this will necessitate a reexamination of the statistical basis of sampling design. For example, if the mean value of an algal variable from an affected site is not significantly different from that at an unaffected one, does this mean that there is really no difference between the two sites or, alternatively, was the sampling strategy inadequate to detect the change?

The short generation times of many microalgae, combined with their susceptibility to hydrological events, means that temporal scale is an important issue when designing a monitoring program. This also has implications for how resources are allocated to studies. Assuming a finite budget, then basic data collected frequently might be of more long-term value than detailed data collected less often. From the point of view of detecting a change, then the sensitivity of any statistical analysis will depend on understanding the scale of within-year and between-year variation at a site.

For example, temperate rivers often experience a spring bloom of diatoms, during which the concentration of cells increases by several orders of magnitude over the course of a few weeks. The onset of this bloom depends on factors such as water turbidity, which

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is related to the amount of detrital material washed into the river following heavy rain. Marker and Collett (1997) noted that the spring bloom of phytoplankton in the River Great Ouse (United Kingdom) started 2 months earlier in 1990, when the last major spate of the winter was in early February, compared with 1989, when the late winter–early spring period was characterized by several major floods. Under circumstances such as these, a single sample cannot be considered to be representative, and it is accepted practice for phytoplankton studies to be based on a series of samples collected over the course of a year.

The frequency at which phytoplankton assemblages are sampled is therefore an important question when designing monitoring program. Kiss et al. (1996) examined a dataset of phytoplankton samples collected at weekly intervals from the River Danube at Göd (Hungary) and then used this dataset to simulate the effect of sampling at fortnightly, monthly, or quarterly intervals (Fig. 4.1). While the simulation of fortnightly sampling detected most of the main trends in the data, sampling at coarser temporal scales led to a loss of the main characteristics of the seasonal changes in phytoplankton density.

Taxonomy

Algal taxonomy can appear daunting to a nonspecialist. Many algal "species" are determined on morphological criteria alone, and in many cases, environmental rather than genetic factors have been shown to be responsible for much natural variability (Wood and Leatham, 1992). The inevitable outcome is a confusing morass of nomenclature caused by different people studying the same organism in different habitats. Many regions of the developed world lack specialist floras on all groups, and workers in these areas have to resort to foreign-language publications. Such problems inevitably can discourage nonspecialists with limited time and budget from maximizing the value of algal-based monitoring.

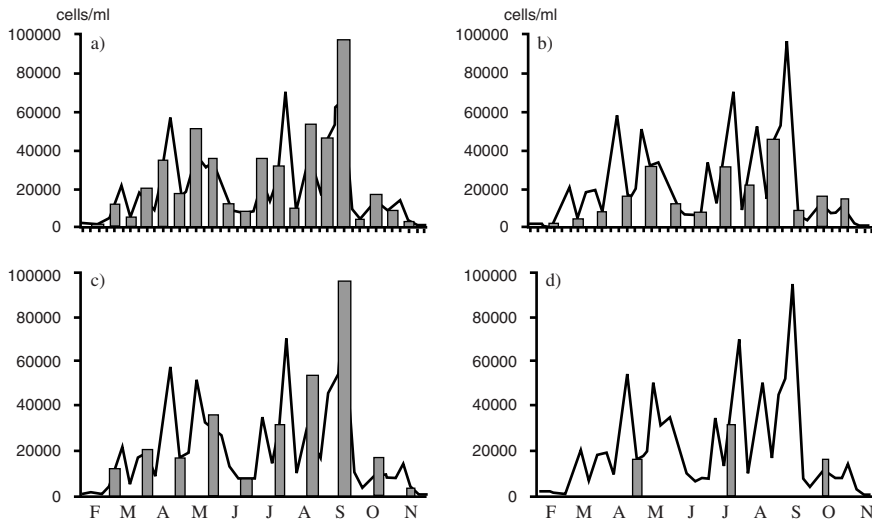

FIGURE 4.1 Change of phytoplankton density at Göd (Hungary) in 1979. The solid line links weekly samples; bars represent subsets of samples chosen to simulate (*a*) fortnightly, (*b*) three-weekly, (*c*) monthly, and (*d*) quarterly sampling intervals.
(From Kiss et al., 1996.)

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General principles that result from this situation include the need for a consistent approach to taxonomy within a study—using taxonomic conventions embodied in a relevant national checklist of flora and the importance of archiving material in local and national herbaria for future reference (see below).

A further important consideration is to concentrate on a level of taxonomy that is achievable under all situations. A trend of recent years has been to develop diatom-based indices based on finite numbers of taxa, lumping rarer species together in order to ease the burden on analysts (Kelly, 1998b; Lenoir and Coste, 1996; Rumeau and Coste, 1988). Nomenclatural disagreements tend to increase at successively finer taxonomic levels (see Kelly, 1999b), and while the establishment of taxonomic standards for a study will not overcome these completely, they at least provide a common measure against which samples can be compared. The problem with such an approach is that the value of the data for long-term monitoring is reduced, although archiving material, whenever possible, allows reexamination when necessary.

Quality Assurance

As the importance of ecological data to environmental decision making increases, so the necessity for quality assurance of these data also increases. The principles of quality assurance (QA) are widely understood (see, e.g., American Public Health Association, 1989), and the principles of international quality standards such as ISO 9000 (International Standards Organization, 1994) can be applied to analytical laboratories. However, there are relatively few methods specifically describing QA methods suitable for algae. Kelly (1999b) provides an overview of the issue for benthic diatoms and phytoplankton, whereas Kelly (2001c) proposes an audit protocol in which the Bray-Curtis similarity measure is used to compare the taxonomic composition of two samples.

USE OF PLANKTON

There is an enormous literature on the ecology of phytoplankton in both freshwater and marine environments (e.g., Reynolds, 1984). Due to the impact of eutrophication on water supplies and the aesthetic and amenity value of lakes in particular, there have been many attempts to use algae as part of monitoring and management programs. The subject is highly technical, and only a few brief guidelines can be offered here. More details of practical techniques can be found in manuals such as American Public Health Association (1989) and Olrik et al. (1998).

In monitoring studies, there is a choice between direct measurement of the phytoplankton assemblage, typically involving identification of some or all taxa along with manual counting, and indirect measurements. The latter include measurements of chlorophyll concentration, in vivo fluorimetry, and turbidity. Identification and enumeration of phytoplankton assemblages provide good insights into the underlying ecological processes that drive community change within water bodies but are time-consuming and require a high level of expertise. By contrast, chlorophyll analysis can be performed quickly and cheaply by most water analysis facilities. Typically, chlorophyll is collected and analyzed along with chemical determinants during routine sampling runs, and the relative low cost of analyses allows for more frequent sampling than is possible when undertaking direct methods. Turbidity is measured most easily as the inverse of lake transparency, which can be measured very quickly and cheaply in situ with a Secchi disk. Turbidity usually is correlated closely with chlorophyll (Harper, 1992) but can be derived from other sources (e.g.,

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humic materials, boat traffic stirring sediment in shallow lakes and rivers, etc.) and therefore needs to be interpreted with caution. Indirect methods of analysis work best where communities are overwhelmingly dominated by a single taxon; where this assumption does not hold, then there is no substitute for direct methods of identification and enumeration.

These data can be used to classify lakes into one of a number of categories depending on the level of eutrophication. The most widely used classification for lakes and reservoirs is that developed by the Organization for Economic Cooperation and Development (Table 4.1). However, all data interpretation should take into account year-to-year variation as well as within-year variations (see above). Measurement of other variables such as Z_m, the depth to the thermocline, provide useful insights into the physical processes that will drive the phytoplankton sucession through the year (Reynolds, 1984).

An important focus of much phytoplankton monitoring by regulatory authorities is to determine the risk of toxic algal blooms. These include blue-green algae (cyanobacteria) in freshwaters and dinoflagellates and, to a lesser extent, diatoms in the marine environment. Identification and enumeration play an important role in such risk assessments, although where large numbers of lakes have to be screened, it is possible to use relatively quick semiquantitative analyses of key species (National Rivers Authority, 1990). Computer models such as PROTECH (*Phytoplankton Responses to Environmental Change*) can be used to predict the risk of such blooms occurring (Reynolds and Irish, 1997).

The same principles as described for lakes also apply to rivers, although hydrological events have a more pronounced effect on species composition and abundance than in the relatively stable environment of a deep lake (Reynolds, 1994; Marker and Collett, 1997). Nonetheless, regular sampling can reveal long-term trends [e.g., Hindák and Makovinská (1999) for River Danube]. Valuable information for identifying long-term trends can be obtained from routine chlorophyll analyses (Balbi, 2000; Kelly and Whitton, 1998); however, a case also can be made for identification and enumeration (Noppe and Prygiel, 1999). Since different groups of algae have different seasonal trends, such data also provide a better basis for developing predictive models of phytoplankton behavior than chlorophyll data alone (Billen et al., 1994; Kowe et al., 1998).

USE OF BENTHIC MACROALGAE

A number of algae are large enough to be recognizable with the naked eye. These include the seaweeds of the marine and brackish littoral zone, along with several species found in freshwaters. Techniques for using these algae for monitoring can be divided into two broad

TABLE 4.1 Boundary Values for Lake Trophic Categories

Trophic category	Total Phosphorus	Chlorophyll	Maximum chlorophyll	Secchi depth	Maximum Secchi depth
Ultraoligotrophic	≤4	≤1	≤2.5	≥12	≥6
Oligotrophic	≤10	≤2.5	≤8	≥6	≤3
Mesotrophic	10–30	2.5–8	8–25	6–3	3–1.5
Eutrophic	35–100	8–25	25–75	3–1.5	1.5–0.7
Hypertrophic	≥100	≥25	≥75	≤1.5	≤0.7

Note: All variables in micrograms per liter except Secchi depth (in meters).
Source: Modified from Organization for Economic Cooperation and Development (1982).

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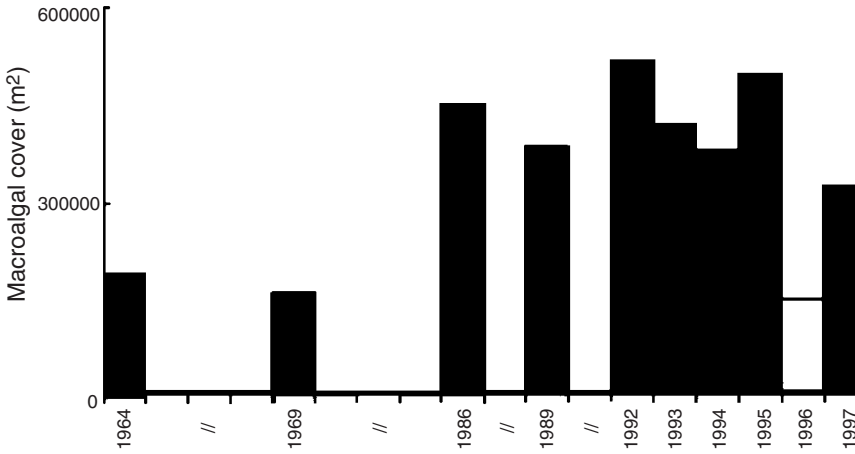

FIGURE 4.2 Coverage of intertidal flats in the Ythan estuary (Scotland) by macroalgal mats (>1 kg/m^2), estimated from aerial photographs.
(From Raffaelli et al., 1999.)

categories: survey methods that rely on measuring the abundance of one or more indicator species and those which measure physiological properties of these species.

Surveying Species Composition and Abundance

While techniques of terrestrial ecology (e.g., point transects) can be adapted to provide semiquantitative estimates of abundance, such procedures are time-consuming, and simple visual estimates often provide sufficient information to be valuable for management purposes. Several survey techniques for macroalgae in rivers have been developed, often as part of more general surveys of all photosynthetic organisms (Standing Committee of Analysts, 1987; Österreichisches Normunginstitut, 1995; Jarlman et al., 1996). Similar techniques also exist for the marine and estuarine environment.

Three examples of how macroalgae abundance data can be used in practical monitoring situations are described below:

1. *Control of filamentous algae in River Sihl, Switzerland* (Elber et al., 1996). The natural flow of the River Sihl was disrupted in the 1930s when a pressure tunnel diverted water from an upstream lake (Sihlsee) through a hydroelectric plant and then to Lake Zurich. One effect of the reduced flow was less dilution of effluents from sewage discharges entering the river downstream of this point, leading to profuse algal growth and associated fish kills. Elber et al. (1996) quantified the relationship between algal density (classified on a simple six-point scale) and discharge. Noting that high discharge (associated with spates) lead to a reduction in the density of filamentous algae, they proposed a management strategy that involved regular monitoring using the six-point scale. If density exceeded point 4 on this scale, then the next natural high-water event is supplemented by water from the Sihlsee in order to ensure that discharge exceeds a critical point where filamentous algae are scoured away.
2. *Detection of eutrophication in Scottish streams* (Marsden et al., 1997). New regulatory requirements necessitated collecting data on trophic status of a large number of streams

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TABLE 4.2 Classification Limits Used to Describe the Trophic Status of Streams and Rivers in the Forth Catchment

	Total reactive phosphorus (mg/liter)	Algal abundance index (AAI)
Oligotrophic	<20	<20
Mesotrophic	≥20, <99	≥20, <49
Eutrophic	≥100, <499	≥50, <69
Hypertrophic	>500	>70

Source: Modified from Marsden et al. (1997).

in the Forth catchment in Scotland during the early 1990s. Many of these streams were already visited as part of a routine invertebrate sampling program, and benthic algal cover had been recorded on these visits using a semiquantitative scale of abundant, common, present, rare, and none. These data were converted into a simple scale, the *algal abundance index* (AAI), using the following formula:

$$\text{AAI} = \frac{2\,(\text{number of abundant records}) + \text{number of common records}}{\text{number of site visits}} \times 100$$

A simple scale was used to relate AAI to phosphorus concentrations in the river (Table 4.2), and as a result, the trophic status of 67 percent of the 3247 km of rivers in the catchment was defined. Twenty-six percent of these were classified as eutrophic according to currently accepted guidelines (described in Marsden et al., 1997), and these could then be subjected to more detailed study. Although the AAI is very simple, it is a good example of how simple observations can provide valuable data for management purposes.

Repeated visits to the same site overcome the temporal variability in filamentous algal abundance, as highlighted by the Elber et al. (1996) study. However, a further issue when studying macroalgae is that of spatial variability and, in particular, the reliance on suitable substrata for macroalgal growth. The *mean trophic rank* macrophyte index (which includes algae such as *Cladophora* and *Enteromorpha*) includes special procedures to ensure that comparisons between sites above and below sewage discharges of interest are not distorted by changes in substrate composition (Holmes et al., 1999). A final cautionary note is that under some circumstances excessive algal growth can be caused by an absence of grazers rather than an excess of nutrients. Streams with high levels of heavy metals are a case in point (Armitage, 1979). Light availability and water temperature are also important factors influencing macroalgal biomass.

3. *Detection of eutrophication in River Ythan estuary, Scotland* (Raffaelli et al., 1999). This example involves estimating changes in macroalgal cover on intertidal mudflats using aerial photographs. Comparisons between surveys in the period 1986–1997 with earlier surveys show a clear trend toward higher macroalgal abundance in the estuary as a whole (Fig. 4.2) and a change in spatial patterns of macroalgal cover. These changes are consistent with predictions concerning the effects of eutrophication. The low algal abundance in 1996 was attributed to severe floods in September 1995 that probably scoured away much of the overwintering biomass that forms the inoculum for the spring bloom. Raffaelli et al. (1999) were able to calibrate the aerial surveys to establish a detection limit of about 1 kg/m^2 of algal biomass measurable from aerial surveys. Limitations of the method include the inability to identify individual algal genera, but in this case the information was already well known, with *Enteromorpha* most common at downstream sites and *Chaetomorpha* and *Ulva* more abundant at upstream sites. This

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study also illustrates that it is important to extend the sampling program over several years in order to understand the extent of between-year variation and to reduce the probability of a freak year such as 1996 influencing interpretation.

These three examples are linked by their relative simplicity, achieved through concentrating efforts on the dominant photosynthetic organisms in the system at the expense of rarer organisms. As such, they may not be suitable for some monitoring purposes (e.g., biodiversity studies); however, in the case of eutrophication, excess growth of dominant photosynthetic organisms often has deleterious effects on other trophic levels of the ecosystem (Raffaelli et al., 1998). The conceptual model of Biggs et al. (1998) for stream periphyton dynamics provides some theoretical support for this approach to monitoring.

Measuring Tissue Concentrations of Contaminants

The ability of macroalgae (along with bryophytes) to accumulate heavy metals has been proposed as a monitoring tool in both freshwater (e.g., Whitton et al., 1989) and marine (e.g., Say et al., 1990) environments. The issue has been reviewed in Whitton and Kelly (1995), and only brief comments will be made here.

Whitton et al. (1991) summarize methodology. Briefly, plants are harvested and transferred to the laboratory in a moist condition, where they are washed in distilled water to remove sediment, etc. Dependng on the study, either whole plants or tip material (typically the first 0 to 2 cm) is removed. This material can then be either air dried for long-term storage or digested in acids and analyzed for metal content directly.

Although efforts have been made to quantify the relationship between metals accumulated in the alga and water, the most effective, practical use of algae (and bryophytes) has been to indicate the presence of intermittent discharges in rivers or to locate "hot spots" of metal pollution in estuaries where dissolved metal concentrations are highly variable due to tides (Kelly, 1989). Such techniques are not confined to heavy metals; they also have been used as monitors of radionuclides (Howe and Hunt, 1984; Howe and Lloyd, 1986) and organic pesticides (Mouvet et al., 1993). The latter study used the moss *Cinclidotus danubicus,* but the same principle could be applied easily to macroalgae.

USE OF BENTHIC MICROALGAE

A large number of methods for monitoring rivers based on benthic microalgae have been developed in recent years. Early methods were elaborations of the Kolkwitz and Marsson (1908, 1909) saprobic system and included all taxonomic groups (Zelinka and Marvan, 1961; Sládacek, 1973), although more recently attention has concentrated on the diatoms. Diatoms have several advantages for environmental monitoring: They are one of the most common groups of benthic algae in rivers, their taxonomy is relatively well understood, and the properties of the silica cell wall (or frustule) mean that permanent slides can be prepared and stored indefinitely. Finally, quantification of diatoms on permanent slides is much easier than that of assemblages of the entire algal community (a mixture of unicells, colonies of various sizes, and filaments), for which special counting chambers are required. A few recent studies have concentrated on other groups such as epilithic cyanobacteria (Perona et al., 1998), but the practical usefulness of such work remains to be tested.

Sampling of benthic diatoms from running waters is relatively simple: If cobbles or small boulders are present, then the upper surfaces of at least five replicates are scrubbed with a hard toothbrush to remove the brown surface film. This is then collected in a sam-

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ple bottle for transfer to the laboratory, where it is treated with one or more oxidizing agents to remove organic material, and permanent slides are prepared (Kelly et al., 1998). If cobbles and boulders are not present, then there are various options, including the use of artificial substrates or sampling from submerged or emergent macrophytes.

Organic Pollution

Two groups of indices based on diatoms are widely used. Many German-speaking countries use modifications of a saprobic zoning system proposed by Lange-Bertalot (1979), whereas French-speaking countries have tended to develop water quality indices based on the index of Descy (1979). In particular, Michel Coste has developed indices based on species-level identification [*indice de polluosensibilité:* (IPS); Coste in CEMAGREF, 1982] and generic-level identification [generic diatom index (GDI); Rumeau and Coste, 1988]. The latter is very easy to use, but its effectiveness is variable. Some workers (e.g., Coste et al., 1991; Kelly et al., 1995) found very good relationships between IPS and GDI, whereas others (van de Vijver and Beyens, 1998) found a poor relationship. To overcome some of these problems, indices based on intermediate levels of taxonomy have been developed for practical use in France (Lenoir and Coste, 1996).

pH

Battarbee et al. (1999) describe the historical development of these methods. Most recent work has used statistical techniques such as weighted averaging to assign pH optima and pH tolerances for taxa (Birks et al., 1990). These values generally are derived from training sets of sites in the same region as the site of interest. One of the most impressive uses of diatoms for monitoring has been the reconstruction of pH using diatoms preserved in lake cores. These transfer functions should be used with caution in streams; however, a few studies have concentrated particularly on pH and stream diatoms (e.g., van Dam and Mertons, 1995; Pan et al., 1996). The study of Lancaster et al. (1996) deserves special mention because it describes techniques by which long-term trends in acidification (and other pollutants) can be monitored.

An alternative approach to monitoring pH was developed by Coring (1996). His *diatom assemblage type analysis* (DATA) does not attempt to model the relationship between community composition and pH but instead attempts to differentiate between permanently acidic streams, periodically acidic streams, and circumneutral streams using the following types:

1. *Permanently neutral, alkaline;* pH never <7.0, no danger of acidification.
2. *Endangered by acidification;* pH minimum never <6.0; pH generally <6.5 and mostly about 7.0.
3. *Episodically slightly acidic;* pH similar to types 1 and 2, but rare pH depressions not <5.5.
4. *Periodically acidic streams;* pH normally <6.5, minimum <5.5.
5. *Permanently acidic streams;* pH <5.5, minimum often <5.0, sometimes <4.3.

There is also a separate category for dystrophic streams. Coring (1996) contains a classification scheme, based on Hustedt's (1938–1939) pH groups (Table 4.3) plus a key to aid assessment of acidity in calcium-poor, low-buffered mountain streams. This key is very useful for quick assessments of pH.

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Eutrophication

Eutrophication only recently has been recognized as a serious problem distinct from organic pollution, and development of diatom-based indices is, as a consequence, only just beginning. Early attempts include a modification of the zoning system of Lange-Bertalot (1979) to take account of inorganic nutrient enrichment. This system, developed by Steinberg and Schiefele (1988), was based on 50 species and subsequently was developed into a quantitative weighted-average-based index by Schiefele and Kohmann (1993). This index was tested by Kelly et al. (1995) and found to be relatively insensitive to U.K. conditions. This, in turn, stimulated the development of the trophic diatom index (TDI) in the United Kingdom (Kelly and Whitton, 1995; Kelly, 1998b). More recently, trophic indices have been developed in Germany (Coring et al., 1999) and Austria (Rott et al., 1999). Interestingly, all these studies, along with that of Pan et al. (1996), produced indices that, when regressed against the variable of interest, had R^2 values that were lower than for comparable models of stream pH. Pan et al. (1996) suggested that this reflected the greater temporal and spatial variability of phosphorus compared with pH. Despite this, however, the United Kingdom TDI has been used widely as part of a suite of methods to implement tighter nutrient controls on large sewage works (Harding and Kelly, 1999).

The experience in the United Kingdom led to some insights relevant to data interpretation in other environments. These included the importance of not confusing the response of organic pollution with that of eutrophication and the necessity of understanding the limits of community-based indices (Kelly, 1998a). To date, most trophic indices assume that phosphorus is the limiting nutrient. In practice, the role of nitrogen is difficult to separate from that of phosphorus. If the objective of the monitoring program is to manage phosphorus (as it was in the United Kingdom), then the TDI would not be appropriate in a river where primary production was limited by nitrogen (Kelly, 1998a). Finally, it is important that interpretations are based on surveys with sufficient temporal replication to account for within-site variations.

Species Diversity

A wide range of species diversity measures are available, and Magurran (1988) provides a helpful review. The use of species diversity as a direct measure of pollution has been tested frequently and found to be inadequate (van Dam, 1982; van de Vijver and Beyens, 1998). Unpredictable and unstable environments are dominated by one or a few very common

TABLE 4.3 Classification Scheme for the Estimation of Types of pH Responses in Streams Using the DATA System of Coring (1993, 1996)

	Percentage of Hustedt's pH groups			
	Acidobiontic	Acidophilous	Circumneutral	Alkaliphilous
Type 1	<10		30–60	30–80
Type 2	<10		50–90	<10–50
Type 3	<20	5–50	30–70	<20
Type 4	15–70	5–50	10–40	<10
Type 5	20–90	10–70	<10	<5

Note: Based on the pH classification of Hustedt (1938–1939). Acidobiontic taxa have an optimal distribution at pH 5.5 or below; acidophilous taxa have an optimum between pH 5.5 and pH 7; circumneutral taxa ("indifferent" in Hustedt's original classification) have an optimum of about pH 7; and alkaliphilous taxa have an optimum of greater than pH 7.

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species and a smaller number of rarer species (May, 1975); such conditions are typical of flashy streams even in the absence of pollution. Indeed, moderate levels of enrichment can lead to increases in diversity, although interpretation is difficult. In the case of the River Wear, upstream sites consistently have lower diversity than sites further downstream, but the range of diversity values at all sites is wide (Fig. 4.3, based on unpublished data collected by the author). This, in turn, reflects conditions within the river; any factor that permits a single taxon to flourish at the expense of others will lead to low diversity values. At the upstream sites, this may reflect the harsh environment created by fast current velocities, whereas at the midstream and downstream sites, low diversity was observed frequently in

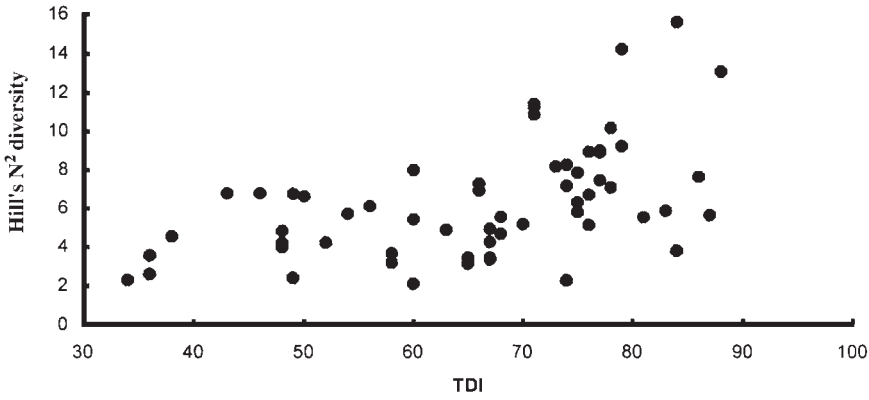

FIGURE 4.3 Longitudinal changes in diversity (as Hill's N_2 diversity) at sites along the River Wear, County Durham, NE England, between 1993 and 1997.

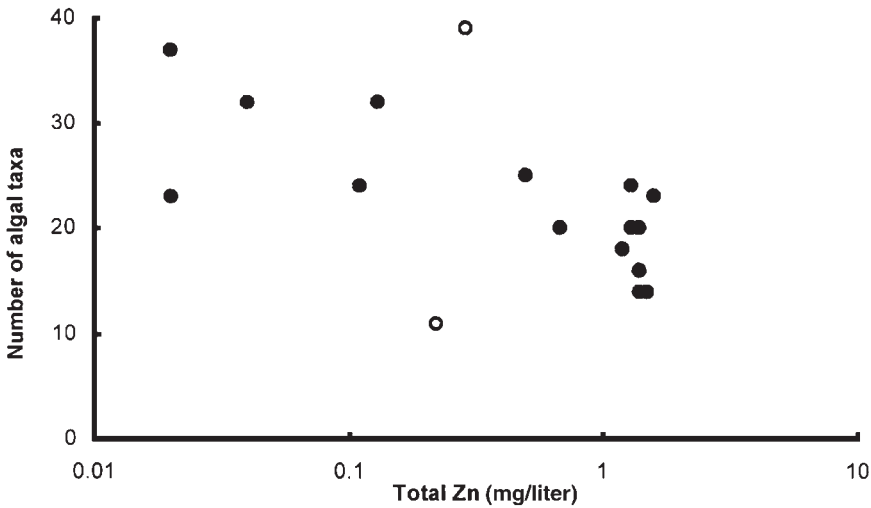

FIGURE 4.4 Relationship between total zinc and the number of algal taxa in streams in the northern Pennine orefield. Open circles represent two outliers representing a particularly species-rich environment (downstream of the confluence between rivers contributing different inocula to the flora) and a particularly impoverished site very close to a stream source. Equation for the relationship (excluding outliers): Number of taxa $= -0.082 \log \mathrm{Zn} + 1.48$; $R^2 = 0.76$; $F = 17.9$; $P < 0.001$.

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the summer when one species (often *Cocconeis placentula*) dominates due, presumably, to selective grazing by benthic invertebrates. Species diversity indices are useful as adjuncts to pollution indices when interpreting results, but they are of otherwise limited usefulness for environmental monitoring purposes.

One example of where a species diversity measure may be of value is for monitoring heavy metals. A very simple measure, the number of taxa recorded, decreases as heavy metal concentrations increase (Kelly, 1999a), and this was used as part of a study on the potential for rehabilitation of streams draining an abandoned lead-zinc mining area (Fig. 4.4). The potential benefit of various remediation schemes on water quality (estimated from hydrological models) could then be translated into an ecological benefit using the relationship between species numbers and total zinc in streams in the vicinity. Although very simple, it provided a rapid and cost-effective insight into the problem.

ASSESSING BASELINE CONDITIONS

As ecological principles are gradually incorporated into environmental legislation, so the role of biological monitoring is changing gradually, from a reconnaissance and investigative tool that supports legislation that usually is drafted in terms of chemical variables to a means of quantifying a fundamental characteristic of an aquatic ecosystem. Terms such as *biological* (or *ecological*) *integrity* and *ecosystem health* are being used with increasing frequency not just in the scientific literature (e.g., Rapport, 1992), but also in legislation and monitoring and restoration programs. The objective is to define a pristine (or at least preimpact) state for a particular ecosystem, against which anthropogenic pertubations can be measured.

In the case of standing waters, it is possible to identify the preimpact state using palaeolimnological methods to identify fossil remains in sediment cores. The best example is the use of diatoms in such cores to demonstrate the acidification of lakes in regions with low natural buffering capacity (Battarbee et al., 1999). By linking changes in dated cores with known historical events, this work played a significant role in shaping public policy toward sulfur dioxide emissions in the United Kingdom during the 1980s. It does, however, raise an interesting philosophical point. Identification of the factors responsible for floristic changes helps to define a trajectory for subsequent remediation. However, in the case of the liming of Loch Fleet (southwest Scotland) to restore chemical conditions capable of supporting fish life, the diatom assemblage after restoration was significantly different from that of the preimpact state of the lake (Flower et al., 1990). The role of diatoms in studies such as these and elsewhere (e.g., establishing the natural trophic state of lakes; Bennion et al., 1996) lies in determining whether or not changes are due to anthropogenic causes. The decision about appropriate targets realistically is a matter of aesthetics, amenity, and economics as much as it is one of ecological niceties.

Such palaeolimnological studies are necessarily confined to depositional environments, and efforts to extend the methodology to running waters (e.g., Reavie et al., 1998) are unconvincing. Alternative approaches include the analysis of material stored in herbaria: either archived diatom slides (Battarbee, 1981; Flower, 1986) or diatom epiphytes dried on macrophyte specimens (van Dam and Mertens, 1993). Investigating a macrophyte-rich shallow lake in the Netherlands, van Dam and Mertens (1993) were able to demonstrate a shift from species typical of oligotrophic conditions for samples collected in 1934 to species typical of meso- and eutrophic conditions from samples collected in 1989.

If such historical reconstructions are not possible, then another option is to develop an artificial index of biological integrity. Development of such indices for diatoms is still at an early stage, but they typically involve a statistical comparison between a sample site and a group of (relatively) unaffected reference sites that match the site of interest in physical and geomorphologic characteristics. Chessman et al. (1999) adopted the approach developed for

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the invertebrate-based RIVPACS (see references Chap. 1) and classified a series of reference sites using cluster analysis and then used discriminant analysis to relate the clusters to environmental variables (mainly geomorphological characteristics unaffected by human activity). Test sites could then be related, via discriminant analysis, to the most appropriate cluster, and then the ratio of observed to expected characteristics such as number of genera, water quality indices, etc.) could be calculated. However, this model was relatively unsuccessful at allocating sites to the correct cluster, possibly due to the fact that generic, rather than specific, determinations were used (Chessman et al., 1999).

A second approach to evaluating biological integrity is to use the average (or sum) of several attributes of the assemblage. This is known as the *multimetric approach* and is particularly common in the United States. Kentucky Division of Water (1994) have developed one such approach, the *diatom bioassessment index* (DBI), that uses five variables: taxa richness, diversity, pollution tolerance index, percentage abundance of pollution-sensitive species, and percentage similarity of assessed and reference sites (Table 4.4). Low values of the DBI indicate severe impairment, whereas high values indicate excellent ecological integrity. Another approach is described by Hill et al. (2000). Their *periphyton index of biotic integrity* (PIBI) is not limited to diatoms and includes measures of biomass and enzyme (alkaline phosphatase) activity as well as analyses of the algal taxa present at a site (Table 4.5). For the Mid-Appalachian region of the United States, where the index was developed, acceptable stream conditions were defined as the upper 25th percentile of sites (PIBI $\geq$ 72), although the authors also noted significant between-year variations in PIBI that may confound interpretation. Many ecologists may quibble with the details of these multimetric indices, and my earlier comments on the use of species diversity highlight one weakness with both the DBI and PIBI. However, Hill et al. (2000) stress that this type of simplification is necessary if it is to be understood by nontechnical resource managers. More work clearly is needed on techniques such as this.

Some progress also has been made toward a system for classifying the ecological integrity of running waters in Austria based on the entire algal community at a site (Pipp and Rott, 1996).

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The problems of establishing a baseline reflect the extent to which the demands made by current legislation have pushed the monitoring agenda in hitherto unforeseen directions.

TABLE 4.4 Variables and Scoring Ranges Used to Calculate the Diatom Bioassessment Index (DBI) of Kentucky Division of Water

Score	Taxa richness	Diversity	DTI	RA(s)	PSc
1	<20	<1.5	1.0–1.5	<0.1	<10
2	20–30	1.5–2.5	1.5–2.0	0.1–1	10–30
3	30–50	2.5–3.5	2.0–2.5	1.0–5.0	30–50
4	50–70	3.5–4.5	2.5–3.0	5.0–20	50–75
5	> 70	> 4.5	> 3.0	20–100	75–100

Note: Taxa richness is based on number of taxa in a count of 500 to 1000 valves; diversity uses Shannon's (1948) index; DTI is a pollution index similar to the diatom-based indices discussed elsewhere in this chapter; RA(s) is the relative abundance of sensitive species (using the pollution tolerance ranks of the DTI; PSc is the percentage similarity of the assessed and reference assemblages. DBI is the mean of all five metrics.

Source: Modified from Kentucky Division of Water (1994).

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TABLE 4.5 Measurements (Metrics) Included in the Periphyton Index of Biotic Integrity (PIBI)

Metric	Calculation	Range	Score*
Relative taxa richness	No. of algal genera/expected no. of algal genera†	0–1	0–10
Diatom metric	No. of diatom cells/total no. of algal cells	0–1	0–10
Cyanobacteria metric	1 − (no. of cyanobacteria cells/total no. of algal cells)	0–1	0–10
Dominant diatom metric	1 − (no. of dominant diatoms/total no. of diatoms)	0–1	0–10
Acidophilic diatoms metric	1 − (no. of acidophilic diatoms/total no. of diatoms)	0–1	0–10
Eutraphentic diatoms metric	1 − (no. of eutraphentic diatoms/total no. of diatoms)	0–1	0–10
Motile diatoms metric	1 − (no. of motile diatoms/total no. of diatoms)	0–1	0–10
Chlorophyll metric‡	6.67/[absolute value of 6.67 ±Chl (mg/m^2)]	0–1	0–10
Biomass metric‡	0.006/[absolute value of 0.006 ±AFDM (g/m^2)]	0–1	0–10
Phosphatase activity metric‡	18.2/[absolute value of 18.2 ±APA (nmol/g/h)]	0–1	0–10
Range of potential PIBI scores			0–100

Note: AFDM = ash free dry mass; APA = alkaline phosphatase activity; Chl = chlorophyll.

*Score range is calculated by multiplying raw range by 10, so the 10-metric PIBI total equals 0 to 100.

†Expected number of genera is the observed maximum genera richness for each year.

‡Chl, AFDM, and APA are two-tailed metrics that have low scores when both are lower and higher than the median standing crops. Median values for each metric are given in the numerator of each formula.

Source: Hill et al. (2000).

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What will the next generation of monitoring biologists want to measure, and where will they find their baseline data?

The ease with which permanent slides of diatom samples can be prepared makes this group an ideal candidate for a record of contemporary conditions that future generations can reanalyze, if necessary, in various means. The situation at present is that the best-studied sites are not necessarily those of most interest to regulatory agencies, and the level of documentation is not always sufficient. Kelly et al. (1996) suggest that samples collected from contemporary monitoring programs should be archived routinely in national herbaria.

A second possibility is that macroalgal tissues are dried and stored in herbaria for future analysis of contaminants. Again, contemporary analyses depend on the availability of material from relevant sites and are destructive to the tissue in question. Material is cheap to collect and process to a state where it can be stored and provides a valuable database to monitor trends in variables that may not be considered problematic at the time of sampling (Whitton and Kelly, 1995; Kettrup and Marth, 1998).

CONCLUDING COMMENTS

Algal-based monitoring is a large and rather diffuse field. It is also one in which the literature contains rather more good ideas than actually survive the transition from academic research laboratory to practical management tool. In this review, I have attempted to provide as many practical examples as possible. While much of the literature makes too many assumptions about the taxonomic expertise of end users, I have tried to emphasize instead the need for consistent and reliable techniques that can be repeated over several years in order to give a picture of between-year variation.

The changes over the past two decades have been dramatic as new legislation has forced regulatory agencies to explore new techniques. As public perceptions of the environment increase, so too does the need for robust monitoring tools. Some of the methods described here have provided evidence on which multimillion-pound investments are made. This success has, in itself, brought new challenges not just in data interpretation but also in issues such as quality assurance.

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CHAPTER 5
BIOLOGICAL MONITORING AND ASSESSMENT USING INVERTEBRATES

Ian C. Campbell

INTRODUCTION

This chapter will focus primarily on the use of benthic macroinvertebrates for monitoring freshwater ecosystems. Many of the techniques and principles discussed are equally applicable to marine systems or the use of zooplankton for water quality monitoring, but given the constraints of a single chapter, it is not possible to encompass these other systems in any detail.

Biological versus Chemical Monitoring Programs

The selection of biological versus chemical monitoring and the balance between the two will depend on the purpose of the monitoring program. Biological monitoring has the capability of detecting unexpected impacts on aquatic systems because the biota will respond to any impacts whether expected by the investigator or not. Biological data are more directly related to the ecological condition or "ecological health" of aquatic ecosystems than chemical data, although the concept of ecological health is itself somewhat problematic (Fairweather, 1999; Norris and Thoms, 1999; Wicklum and Davies, 1995). However, biological data are less specific than chemical data, and it may not be obvious whether an affected biological community is responding mainly to poor water quality or poor habitat quality, for example. The two are often linked.

Chemical water quality monitoring has the advantage of specificity. If a water body is being monitored for the pesticide lindane, for example, and high levels are found, it is clear that the water body has been contaminated with lindane. Continuing the monitoring will demonstrate clearly whether contamination is continuing and, when it ceases, the pattern of decline of lindane concentrations. This sort of information is essential to determine whether abatement or policing practices are effective and the safety of the water for human use. However, chemical monitoring requires the specific chemical contaminants to be known prior to the sampling program commencing. A monitoring program for lindane will not detect contamination by mercury, and if contamination by mercury is not expected and therefore not tested for, it will not be discovered.

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In a number of examples, contamination of aquatic ecosystems remained undetected despite chemical monitoring programs because the nature of the contamination was unexpected. For example, McKaige (1986) conducted a 1-year study of the invertebrate assemblages of the Thredbo River in southeastern Australia. The stream, which is located in Kosciusko National Park, had been the subject of several previous investigations of chemical water quality because of particular concerns about the impact of sewage effluent from the Thredbo Ski Village on the river (Hogg, 1984). However, McKaige (1986) found that at a site downstream of the village in July (southern hemisphere winter), species richness was reduced to 50 per Surber sample compared with 60 and 63 at the two upstream sites. Total number of individuals was depressed to 330 per sample ($0.05/m^2$) compared with 1500 and 1502 at the two upstream sites. These results are consistent with toxic pollution, presumably from leachate from the village waste dump, rather than sewage impacts, which would depress species numbers but increase total numbers of organisms. Toxic leachate had not been suspected previously as a problem, and thus no chemical monitoring for toxicants had been conducted previously.

Biological monitoring can detect the impacts of all stressors present. It is thus ideally suited to routine ambient monitoring programs and to broad-scale environmental condition surveys. Chemical monitoring is far more suitable for compliance monitoring and the monitoring of specific sites where problems have been clearly identified and the nature of the contamination is established.

Why Use Invertebrates?

The invertebrates are one of the components of aquatic ecosystems most widely used for biological monitoring for a number of reasons. These have been documented by numerous previous authors (e.g., Hynes, 1960; Hellawell, 1986; Rosenberg and Resh, 1993). The first and most obvious reason is the diversity of invertebrates, particularly insects, which make up about 54 percent of all described species of organisms (Wilson, 1988). Any biological monitoring program that does not include invertebrates is likely to be excluding much of the biodiversity present at a site. Intuitively, groups with many taxa present at a site are likely to contain more specialists, which are likely to be sensitive to environmental change.

Second, invertebrates are almost ubiquitous in aquatic systems—wherever there is water, there are likely to be invertebrates. Consequently, seldom can invertebrates not be used for monitoring because they are absent from the system to be monitored. Third, invertebrates have limited mobility, so they are not able to move out of an area if conditions deteriorate and then quickly return later. They thus reflect the history of the site, enabling intermittent contaminants to be detected. Finally, their life cycles are usually on the order of months to years long, which also limits their ability to recolonize sites rapidly.

Types of Biological Monitoring

Biological monitoring is carried out most frequently for large-scale assessment of ecosystem condition, routine ambient monitoring, or to assess local environmental impacts. Monitoring of the first type would be used for state-of-the-environment reporting, and the second type would be used to establish whether the waterways of a particular region are deteriorating, improving, or stable in terms of their overall ecological condition. Monitoring of the third type is at a smaller scale, attempting to answer questions about the impact of a particular discharge or other activity on a particular stream or other water body. Monitoring may use the entire biological community or, more commonly, a subset of it, such as invertebrates, algae, or fish. More restricted subsets also are used frequently, such as the EPT (Ephemeroptera,

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Plecoptera, Trichoptera) orders (e.g., Lenat, 1988) or single species, as in fluctuating asymmetry in Chironomidae and other invertebrates (e.g., Clarke, 1993). Various physiological responses, such as changes in respiration rates in fish or invertebrates, also may be used for continuous effluent monitoring (e.g., Morgan, 1976). This chapter will emphasize invertebrate assemblage analysis because this is the most widely practiced form of invertebrate monitoring, but the use of fluctuating asymmetry also will be briefly discussed.

DESIGN OF MONITORING PROGRAMS

The design of biological monitoring programs has always been problematic (Rabeni et al., 1995; Resh et al., 1995). Monitoring at a single site over time is relatively straightforward. As long as the sampling and sorting methods and the taxonomic resolution remain uniform, change through time can be detected, although see Linke et al. (1999). For broadscale ambient monitoring, the detection and measurement of change may be sufficient to answer questions about the trends in environmental quality. However, there are two areas where difficulty arises.

The first difficulty occurs when we wish to identify causes of environmental impacts. Standard scientific procedure requires the use of controls, in this case a similar site or sites unaffected by the putative impact. The simplest experimental design involves selection of sites prior to impact commencing, including one site or group of sites that is subjected to the impact and one that is not—the so-called BACI design (before after control impact) (Green, 1979; Underwood, 1991). Difficulties arise in use of these designs in studies of streams and rivers because the control sites often are upstream of the impacted sites, which becomes a confounding factor in the design. There is also an assumption required for the statistical analysis of BACI designs that the control and impacted sites are independent of each other, even though much of stream ecological theory is based on the assumption that downstream sites are influenced by and not independent of upstream sites.

BACI designs are not always possible in biomonitoring. For example, there is often a need to assess the impact of an activity that has already commenced and may have been operating for a number of years. The difficulty lies in establishing what the biota of a site would have been in the absence of any impact. It is well established that spatial variations in invertebrate communities are considerable even in the absence of any impacts (e.g., see Hynes, 1970). Control sites, in the sense of sites apparently unaffected, may be available, e.g., upstream sites in rivers, but in many cases control sites on the same river may not be available. Where unaffected sites are available, it is important that several are sampled to provide data with which the data from the putatively affected site can be compared. This at least allows the investigator to see whether the data from the impact site lies within or outside the range of that from the control sites.

The second difficulty arises when there is a requirement to make a judgment about the environmental quality of a site. While detecting trends is simple, to judge the quality requires some assessment of what the assemblage at the site would have been in the absence of human disturbance. This problem is related to the preceding problem. Is there an objective method of assessing what the biological community at a site would have been prior to human impact? Three approaches have been employed to solve this problem. One is the selection of control sites on the same stream, as discussed previously. The second approach has been to find *reference sites,* i.e., sites with little or no impact that may be on the same stream or on other streams in the same region to which the fauna of the impact sites can be compared. The third approach has been to develop models to predict what the fauna at the impact site should have been in the absence of impact and compare the existing fauna with that. This third approach will be discussed in more detail below.

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The difficulty with the reference-site approach is that of finding unaffected sites or even sites that are only slightly affected. For smaller streams, most regions have some sites that are in relatively good ecological condition, but the problem is acute for assemblages in large rivers. Each large river is virtually always the only large river in its region. With what could one compare invertebrate assemblages from the Mississippi, the Murray, or the Mekong? Yet large rivers are also the recipients of the problems of all their tributaries, so frequently the whole main channel is degraded to a significant extent.

For smaller streams, reference sites on other streams are more likely. One issue may be deciding when a site is too distant to act as an effective reference. Within the United States, ecoregions have been mapped that are based on soils, land use, land surface form, and potential natural vegetation (Bailey, 1976; Omernik, 1987; Gallant et al., 1989). This has been done to assist managers of aquatic resources to understand regional patterns of attainable quality. Aquatic biologists have suggested that reference sites should be located within the same ecoregion as the site to be evaluated. However, the ecoregions do not incorporate biogeographic information on aquatic invertebrates and a quick comparison of the patterns of ecoregions (Omernik, 1987) with the distribution patterns of North American mayflies (Allen, 1990) indicates little correspondence. Thus it is unlikely that the U.S. ecoregion approach will be a successful predictor of aquatic invertebrate assemblage composition. Marchant et al. (1999) found that terrestrial biogeographic regions were a poor predictor of stream invertebrate assemblage composition in southeastern Australia. The issue has been addressed recently by a full issue of the *Journal of the North American Benthological Society* (see Hawkins and Norris, 2000), with 15 papers all concluding that the terrestrial ecoregions approach was not successful in predicting invertebrate community distributions. Curiously, none of the papers took the relatively simple approach of comparing published biogeographic data with published ecoregions.

SAMPLING METHODS

Standardization

Biological monitoring and assessment are essentially comparative studies—comparing the biota of a site at a given time with that at the same site at another time or comparing unaffected with putatively affected sites. The key factor in selection of sampling methods for biological monitoring or assessment, therefore, is repeatability. The suite of techniques used must be equally applicable at all sampling locations and at all sampling times and must be adhered to rigidly. If this is not the case, there is no way of determining whether differences between samples are caused by environmental impacts or simply are artifacts of the sampling process or changes in the procedure. While these principles may appear obvious, it is astonishing how often they are not followed, often because someone decided that there was a better sampling procedure than that being followed. For most monitoring programs, it is far less important that the samples provide the best possible representation of the system being sampled than that the sampling procedure is replicated identically.

The particular sampling method selected will depend on the specific environment. For plankton samples, either nets that filter out the plankton or water samplers that collect a fixed volume could be used equally well at any site. Benthic environments are far more heterogeneous, and the Surber or Hess samplers that are suitable for use in stony cobble stream beds cannot be used to sample fine silt or wood habitats. For benthic studies, detailed descriptions of sampling equipment are provided by Welch (1948), Hauer and Resh (1996), Smock (1996), Hellawell (1978), Merritt and Cummins (1996), Southwood (1978), Weber

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(1973), and Britton and Greeson (1987). Many rapid assessment methods now simply use standardized pond nets, which do not provide quantitative samples but can be used in a variety of habitats (e.g., see Wright, 2000).

Sampling Natural Substrates

Sampling of natural substrates generally is preferred in biologic monitoring of benthic assemblages primarily because the sample represents the natural system. The difficulty is that the spatial and temporal physical variability of the benthic environment adds a significant noise component to the data obtained. Benthic invertebrate abundance and distribution have long been known to be strongly influenced by the nature of the physical habitat (e.g., Cummins et al., 1966; Hynes, 1970). The variability in natural habitats, both spatial and temporal, is often a significant confounding problem. For example, if a benthic invertebrate monitoring program were required to sample the entire length of a river from the mountains to the sea, there would be great difficulty in using a single sampling procedure. The upland erosional section of the river probably would have a bed of rock, boulders, and stones, whereas the downstream depositional section would have a bed of sands and silts. No sampling apparatus appropriate for one type of substratum would be successful for the other. There are several possible solutions. One is to use a sampling technique that samples benthic invertebrates indirectly, such as drift sampling (e.g., McKaige, 1987). Drift sampling could be used wherever there was sufficient current, which may or may not be possible in the lower reaches of a river. A second possibility is to use an artificial substratum method, although an artificial substratum appropriate to the upper reaches may not be appropriate for the lower reaches. A third possibility is to use several different techniques and spatially overlap them. For example, Surber sampling could be used at erosional sites and grab sampling at depositional sites, and at several sites in the middle, where both sets of substrates occur, both erosional and depositional habitats could be sampled so that the two sampling methods could be calibrated against each other.

Temporal overlap also can be used where the sampling technique is to be changed for some reason. The new and old techniques can be operated in parallel for some period so that the new method is calibrated against the old. It will then be clear whether any changes in the data resulted from changes in the sampling method or from some other factor.

Sampling Artificial Substrata

Use of artificial substrata in invertebrate biomonitoring has been reviewed by Rosenberg and Resh (1982). Artificial substrata include structures such as Hester-Dendy plate samplers, bags of stones or wood, and crumpled nylon bags. Some, such as the bags of stone or wood, are intended to mimic natural substrata, but samplers such as the plate samplers or the ground-glass slides used for sampling stream algae are designed primarily to facilitate extraction or examination of the biota.

Artificial substrata have the advantage over natural substrata of greater uniformity. Variation between samples caused by differences in the nature or amount of the sampled substratum will be reduced. The disadvantage is that it is never quite certain what the biota that colonizes the substratum actually represents. If the biota in the artificial substratum is depauperate, does this indicate a depauperate biota in the river or merely that the site had few organisms capable of colonizing the substratum?

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Sample Size and Number

Because sample processing (sorting, identifying, and counting of invertebrates) is the most time-consuming part of a biological monitoring program, there is considerable pressure to minimize the number of invertebrates processed to the fewest consistent with the sensitivity required for the study. Two approaches have been used to achieve this aim. The first is to subsample or reduce the area sampled but always to sample a fixed area. The other has been to identify a fixed number of invertebrates regardless of the number present in the sample (as long as this number is larger than the number required).

There has been considerable discussion in the literature about the influence of fixed-sampling-area and fixed-count sampling on the sensitivity of the sampling program. The discussion has focused particularly on the effect on species richness comparisons, a common suite of metrics in water quality assessment (see below). This is not surprising in view of the extensive discussions in the ecological literature about species area relationships (e.g., Arrhenius, 1921; MacArthur and Wilson, 1967; Douglas and Lake, 1994). Courtemanch (1996) argued that sampling a fixed number of organisms would produce unstable estimates of taxa richness and that the measurements thus produced would, as a consequence, not be usable for comparison with reference values. They suggested three alternative strategies: whole-sample processing but with the sampling area adjusted through experience so that median size of the samples was manageable within time and budgetary constraints; a two-phase approach as suggested by Vinson and Hawkins (1996), which used a search of the whole sample for large, rare species followed by a subsample; or a serial processing technique where a fixed number of organisms is counted followed by a search of the whole sample for additional species.

Barbour and Gerritson (1996) argue that fixed-count sampling provides good comparability among samples and provides more effective discrimination between sites than fixed area samples. Vinson and Hawkins (1996) reanalyzed an existing data set to simulate fixed-count sampling, which they compared with the taxon richness based on total taxa identified using area-based sampling. They suggested that where fixed-count sampling was based on less than 150 individuals there may be a loss of sensitivity and decreased ability to detect real differences between collections but that above this number the sensitivity of the technique was similar to that of total counts as long as only comparisons of taxon richness are being made. Where other metrics, such as community similarity or presence or absence of specific indicator groups, are to be used, then fixed-count enumeration may have low power to discriminate between invertebrate assemblages.

Larson and Herlihy (1998) conducted a field test by sampling 35 wadable streams in Oregon. They collected 16 to 50 Surber samples from each stream, calculated species richness at three different sampling areas, and used a rarefaction equation (Hurlbert, 1971) and data from the pooled set of samples at each site to estimate the numerical taxon richness for various fixed counts. They found a high degree of correlation between the two when counts and areas were both high (counts = 500; area = 0.45 m^2) but poor correlations ($R^2 = 0.54$) where numbers and areas were low (count = 100; area = 0.09 m^2).

One of the most thorough assessments of sample size and processing methods on rapid assessment outcomes was conducted by Growns et al. (1997). They concluded that a selective 100-animal subsample was the most cost-efficient technique to obtain effective discrimination between unimpacted and mildly polluted sites around Sydney, Australia. Somers et al. (1998) also found that subsamples of 100 animals were sufficient to distinguish littoral benthic communities of small inland lakes in southern Ontario. They concluded that increased sampling effort (double or triple) produced little additional benefit but that not all the indices they tested were equally effective.

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Sorting and Identification

Sorting the invertebrates from the detritus and other debris present in the sample and identifying them are the most time-consuming components of invertebrate monitoring. A number of methods can be used to speed both processes. Samples may be collected and preserved in the field or sorted in the field. Several field sorting methods have been advocated in the literature (e.g., by Chessman, 1995; Plafkin et al., (1989). Several advantages may accrue from field sorting. The first is time saved through the absence of double handling of samples; the second is that field sorting picks out live organisms. Some organisms, such as many of the stick-dwelling caddises, are easier to locate when they are alive and moving. Finally, field sorting reduces the exposure of sampling staff to preservatives such as ethanol and formaldehyde, commonly used to preserve samples, and reduces the total amount of preservative used because only a small volume of invertebrates is preserved rather than a large sample of invertebrates, water, and debris. The disadvantage of field sampling is a possible bias toward selecting large, active or otherwise conspicuous organisms from the sample.

Where field sorting is not used, samples returned to the laboratory may be fully sorted, so that all invertebrates are removed, using several types of aids. Staining with stains such as rose-Bengal makes invertebrates in the sample more conspicuous, and flotation using calcium chloride, kerosene, or sugar solutions may speed removal of many species, particularly in samples that contain relatively little plant material. However, samples still must be sorted manually for gastropods, bivalves, and many of the cased caddisflies, which cannot be floated off.

Sample processing time can be reduced by subsampling. Subsampling may be carried out as a field exercise; for example, rapid assessment techniques often involve field sorting and the collection of a fixed number of invertebrates from the sample (Chessman, 1995). Alternatively, the sample may be returned to the laboratory and then subsampled, sometimes after the removal of large items of debris. Common splitting techniques include the Folsom plankton splitter (e.g., Waters, 1969; McKaige, 1986), which divides the sample into two equal subsamples on each iteration, or quadrant-based subsamplers such as that developed by Marchant (1989).

Invertebrate Identification

The level to which invertebrates should be identified in biological monitoring exercises has been the subject of considerable debate (e.g., Resh and Unzicker, 1975). There are three sets of issues. The first is the extent to which information is lost when invertebrates are not identified, as often as possible, to species. The second is the cost of identification in both time and money. The third is the practicality of identification.

Several authors have argued that the use of species-level identification in biologic monitoring improves the sensitivity of the monitoring, particularly to subtle impacts (e.g., Furse et al., 1987). Resh and Unzicker (1975) pointed out that many genera of aquatic invertebrates include species with quite different tolerances to organic pollution, for example. Thus they suggested that the presence or absence of particular genera at a site is not likely to be a useful indicator of the water quality.

However, other authors have compared the outputs of water quality assessments or macroinvertebrate community analysis using different levels of identification of the invertebrates. For example, Marchant et al. (1995) compared the outputs of two different multivariate analyses on a suite of data sets from nine rivers that were based on species-level resolution. They then created data sets with taxonomic resolution reduced to the generic and family levels, a data set converted from abundance to presence-absence, and finally, a

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data set based just on EPT (Ephemeroptera, Plecoptera, and Trichoptera). They concluded that the same patterns were evident with both ordination methods and all data sets. Thus species-level identification does not appear necessary at least where reasonably strong environmental gradients are present.

DATA ANALYSIS AND INTERPRETATION

Multivariate Systems

Biological monitoring data are almost always multivariate, consisting of lists of taxa and their abundances (Resh and McElravy, 1993). Multivariate analyses assess the similarities or dissimilarities between samples (Gauch, 1982), and results normally are expressed as cladograms or, more popularly, ordination plots. A wide variety of multivariate algorithms is available, and the results may differ appreciably depending on the algorithm employed. Since multivariate techniques increasingly are included in standard statistical packages and specialized multivariate statistical packages are becoming relatively cheap and accessible, data processing is relatively simple. It is usually advisable to analyze data using several algorithms to test whether the patterns found are robust, i.e., are features of the data rather than artifacts of the analysis. Specific computer packages available for multivariate statistical analysis include MVSP, PC-ORD, PRIMER, and PATN. Most multivariate methods are techniques for finding patterns in data, not for hypothesis testing or assessing environmental quality. They can identify a sample or a group of samples with invertebrate assemblages that differ from others included in the analysis. Some techniques, such as ANOSIM, can determine whether the differences are statistically significant (Clarke, 1993), but they cannot determine whether patterns are attributable to water quality. When environmental data are analyzed along with the invertebrate data using techniques such as MDS or DECORANA, one can identify which environmental parameters are correlated with the invertebrate data. However, correlation does not equate to causality.

Indices and Metrics

The alternative to analyzing multivariate data with multivariate techniques is to collapse the information to a single index or metric. The earliest techniques for biological assessment of water pollution, proposed by Kolkwitz and Marsson (1902, 1906), used such metrics. The simplest measures are those concerned with species richness or species diversity. Of the two, species richness measures generally are to be preferred because diversity measures generally compound species richness and evenness, making comparisons more difficult to interpret (Hurlbert, 1971). It should be noted that although diversity indices are intended to be independent of sample size, they are usually not. Figure 5.1 presents diversity spectra (Margalef, 1968) developed by calculating diversity indices for benthic invertebrate samples collected using a Surber sampler from riffles in the Yarra River, Victoria, Australia (Campbell et al., 1982). Five samples were collected per site per occasion. Index values were calculated for each individual sample, then for each possible combination of two samples pooled, and then each possible combination of three and so on up to five samples. The mean diversity values for individual samples and the various combinations were then plotted. Effectively, this demonstrates how diversity index values change as sample size, in this case equivalent to sampling area, increases. Figure 5.1 presents data for the Shannon and

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Weaver index (1949), but the same pattern was found using a species richness index proposed by Margalef (Hellawell, 1978) and Pielou's (1969) modification of a diversity index proposed by Simpson (1949) (Campbell et al., 1982). At 11 of 15 sites, index values increased appreciably as sample size increased, but of greatest concern were the rates of change; these differed between sites so that the relative rankings of sites changed as sample area increased.

While various measures of taxa richness are now widely used (Resh and Jackson, 1993), there is still considerable debate about which are most appropriate.

Specific metrics for assessment of water pollution use the relative abundances of specific taxa selected for their known tolerance of or sensitivity to water quality or other environmental quality parameters. The most elaborate example is the saprobien system originally developed by Kolkwitz and Marsson (1902, 1906) but since elaborated by Sladecek (1979) and others. Saprobic-based indices are still used in Germany (Persoone and DePauw, 1979) and parts of the Netherlands (Tolkamp, 1985). In Great Britain, the Trent Biotic Index (Woodiwiss, 1964) was developed in the early 1960s but was replaced by the BMWP system (National Water Council, 1981) in the 1980s. In South Africa, an index initially proposed by Chutter (1972) and subsequently further developed and is used widely (Dallas and Day, 1993).

In the United States, a number of different metrics have been proposed. Beck (1955) and Beak (1964) both proposed biotic indices based on indicator groups, Goodnight and Whitley (1961) proposed an index based on the abundance of oligochaets, and Patrick (1949) suggested a method based on species abundances. Most recently, the Index of Biotic Integrity (IBI) developed by Karr and others (Karr, 1981, 1991; Karr et al., 1986) has been used in a number of North American studies (Karr, 1999). The index was based initially on an assessment of the fish assemblage, but modified versions have been based on invertebrates (Karr, 1999).

A problem with any of the metrics proposed for water quality assessment is that of validation. There is no reason to expect that any biological metric will correlate precisely with, for example, chemical or physical water quality parameters. Indeed, if it did, there would be little need for the metric. The difficulty, then, is how to tell whether the results calculated

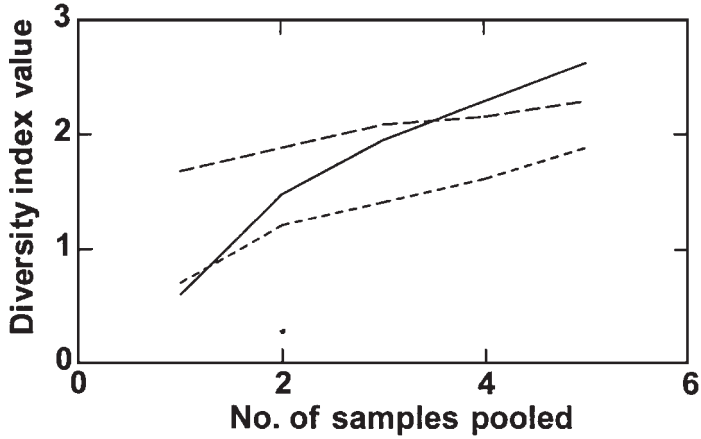

FIGURE 5.1 Changes in diversity index value at three sites on tributaries of the Yarra River, Victoria, Australia, as the effective sampling area was increased. Note that one site with the lowest diversity if only single sample size was considered had the highest diversity of the five pooled samples that were considered.

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using the metric are expressing an ecological reality or are simply an artifact of the metric. The literature on biologic water pollution assessment is replete with examples of modified metrics. In some cases, the metrics have been adapted through biogeographic necessity, as was the case when the IBI was modified for Australia (Harris and Silviera, 1999). In other cases, metrics appear to have been modified because the modified metric gave a better result, which presumably is one that more closely matches the subjective impression of the investigator.

Chessman and coworkers (Chessman, 1995; Chessman et al., 1997) have developed a very successful index called SIGNAL for use in Australia. Many of the validation shortcomings of other indices have been avoided (Chessman et al., 1997), and the index does appear to be particularly sensitive (Chessman, 1999).

Predictive Models

Predictive models are one of the more recent developments in water quality assessment. As noted previously, one difficulty in assessing quality of a site using invertebrates is the lack of information on what the invertebrate assemblage at the site would have been before significant human impact. The modeling approach uses a model to predict the assemblage composition. The actual assemblage found can then be compared with the assemblage expected and the degree of correspondence scored.

The approach was first developed by the Freshwater Biological Association in Great Britain (Armitage et al., 1992; Moss et al., 1999; Wright et al., 1984; Wright et al., 1989; Wright, 2000) and named RIVPACS. As many unaffected sites as possible were sampled, the invertebrates collected, and a variety of physical and chemical parameters recorded. In particular, physicochemical parameters were selected that were unlikely to be altered by the most frequent types of human impact. Thus latitude and longitude, alkalinity, gradient, substrate type, and distance from the source were among those recorded, whereas dissolved oxygen concentrations and phosphorus and nitrogen levels were not measured. Multiple Discriminant Analysis (MDA) (Klecka, 1975) was then used to identify the suite of physicochemical parameters that gave the best fit to the invertebrate assemblage classification. This suite could then be used to predict the assemblage composition at a test site by assuming that the probability of occurrence of any given taxon at a test site was a function of its frequency of occurrence within the appropriate reference classification group and its frequency of capture. The test site could then be sampled and the appropriate physicochemical data collected to allow a prediction of the test-site invertebrate assemblage. An index of quality can be determined using a ratio of the number of taxa observed to number of taxa expected at some predetermined level of probability.

The technique has passed through a number of iterations in Great Britain (Wright et al., 1989; Wright, 2000) and has been based on data from 614 sample sites in Great Britain and a further 70 sites in Northern Ireland. It also has been applied with apparent success in Spain (Armitage et al., 1990). In Australia, the method has been developed further by combination with rapid-assessment protocols similar to those developed in the United States by Plafkin et al. (1989) and named AUSRIVAS (Davies, 2000).

Rapid-Assessment Methods

A problem with traditional biologic assessment techniques has been the length of time required to process samples and interpret the data. This slowness is problematic because of its impact on the speed of feedback, which made these methods unsuitable for short-term impact monitoring. If the samples take weeks to months to process, the results are obtained too late to

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inform many of the decisions about effluent standards. Slow processing is particularly labor-intensive, which made large-scale programs using these methods extremely expensive.

Two solutions have been applied. The most widely applied solution has been rapid field assessment methods such as those developed in the United States by Plafkin et al. (1989) and discussed previously. These methods attempt to reduce the time taken to sort and identify invertebrates.

Alternative Monitoring Strategies

Alternatives to community monitoring use particular species or species groups. One alternative to ambient community monitoring, which has a growing number of adherents, is the evaluation of fluctuating asymmetries.

Fluctuating asymmetries are minor morphologic deviations from normal symmetries, which are detected as nondirectional differences between left and right members of paired bilateral characters in animals (van Valen, 1962). They have been suggested as potentially sensitive biologic indicators of environmental stress (Valentine et al., 1973; Leary and Allendorf, 1989; Parsons, 1990; Clarke, 1993). In aquatic systems, this approach has been applied most widely to the impacts of toxic contaminants such as trace metals and organic toxicants on fish (e.g., Utayopas, 1996) and chironomid mouthparts (Wiederholm, 1984; Diggins and Stewart, 1998). Several studies that considered the total chironomid fauna failed to find a significant relationship between the frequency of chironomid mouthpart deformities and levels of toxicants in sediments. However, investigations limited to particular suites of sensitive species such as the *Chironomus thummi* group (Diggins and Stewart, 1998) and the *Chironomus plumosus* group (van Urk et al., 1992) have been more successful, in both cases finding significant regressions between percentage of deformed individuals and principal components analysis (PCA) factor scores for toxic contaminants in the sediments.

Another alternative that can provide very rapid feedback in a monitoring program is the establishment of some form of continuous monitoring, either in-stream using enclosures or on effluent prior to discharge into a receiving water. In-stream enclosure methods have been applied most frequently with sedentary species such as mussels (e.g., see Walker, 1981) but also with plants and fish (Hellawell, 1986). Continuous biologic effluent monitoring has been practiced most widely with fish (e.g., see Morgan, 1976; Dickson et al., 1980), but similar systems also have been used for oyster larvae (Roberts, 1980).

Statistical Power Considerations in Environmental Monitoring

Environmental monitoring of any kind is carried out most frequently with the purpose of detecting whether or not a change has occurred. Standard statistical tests are designed primarily to avoid type I errors that occur when a test shows that a change has occurred when in fact no change has occurred. In environmental monitoring, it is type II errors that are normally of greater concern; these occur when the test shows no change when in fact there has been a change (Fairweather, 1991). In much of our environmental monitoring, particularly of relatively unaffected systems, we are hoping that the system has not changed since the previous set of measurements and that degradation has not occurred. In order to have confidence that results showing no statistical difference reflect the ecological reality, we need to know how large an effect must occur before our sampling program can detect it.

Power analysis can be used to determine the type II error rate, as well as the minimum effect size that could have been detected with a given sampling design. Alternatively, it can be used to determine the number of samples necessary to detect an effect of a given size (Cohen, 1988). Power analysis is as yet a greatly underused tool in water quality monitoring.

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CHAPTER 6
MONITORING OF TRACE METALS AND METALLOIDS IN NATURAL WATERS

Simon C. Apte, Graeme Batley, and William A. Maher

INTRODUCTION

Metals* are ubiquitous contaminants of the aquatic environment. Regulatory concerns arise from their potential toxicity to aquatic biota and detriment to human health through ingestion of waters and contaminated foodstuffs. Water quality legislation (e.g., ANZECC/ARMCANZ, 2000; U.S. Federal Register, 1998; Gardner and Zabel, 1989) normally focuses on regulating dissolved metals because these are considered to be the most bioavailable to aquatic organisms (Campbell, 1995; Luoma, 1983). The trace metals of greatest concern include aluminium, arsenic, cadmium, copper, lead, nickel, mercury, selenium, silver, and zinc. The maximum tolerable concentrations, as defined by various water quality guidelines, typically are in the 1 to 100 μg/liter range; however, some forms of organometallic compounds (e.g., methylmercury and tributyltin) are highly toxic at quite low (nanogram per liter) concentrations.

Metals have both natural and anthropogenic sources. Natural background concentrations largely are determined by catchment geology and can be very variable (Jacinski, 1995). The waters draining mineralized regions may contain naturally elevated metal concentrations. For example, surface waters in the geothermal regions of New Zealand contain high concentrations of arsenic and mercury (Craw et al., 2000). Acid-rock drainage resulting from the natural weathering of sulfidic ores can be responsible for elevated dissolved metal concentrations in some water bodies (Furniss et al., 1999).

Anthropogenic sources of metals include point-source inputs such as industrial discharges, sewage treatment effluents, mining discharges (e.g., tailings, waste rock, mine drainage), mineral processing, and power generation (Jacinski, 1995). Diffuse inputs arising from stormwater and road runoff have been identified as the major sources of zinc, lead, and copper in urban environments (Makepeace et al., 1995). Atmospheric sources can be significant for some metals (e.g., lead and platinum) and are associated with vehicle emissions (Barefoot, 1999; Weiss et al., 1999), and mercury is associated with coal combustion (Pirrone et al., 1996). Shipping could be considered a diffuse source of metals largely derived from antifouling paints (copper and tributyltin) (Batley et al., 1989).

*The term *metals* is also used in this chapter to cover metalloids.

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Contaminated benthic sediments, which are common in many aquatic systems, also can be a diffuse source of metals to the water column. Metals such as copper, cadmium, lead, and zinc can be mobilized during the oxidation of anoxic sediments through the oxidation of sulfide phases (Kerner and Wallmann, 1992) and the oxidation of organic matter (Forstner et al., 1989).

If we are to understand the fate and effects of metals in aquatic environments and meet water quality guidelines, accurate measurements of metal concentrations are required. This chapter critically reviews the field and laboratory procedures for monitoring metal concentrations in fresh, coastal, and estuarine surface waters. The highly specialized area of ultratrace open-ocean sampling and analysis is not considered. For further information on this topic, the book by Grasshoff et al. (1999) is recommended.

FORMS OF TRACE METALS AND RELEVANCE TO MONITORING: WHAT SHOULD BE MEASURED?

Trace metals in natural waters may be present in a variety of forms (Fig. 6.1) having different reactivities and bioavailabilities. Unfortunately, analytical techniques are not available to measure all these species. The metal fractions typically measured in natural waters are summarized in Fig. 6.2. All these measurements are operationally defined and bear little relation to the true forms of the metals existing in solution (see Fig. 6.1). For example, filtration using a 0.45-μm membrane filter is used widely to differentiate between dissolved and particulate forms of trace elements (Hunt and Wilson, 1986). This definition of dissolved metals ignores the true form of metals in the dissolved phase (see Fig. 6.1). The dissolved fraction isolated by this procedure is more appropriately termed *filterable metals.* Filtration is covered in detail in a later section. The filter pore size and structure will determine the amount of colloidal material (including bacteria and other organisms) that will pass through the filters (Danielsson, 1982). This will influence the dissolved metal concentration measured.

The measurement of total metals can be questioned in terms of its relevance. Apart from giving estimates of trace metal loads from various sources, total metal concentrations give little information on processes or biological impacts. In most aquatic systems, sediments contain the most metals, and the suspended sediment concentrations largely determine the total metal concentrations. It can be reasonably argued that those metals which are not solubilized by dilute acid need not be considered as having potential bioavailability. For this reason, the standard methods adopted by agencies such as the U.S. Environmental Protection Agency (EPA) have involved sample acidification (Martin et al., 1986, 1991).

While regulating metals based on their total concentrations is a first step, this alone is insufficient to address the important issues of metal bioavailability and toxicity. Generally, a poor correlation exists between total trace metal concentrations and biological effects (Allen et al., 1980; Campbell, 1995). This is so because metals in natural waters can be present in a variety of forms or species that have different reactivity, bioavailability, and toxicity to aquatic organisms (see Fig. 6.1). For several metals, bioavailability is better correlated with the concentration of simple aquated ion and inorganic complexes (Campbell, 1995). Metal speciation is influenced by pH, alkalinity, and the presence of natural organic matter. In order to gain a better understanding of these important issues, a second tier of environmental monitoring in systems where elevated metal concentrations already have been identified as a concern involving speciation measurements together with ecotoxicological investigations is advisable. The measurement of trace metal species that are more relevant measures of toxicity and bioavailability are covered in a later section.

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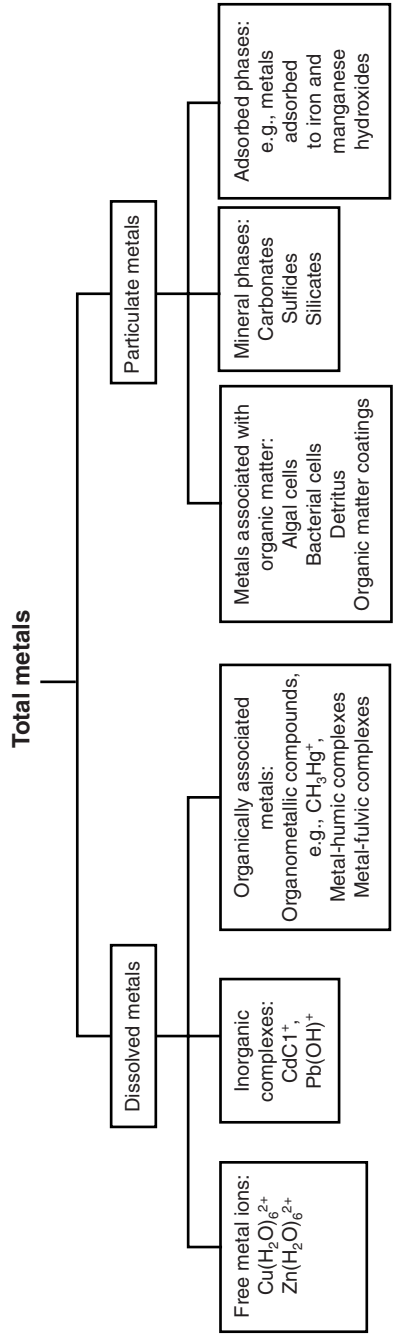

FIGURE 6.1 Some examples of dissolved and particulate metal species in natural waters.

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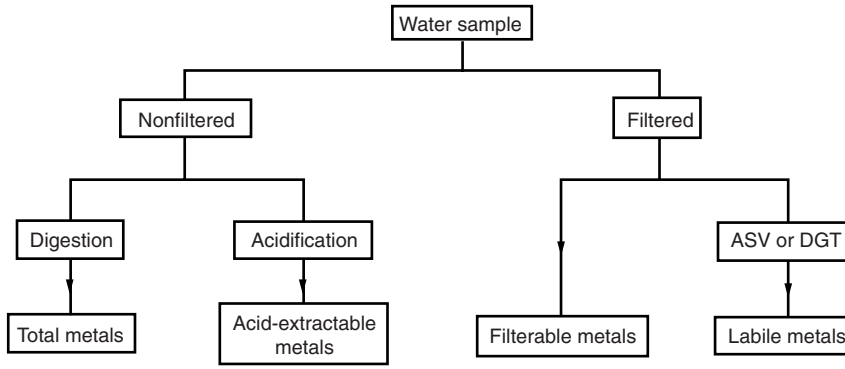

FIGURE 6.2 Some examples of operationally defined metal fractions in water samples.

DESIGN OF MONITORING PROGRAMS

The essential processes involved in developing a monitoring program are discussed in Chap. 2. These include defining the objectives of a monitoring exercise and addressing the why, what, where, when, and how questions. Development of the sampling program involves consideration of system heterogeneity and hence variability and the minimum spatial and temporal resolution needed. This will determine the number of sampling sites and replicates required to address the study objectives satisfactorily. The number of samples and statistical considerations are covered by in the book by Keith (1996).

Monitoring programs for trace metals can be classified broadly into two groups: those which aim to measure metal concentrations accurately in a water body and those which wish to check compliance against fixed values such as water quality guidelines. In most water bodies, actual metal concentrations are well below compliance concentrations. Greater rigor is required to measure actual trace metal concentrations accurately compared with the efforts required for compliance monitoring. The data obtained using less stringent protocols may overestimate the true trace metal concentrations. This can create problems if such data are later used for other purposes, such as compilations of background water quality.

Care should be taken to ensure that monitoring exercises are resourced appropriately and have a sufficient level of quality assurance. Cost-driven monitoring is invariably a false economy. Based on our own experiences, there have been many cases where perceived metal contamination problems actually were problems with the quality and representativeness of monitoring data. Significant effort and resources are then wasted fixing problems that do not actually exist.

Environmental samples must be representative of the portion of the environment being investigated. The behavior of metals will be influenced by physical and chemical parameters such as temperature, flow, pH, hardness, salinity, dissolved organic carbon, redox potential, and total suspended solids (TSS). Physical processes such as water column stratification, river flow, mixing of water streams at a junction, tidal movement, wind-induced turbulence, and sediment resuspension events contribute to the observed variability in metal concentrations. Seasonal and climatic variability also may be important. Consideration of these processes for the system of interest is essential in designing a meaningful monitoring program. Exploratory monitoring surveys are often of value for scoping problems and establishing the level of replication required to achieve the desired statistical power. Consideration also needs to be given to any additional parameters that should be

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MONITORING OF TRACE METALS AND METALLOIDS IN NATURAL WATERS

measured, e.g., TSS, pH, temperature, dissolved oxygen (DO), and discharge. Both process-based models and empirical relationships can be derived from such data that are invaluable in refining monitoring programs.

Monitoring typically comprises three phases: sample collection, sample pretreatment, and sample analysis. These will be dealt with separately in the ensuing sections.

SAMPLE COLLECTION

Water sampling generally involves collecting volumes of water at precise locations in both space and time. Depending on the nature of the sampling site, this may involve sampling by hand from bank locations, by boat, or from some sort of structure such as a bridge, jetty, or discharge pipe. Samples also may be taken at various positions within the water column (e.g., surface, mid-depth, and bottom). Sampling frequency may be at a regular time interval (e.g., daily, weekly, or monthly) or may be event-related (e.g., taken at certain flow or weather conditions).

Sampling estuarine water bodies is complicated by tidal effects and water-column stratification (freshwater lying above denser seawater). This often necessitates taking samples based on the salinity of the water rather than geographic location. Unless tidal effects and changes in salinity are taken into account, data interpretation can be very difficult. Metal concentration versus salinity plots give important information on mixing processes that can assist in data interpretation (Burton and Liss, 1976; Howard et al., 1984). Freshwater bodies (especially lakes) also may become thermally stratified at certain times of year. These examples illustrate the need for auxiliary measurements, e.g., conductivity, temperature, and dissolved oxygen, that assist in the identification of physical mixing processes.

Care must be taken to ensure that the actual sampling site is representative of the stretch of water under study. For instance, a river or lake shore sampling location may be subject to backwater effects that make water quality different from that in the middle of the water body. Sewer inflows and groundwater intrusions also may influence local water quality. The selection of representative sampling sites requires some local knowledge and, in many cases, exploratory (pilot) studies where the factors influencing water quality variability at each sampling site are investigated in detail.

Field sampling and sample pretreatment have been identified as the greatest potential sources of errors in any metal monitoring exercise (Batley, 1999). These are likely to be far greater than the errors associated with chemical analysis, especially at ultratrace (submicrogram per liter) concentrations. This emphasizes the need for quality assurance and quality control (QA/QC) protocols that cover field operations as well as laboratory analysis.

Because metals are ubiquitous, a major concern is that samples may become contaminated during the actual process of sampling and during subsequent storage and analysis. There are many potential sources of metal contamination, including the persons involved in sampling, dust from the atmosphere, dirt from the sampling site, and metals released from the sampling equipment or structures from which the samples are taken. Generally, sampling locations are not particularly clean, and apparatus can be dirtied even in storage. Keeping equipment and sample bottles in large plastic bags contained in sealed plastic containers therefore is recommended. Surfaces that come into contact with the water samples are the largest source of contamination. This will include, in the first instance, the sampling device and sample containers. The lavish use of polyethylene sheeting for wrapping equipment and to cover work areas on boats, river banks, etc., is an effective way to minimize field contributions of metals. Dust, powder, skin, and hair are obvious external sources of metals, and rigorous protocols are also required to minimize their effects. Plastic gloves must be used to reduce contamination from skin. However, the type of plastic gloves used

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requires some scrutiny. Gloves containing talcum powder are to be avoided because the talc contains high levels of trace metals.

Ultimately, the skill and care taken by the operator will determine the quality of the results obtained. Detailed protocols for ultratrace sampling have been described in the literature (Ahlers et al., 1990; Apte et al., 1998; Nriagu et al., 1993; Nolting and de Jong, 1994). It is difficult to judge how much care is actually required to avoid contamination because it depends on many site- and laboratory-specific factors. This highlights the need for pilot studies to check out these issues prior to the commencement of larger sampling campaigns.

The recommended sampling protocol for ultratrace analysis uses the dirty-hand, clean-hands approach (Ahlers et al., 1990). This involves two people both wearing (powder-free) polyethylene gloves. Double-bagged bottles are unwrapped sequentially. The first "dirty" assistant removes the outer bag and hands the inner bag containing the bottle to the "clean" assistant, who removes the bottle and then undertakes the sampling. Bottles then are immersed in the water to be sampled by gloved hand or with a sampler or are filled with water collected using an appropriately cleaned depth sampler. Bottles usually are filled with the sample, capped, shaken, and the water discarded two to three times before the final filling. The bottle is then returned to the two bags before storage.

The importance of using such a rigorous procedure has been demonstrated convincingly by Ahlers et al. (1990). Using a less involved bottle preparation and handling procedure, measured zinc concentrations in upland New Zealand rivers showed great variability. With the rigorous protocol, measured concentrations were almost a factor of 3 lower (150–300 ng/liter), with little difference between sampling sites. Similar examples are provided in studies of trace metals in saline waters (Nolting and de Jong, 1994; Apte et al., 1998).

WATER SAMPLING DEVICES

General Considerations

Ideally, sampling devices should not affect the concentration of metals in the sample. However, no form of sampler is perfect, and all devices will contaminate the sample to some extent. The aim should be to minimize contamination to acceptable or nondetectable levels. Sampling devices fall into five basic categories:

1. Grab sampling of surface waters
2. Pumping systems for sampling surface to medium (6–8 m) depths
3. Depth samplers
4. Flow- or time-activated (automatic) samplers
5. Integrating samplers

Grab Sampling of Surface Waters

Many waters bodies are shallow (<5 m depth) and well mixed because of wind action and water currents (Cowgill, 1996). In these situations, surface (0–1 m) water sampling is all that is required to obtain a representative sample of the water column. For this purpose, immersion of a sample bottle by hand to just below the surface (typically 0.25–0.5 m depth) is satisfactory, provided any contribution from surface films is avoided and the sampler (or hand) does not contaminate the water. When sampling from a boat or from the shore, collection is

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best done with the sample bottle held in acrylic jaws at the end of a polycarbonate pole (1–2 m long, 2 cm in diameter) (Fig. 6.3*a*). An alternative is a bottle or bucket fixed to a plastic rope, although this is less maneuverable and difficult to submerge unless weighted. Care should be taken to ensure that the sampling equipment is kept clean between uses.

Boats can be a source of contamination, creating a halo of elevated metal concentrations around the vessel. Boats should be inspected for any obvious signs of corrosion that may contaminate the surrounding water body. Whatever the size of vessel used, it is advisable to minimize the halo effect by positioning the craft into the ongoing current and taking water samples from the front of the vessel (Apte et al., 1998). To avoid contamination, a rubber dinghy often is used and launched from the shore or from a support vessel. In ultratrace studies, the dinghy should be precleaned thoroughly by washing with clean water (obtained from an uncontaminated field site) before launching.

Pumping Systems

Pumping systems generally are not desirable for ultratrace metal sampling because of the large surface area to volume ratio of the tubing that may introduce adsorption/contamination problems, but they are suitable for situations where the tubing can be cleaned and conditioned by pumping large volumes of water. Pumps in which the water passes into internal chambers (e.g., bladder pumps) are not suitable for trace metal sampling because of contamination problems. Peristaltic pumps are preferred. Water is pumped to the surface via appropriate lengths of precleaned polyethylene, silicone, or PTFE tubing (approximately 1 cm in diameter) directly into a plastic sample bottle (Hamilton-Taylor et al., 1996; U.S. EPA, 1996). Online filtration also may be applied (U.S. EPA, 1996). Peristaltic pumps have a lift limitation of about 8 m. Vacuum samplers in which the sampling chamber is located before the vacuum pump (see Fig. 6.3*b*) also may be applied. One potential difficulty with the use of pumping systems is contamination of tubing between use, especially if long lengths are used. This necessitates particular attention to storage and handling issues.

Discrete Volume Depth Samplers

For depth sampling, a range of purpose-built samplers is available (Batley, 1989), most of which were designed originally for oceanographic applications. Their basic operation involves deployment of a bottle (either closed or open) via a wire or plastic line to the required depth, at which filling is triggered by a weight sent down the line. Most commercially available samplers are not designed specifically for the purpose of trace metal sampling, so it is important to test for contamination by filling the sampling device with water similar to the type being sampled for a duration similar to that of the sampling event and analyzing the resulting metal concentrations. Most samplers are made of a tough plastic (e.g., PVC) with some metallic components (see Fig. 6.3*c*). The metal components should be checked for contamination and should be plastic-coated (or replaced with plastic components) where necessary. Samplers that do not use potentially contaminating rubber closures or plastic lines that run through the bottle are preferred. The commercially available Mercos sampler (Freimann et al., 1983) (see Fig. 6.3*d*), which uses a cluster of Teflon bottles, is suitable for obtaining water-column depth profiles of trace metals including mercury at depths to 100 m. The use of metal cables to deploy depth samplers should be avoided because they can be a source of contamination. A variety of strong synthetic fiber (e.g., Kevlar and Nylon) cables and lines are available that may be cleaned thoroughly before use. Since contamination often increases with age of the sampling device, contamination checks should be carried out at regular intervals over the lifetime of the device.

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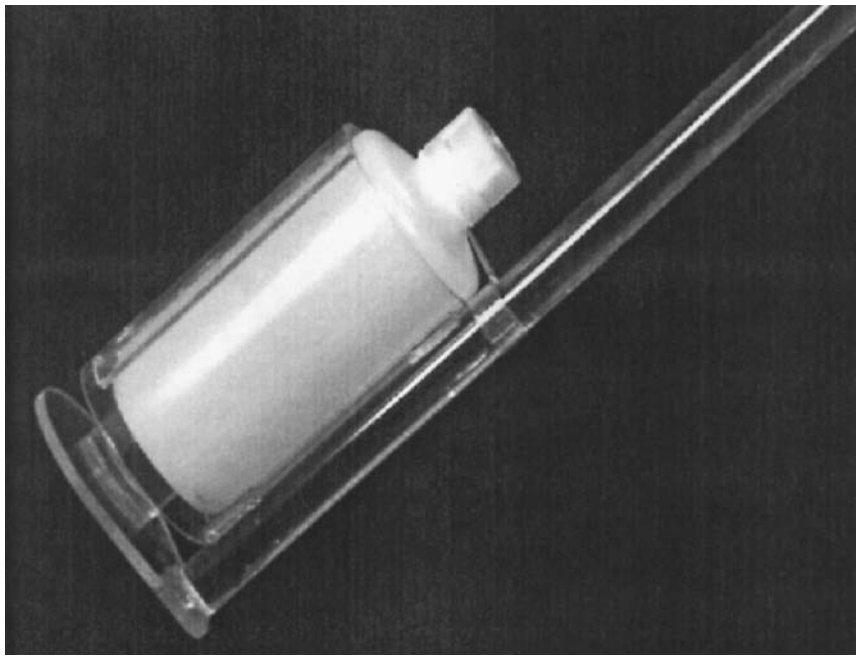
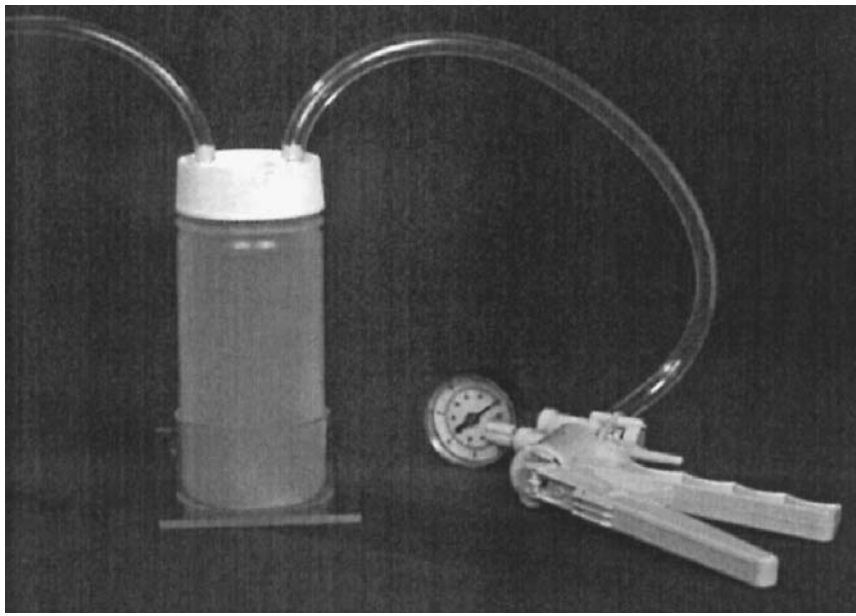


(*a*)



(*b*)

FIGURE 6.3 Examples of water samplers suitable for trace metals. (*a*) hand-held plastic surface water sampler; (*b*) vacuum sampling apparatus; (*c*) Go-flo sampler depth sampler; (*d*) Mercos ultratrace metals sampler.

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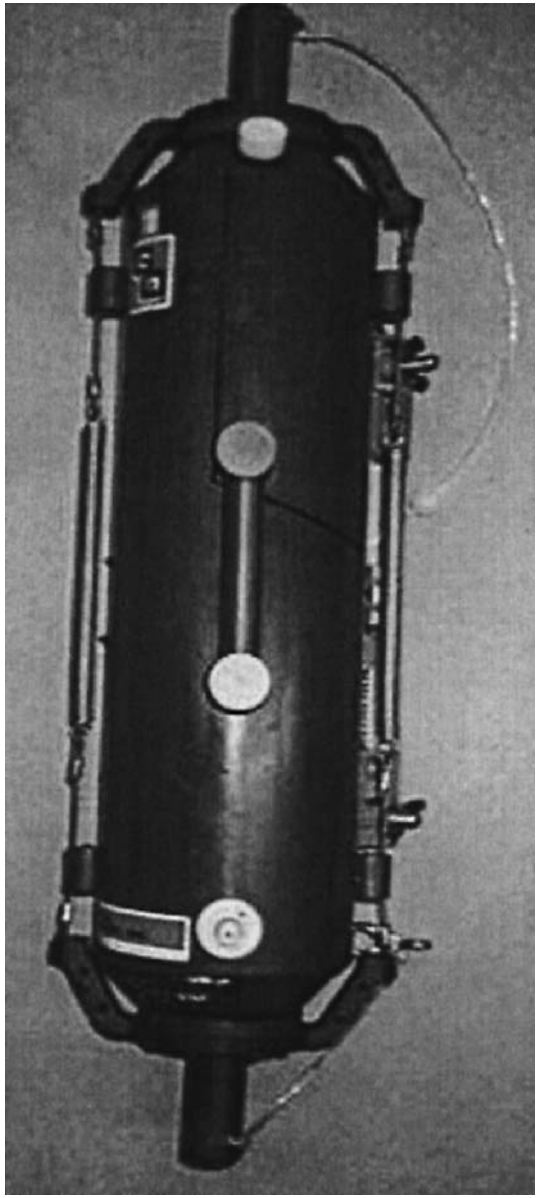

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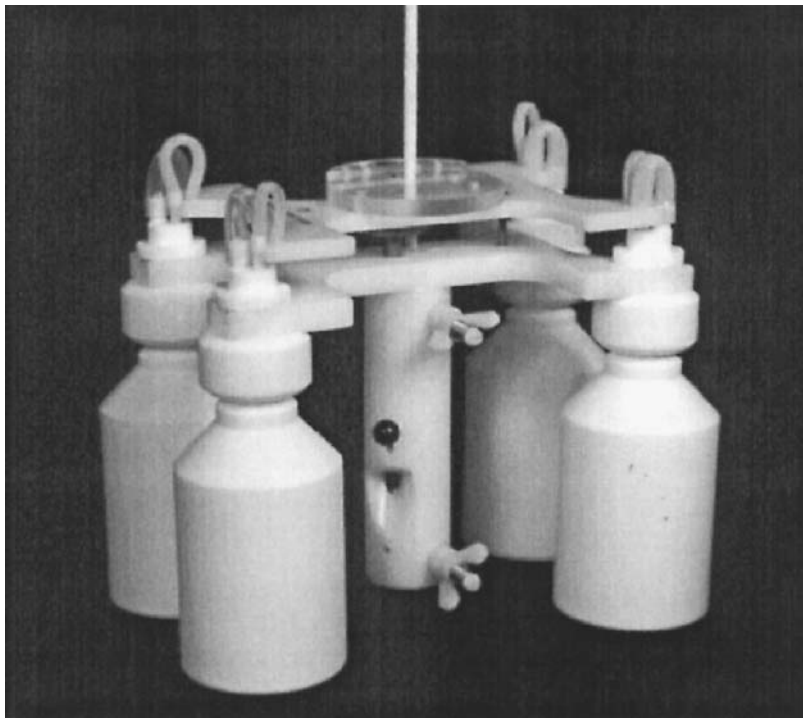

FIGURE 6.3 (*d*) Mercos ultratrace metals sampler.

Flow- or Time-Activated Samplers

A number of commercially available devices are used for unattended water sampling (Dick, 1996). These basically consist of a pump system, controller, and an array of sample bottles contained within a protective housing. The samplers can be preprogrammed to collect samples on a flow- or time-related basis. For event-related sampling, such as collecting stormwater runoff, collection can be triggered by water flow or level. The sampling device also may be programmed to collect composite samples. Flow-proportional sampling (nonuniform with time) that takes into account rapid changes in water quality is also possible. As discussed earlier, sample contamination checks need to be carried out at regular intervals. The issue of sample preservation (see below) needs to be addressed if samples are to remain in the sampling device for long periods. Some flow- or time-activated samplers have refrigerated housings for sample storage.

Integrating Samplers

In situations where water quality is highly time-dependent, information provided by discrete samples will not be representative of temporal changes. In these cases, samplers that integrate or time-average metal loads over a fixed time period or volume are an alternative. Davison and Zhang (1994) have developed novel, diffusive gel samplers for this purpose.

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These consist of a 0.45-μm membrane overlying a hydrous polyacrylamide diffusive gel (0.8 mm depth) and a further hydrogel layer impregnated with Chelex-100 resin (0.14 mm depth). These are contained within a polyethylene housing (Fig. 6.4). The samplers rely on the diffusive gradients in thin films (DGT) principle in which the diffusion of large molecules within the gel is slow compared with that of smaller species (Davison and Zhang, 1994). A linear concentration gradient is established within the diffusive gel, and the diffusion coefficient, surface area, and deployment time control the metal concentrations reaching the Chelex collector gel (Zhang and Davison, 1995). Typically, DGT samplers might be deployed for 24 to 72 hours, at the end of which the Chelex gel is removed and placed in a known volume of dilute nitric acid (Davison and Zhang, 1994; Denney et al., 1999). The elutriate is analyzed subsequently for trace metals. It should be noted that these methods measure a labile metal fraction, which is a subset of the total dissolved metals concentration. The proportion of the dissolved metal fraction determined will depend on the rate and extent of metal complex dissociation in the presence of the chelating resin and the diffusion coefficients of the individual metal species. These issues should be checked before full-scale use in monitoring programs. Before using integrating samplers in systems where water quality is highly variable over short time scales, some consideration should be made as to how the data obtained will be interpreted. The use of mathematical models that simulate the actions of the samplers is helpful in this respect (Harper et al., 1999).

SAMPLE BOTTLE SELECTION AND PREPARATION

A number of different plastic and glass bottles have been used for trace metal sampling, and their propensity for sample contamination has been reported thoroughly (Hunt and Wilson, 1986; Reimann et al., 1999). Glass is not favored owing to high concentrations of trace metals in the glass and the potential for adsorptive losses. Polyethylene (low or high density)

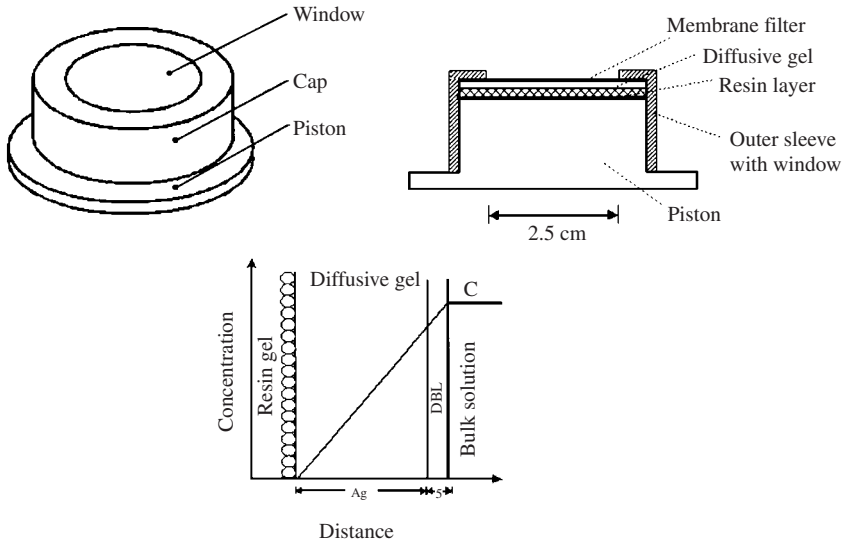

FIGURE 6.4 Construction of DGT assemblies for time-integrated sampling (DBL is the diffusive boundary layer).

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or Teflon FEP bottles are the most favored types owing to their low metal content and ease of cleaning Moody and Lindstrom, 1977). Clear plastics are preferred because the pigments added to colored plastics often contain metals. Fluorocarbon polymer [PTFE (Teflon) or FEP] bottles are usually used only for collecting samples for mercury analysis owing to their high cost. These are preferred for their low mercury content, ability to withstand very strong acids, and low permeability toward elemental mercury vapor (diffusion of mercury from the atmosphere into the sample on storage is a major potential source of contamination). Polyethylene terephthalate (PET) bottles have been proposed recently as a low-cost alternative for the collection and storage of mercury-containing samples (Fadini and Jardim, 2000). Pyrex glass (impermeable to mercury vapor) also may be used for mercury-containing samples.

High-quality bottles are recommended, e.g., Nalgene, because these have good closures that prevent sample leakage. Such bottles are strong and do not rupture on storage or rough treatment. The additional cost of using superior-quality bottles generally is small compared with other field costs.

Prior to use, bottles require cleaning to remove trace metals and unwanted residues from the manufacturing process. This usually involves soaking in acid. The rigor of this procedure depends on the intended application and concentration range of metals to be investigated. Some workers have advocated direct use of certain bottles types without the need for any cleaning (Reimann et al., 1999). Such generalizations are ill advised given that the quality of materials and degree of metal contamination often changes between manufacturing locations and between batches. The need for each laboratory to perform its own tests on locally available materials cannot be overstressed.

In our laboratories, the minimum cleaning procedure for trace metal sampling at the microgram per liter level involves soaking the bottle in 10% (v/v) nitric acid for at least 24 hours, followed by rinsing with copious quantities of deionized water. The cleaned bottles are double bagged using two Ziploc polyethylene bags and stored in plastic containers that are transported into the field. Such precautions are worthwhile on most occasions, given the cost of sampling (especially if helicopters or boats are involved). Acid washing is carried out in a dedicated dust-free laboratory, with the acid baths stored in a bunded and vented area. For sampling at the submicrogram per liter level, additional care is required. In our laboratory this involves successive soaking of bottles in detergent solution (to remove grease), strong acid, and then weak acid. The bottles are rinsed between each stage with high-purity water. Ahlers et al. (1990) advocated that Nalgene bottles for zinc analysis be soaked in hot 50% nitric acid for 2 days, rinsed with high-purity water, then leached in 1% nitric acid for 2 weeks. The value of such extreme care was demonstrated clearly in the reliability of the resulting analytical data. Preparing bottles for ultratrace mercury analysis also requires special care. Bottles typically are soaked in strong hydrochloric acid (65–75°C) for several days, followed by exhaustive rinsing with ultrapure water (U.S. EPA, 1996). For some elements/organometallic compounds, contamination from bottles is not an issue, and cleaning is of little value. The actual care required to prepare bottles needs to be assessed by individual laboratories, taking into account the objectives of the sampling program.

QA/QC IN FIELD SAMPLING

Given the issues already identified, appropriate QA/QC for field sampling should seek to check exposure to contamination. The most widely adopted procedures include the use of field blanks and sample duplicates. Field blanks are bottles filled with ultrapure water (or a natural water sample low in trace metals) that are taken on the field trip and subjected to as many of the operations as that of a real sample as possible. On return to the laboratory,

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the field blanks, together with aliquots of the source water used to prepare the field blanks, are analyzed alongside samples. If there is a statistically significant difference between the field blanks and the source water, contamination is indicated. If the level of contamination is of sufficient concern, the sources of contamination can then be investigated and appropriate remedial action taken. While this approach is the most practically feasible, not all aspects of sample contamination can be checked using field blanks; e.g., contamination arising from the sampling device is generally not included. Trip blanks, which focus on contamination during transportation and storage, also may be employed. These represent a subset of the overall field blank. Including a control site where the metals of interest are at background concentrations is an excellent way to provide additional QA. Provided that the metal concentrations are measurable and not below detection limits, this also allows variability resulting from natural processes (e.g., seasonal changes) to be characterized.

Taking replicate samples in the field and comparing them with the typical variability encountered for analytical measurements on a single sample allows some characterization of the variability introduced by sampling. Large variability between field replicates also may indicate sample contamination problems.

Generally, each batch of 10 samples should have at least one field blank and a duplicate sample. Setting action limits for blank contributions and duplicates allows effective management of contamination issues. Typically, blank concentrations should be less than one-tenth the levels to be measured. This is not always achievable, and alternative criteria may need to be applied.

The spiking of samples in the field has been advocated to check for metal losses during storage. This procedure is only applicable if total metals are being determined. If samples are to be filtered, spiking should only be done after filtration. As part of the QA plan, it is advisable to specify holding times between sample preparation, filtration, and preservation. If refrigeration during transportation is required, this may be tracked using a recording thermometer.

SAMPLE PRETREATMENT

Sample Filtration

Although glass and plastic filtration units are available, plastic units are preferred because they are less prone to adsorptive losses. Filtration may be carried out under positive pressure or vacuum. Excessive pressure or vacuum should be avoided because this may cause rupture of algal cells retained by the filter and release of their intracellular contents into the filtered sample (Hunt and Wilson, 1986; Batley, 1989). For filtering small sample volumes, disposable plastic syringes and encapsulated filters are useful. Several detailed reviews of filtration procedures are available (Brock, 1983; Buffle et al., 1992).

Filters having different structures, pore sizes, and composition are available. These can be classified into two broad categories: depth filters having a complex system of channels within the body of the filter and screen filters with a matrix of very uniform sized unbranched pores. The effective pore size of depth filters changes as the filter becomes more loaded with particles, whereas the effective pore size of screen filters is not affected by filter loading. The most widely used filters in water analysis are cellulose-based (depth) membrane filters (e.g., Millipore HA). Glass fiber (depth) filters are not normally used for trace metals analysis but can be used for the filtration of samples prior to mercury analysis because they can be cleaned effectively by heating to 500°C (Fitzgerald and Gill, 1979). Etched-track polycarbonate filters (e.g., Nuclepore) are the most commonly used screen filters; however, their use is limited by their cost and low sample volume capacity.

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It is essential that the filters and filter units are decontaminated before use. Filter units should be acid washed using similar procedures to those used for sample bottles. The closures of some plastic filter units are sealed with silicone O-rings that are not suited to cleaning with strong acids. In our laboratory, these are separated from the filter units and soaked in 1% nitric acid for a few hours, followed by rinsing with deionized water. Alternatively, they can be replaced with Teflon O-rings. Acid-washed PTFE tweezers are used for all delicate handling operations, including reassembly of the filter units. Prior to use, the assembled filter units are stored in resealable plastic bags. Filters may be precleaned by filtering aliquots of dilute acid and then deionized water through the filter, followed by a small aliquot of the sample (filtrate discarded to waste). Apart from cleaning the filter, this acts as a conditioning step and reduces adsorptive losses. When using this procedure, it is essential to thoroughly rinse the filter unit to remove all traces of acid. Otherwise, the sample pH may drop, resulting in release of metals from particulate material. Touching filters and the inside of the filter units with fingers must be avoided. Following the preceding washing process, a volume of sample is then filtered and discarded to waste. The use of gridded filters (as used in microbiological analysis) should be avoided. This is so because the inks used to produce these filters may contain metals that can dissolve and contaminate samples.

An alternative approach involves in-line filtration. This can use encapsulated filters (available from most suppliers of filtration equipment) or commercially available filter holders that are loaded with filters before use. Plastic tubing and a peristaltic pump are used to pass the sample through the filter assembly. This procedure is particularly suited to the filtration of large sample volumes (>1 liter). Decontamination is carried out by passing volumes of dilute acid and then high purity water through the assembly. This procedure may be combined with pump sampling (see earlier section) and used in the field.

Adsorption of metals may occur onto the inner surfaces of the filtration unit or the filter itself. Adsorptive losses generally are lower in samples having high calcium and magnesium concentrations (seawater, hard waters) or low pH and are highest in low-hardness waters and alkaline solutions. This is so because of competition from alkali earth metals and protons for potential metal binding sites that reduces adsorptive losses (Hunt and Wilson, 1986). High dissolved organic carbon (DOC) concentrations also can reduce the losses of some metals either by forming soluble complexes that do not adsorb onto the surfaces of the filter unit or by coating the surfaces of the filter unit, thus blocking access to potential metal adsorption sites. The relative importance of these two mechanisms depends on the nature of the metal and its binding affinity for DOC. Assessing the extent of metal sorption is difficult. Testing for adsorption by spiking samples with ionic metals is likely to overestimate metal losses because the ionic forms may not fully equilibrate with all the natural metal forms in solution and therefore may behave differently. Refiltering a filtered sample and comparing concentrations before and after, although not ideal, is probably the most reasonable approach for evaluating adsorptive losses.

Filtering turbid samples often can be a problem because filters easily clog. The simplest solution is to allow the sample to settle for a period of time (minutes to hours). Use of a coarse prefilter before the main filter can be effective in removing coarse particles but will not alleviate problems caused by fine particulates. Centrifugation prior to filtration also may be effective. This problem is best resolved by using in-line filtration with high-capacity disposable cartridge filters. The cartridges, which are constructed from synthetic polymers, are available commercially (0.2- and 0.45-μm pore sizes) from a number of suppliers and are particularly useful for filtering large sample volumes (20–100 liters). They can be precleaned before use by filtering successive volumes of acid solution and deionized water. As with other filtration procedures, a volume of sample is filtered to waste in order to condition the filter. The main disadvantage is the high cost of these disposable devices.

Filtration normally is carried out in a laboratory; however, it may be carried out in the field. Small nitrogen/air cylinders are used for positive-pressure filtration. Both hand- and battery-powered vacuum pumps are available for field use.

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It is important to minimize the time between sample collection and filtration because adsorption/desorption reactions involving particulates and bacterial activity can lead to changes in sample composition (Hunt and Wilson, 1986). These effects may be minimized by storing samples at 4°C in the dark. This often necessitates storing collected samples in ice-packed containers or portable, battery-powered refrigerators. Maximum holding times should be specified.

Sample Storage and Preservation

Sample acidification to a pH of below 2 is the most widely used form of stabilization for trace metals analysis. This procedure halts most biological activity and limits adsorption onto container walls. Nitric and hydrochloric acids are the most commonly used acids because they are readily available in high-purity grades. Typically, between 2 and 10 ml of concentrated acid is added per liter of sample. Given that the added acid is a potential source of metals, it is advisable to add the minimum amount of acid. The metal content of acids varies between batches, and the purity of each acid batch should be screened before use. The compatability of the preservation acid with the metal analysis procedures also should be checked. For instance, nitric acid is preferred for graphite furnace atomic absorption spectrometry (GFAAS) and inductively coupled plasma mass spectrometry (ICP-MS) because high chloride concentrations can interfere with both techniques (May and Weidmeyer, 1998).

The addition of an oxidizing agent such as acidified bromine monochloride (5 ml/liter) has been recommended for the preservation of mercury samples (U.S. EPA, 1996). This prevents the formation of volatile elemental mercury. Recently, an artifact has been reported to affect the sampling and preservation of sulfidic waters (Simpson et al., 1998). In the presence of high sulfide concentrations, copper forms soluble sulfide species. On acidification, these complexes dissociate and form copper sulfide (insoluble in dilute acid), which adsorbs onto the container walls. Samples preserved using the conventional preservation procedure are likely to underestimate copper concentrations. This artifact can be avoided by adding an oxidizing agent prior to acidification.

TRACE METALS ANALYSIS

Selection of Analytical Methods

The most widely used methods for the determination of metals in waters and their detection limits are summarized in Table 6.1. For further details on these procedures and background to the analytical techniques employed, the reference text *Standard Methods for the Examination of Water and Wastewater* and (APHA, 1998) on standard methods for the examination of water and the books by Grasshoff et al. (1999) and Ebdon et al. (1998) are recommended.

The selection of an appropriate method involves consideration of all or some of the following factors:

- The chemical form of the metal to be analyzed
- The range of analyte concentrations to be measured
- The lowest concentrations of interest
- The sample matrix and potential interferences

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TABLE 6.1 Typical Limits of Detection (μg/liter) of Commonly Used Analytical Methods

Element	Flame atomic absorption spectrometry*	Graphite furnace atomic absorption spectrometry	Hydride/cold vapor atomic absorption spectrometry	Inductively coupled plasma emission spectrometry (axial)	Inductively coupled plasma emission spectrometry (radial)	Inductively coupled plasma mass spectrometry	Anodic stripping voltammetry	Cathodic stripping voltammetry
Ag	2	0.1	—	0.2	—	0.02	—	—
Al	18	1	—	0.1	0.2	0.01	—	0.1
As	0.11	1	0.2	4	10	0.05	—	0.1
Cd	0.7	0.1	—	1	2	0.02	0.5	0.1
Cr	5	0.1	—	1	2	0.05	—	0.1
Cu	2	0.5	—	1	2	0.005	0.5	0.1
Fe	6	0.5	—	1	2	0.05	—	0.1
Hg	160	—	0.1	—	—	0.02	—	—
Mn	2	0.5	—	0.1	1	0.002	—	—
Ni	8	0.5	—	1	5	0.005	—	0.1
Pb	15	0.5	—	3	—	0.005	0.5	0.1
Se	250	1	0.2	10	—	0.1	—	0.1
Zn	1	0.1	—	1	2	0.02	0.5	0.1

*Detection limits from Ebdon et al. (1998).

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- Required sample throughput
- Cost

It is advisable to define the required performance criteria before considering cost issues. Reduction of sample numbers is often preferable to producing more data of inferior quality.

Contamination Control

As with field sampling, adequate control of contamination is a critical factor in obtaining accurate and precise results. This requires stringent cleaning and washing protocols and a clean laboratory environment. The difficulties encountered in measuring metal concentrations often vary between laboratories and depend on the prevailing sources of contamination. Laboratories in some urban locations may experience problems with lead contamination. Older laboratories with an extensive history of elemental mercury use can suffer from mercury contamination problems. Some combinations of instruments are not suitable in the same laboratory. For instance, equipment that uses mercury electrodes is not compatible with trace mercury analysis using cold vapor generation owing to elevated atmospheric mercury concentrations. Given that it is difficult to generalize on such issues, it is important to conduct in-house tests of contamination and manage each case accordingly. Since working conditions often change, ongoing contamination checks are advisable as part of routine QC. For example, in our laboratory over the last 5 years, episodic problems with copper, nickel, and zinc contamination have occurred that have necessitated tracing of contamination sources and corrective actions. Typical causes of these contamination events have included new batches of reagents and consumable items, modifications to laboratory ventilation systems, and corrosion.

Metal contamination usually arises from three sources: the reagents used in the analytical procedures, the surfaces that come into contact with the samples, and the laboratory environment. The first contamination source is usually characterized by a consistent positive bias and may be reduced by using high-purity reagents and a reliable source of high-purity water. Ultrapure reagents may be purchased from specialist suppliers or selected by screening various reagent sources/batches until a suitable one is found. Alternatively, various procedures are available for purifying reagents, e.g., distillation, coprecipitation, and recrystallization (Grasshoff et al., 1999; Howard and Statham, 1993). Other contamination sources usually manifest as erratic variability. A general rule to minimize contamination is to keep the number of sample-handling steps to a minimum. Laboratory-derived contamination can be reduced by limiting the number of metal surfaces in the laboratory or by conducting analyses in a clean room environment or a class 100 laminar-flow cabinet.

Digestion Procedures

Digestion of water samples is applied prior to total metals analysis to release metals from particles, dissolve mineral phases, and oxidize organic matter. This typically involves addition of an acid or combination of acids with or without some form of heating (e.g., ultraviolet, convection, or microwave heating). Additional oxidizing agents such as hydrogen peroxide also can be added. Nitric acid is the acid of choice because it does not interfere with most instrumental analytical methods; however, hydrochloric, perchloric, and hydrofluoric acids are also used (APHA, 1998). Care must be taken to compensate for any changes in sample volume during digestion. This usually involves a final dilution to a known mass or volume. Convection heating of acidified samples using a water bath, hot plate, or heated aluminium block largely has been replaced by the use of microwave heating.

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Microwave heating in sealed vessels with concentrated acids is the preferred procedure. Dipole heating results in higher temperatures, uniform heating, the effective solubilization of particles, lower reagent use, and lower blanks (Kingston and Jassie, 1988).

Pretreatment prior to analysis is also required when different metal species give different analytical responses: e.g., determination of arsenic species by hydride generation. In some cases, specific oxidizing agents are added to convert all chemical forms of an element to the form required for analysis; e.g., persulfate is added to convert organoarsenic compounds to As(V) (Le et al., 1992) and bromine monochloride is added to convert methylmercury to Hg(II) (Bloom and Crecelius, 1983).

The analysis of trace metals in saline samples is a specialist activity because most metals are commonly present at low nanogram per liter levels and well below the limits of detection of most instrumental methods. Preconcentration of the metals is required prior to quantitation of trace metal concentrations. GFAAS has been the single most important technique owing to its high sensitivity and low sample volume requirement. Analysis often involves a matrix separation (to avoid interferences from the saline matrix) and a preconcentration step. These are normally simultaneous procedures, such as chelation/solvent extraction, involving dithiocarbamate ligands and chlorinated solvents such as Freon, chloroform, or trichloroethane and chelating ion exchange resins, (most commonly Chelex-100) (Kingston et al., 1978). Further details on these methods may be found in the comprehensive text by Grasshoff et al. (1999). Reagent purity and clean-room laboratory techniques are vital to attain accurate results.

ANALYTICAL TECHNIQUES

Atomic Spectrometry

Flame atomic absorption spectrometry has limited applications for metal analysis in natural waters because its sensitivity is usually insufficient for the measurement of most natural trace element concentrations (see Table 6.1). GFAAS offers higher sensitivity and precision at low microgram per liter concentrations. It remains a method of choice for small sample volumes and often is used in conjunction with methods employing sample preconcentration by solvent extraction or uptake onto chelating resins. Chemical and spectral interferences are a particular concern with GFAAS. Spectral interferences should be corrected using Zeeman effect background correction (Ebdon et al., 1998). Chemical interferences should be checked for using spiked-recovery tests. Such interferences may be overcome using matrix modifiers (such as palladium and magnesium nitrate solutions) or matrix-matched standards. Further details of such procedures may be found in the book by Welz and Sperling (1998).

Inductively coupled argon plasma atomic emission spectrometry (ICP-AES) is an extremely versatile multielemental technique with detection limits in the low microgram per liter range. It has a high sample throughput and relatively few matrix interferences. Two configurations, involving radial and axial viewing of the plasma, are used commonly. The axial configuration offers greater sensitivity and better detection limits (Dubuisson et al., 1997) and is the preferred configuration for low-level metals analysis. Care should be taken when analyzing saline waters because for many metals sensitivity depends on the salinity of the sample. This may necessitate sample dilution and the use of standard addition calibration or matrix-matched standards.

ICP-MS employs an argon plasma to atomize elements in the sample matrix, followed by introduction of the atoms into a mass spectrometer and subsequent detection. It has the capacity to measure most metals at concentrations found in natural freshwaters (submicro-

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gram per liter) with the added advantage of near simultaneous multielement analysis (Wolf and Grossler, 1997). Detection limits for commonly analyzed elements are 0.001 to 0.06 μg/liter (Wolf and Grossler, 1997). A potential drawback when analyzing complex samples is the interference caused by polyatomic species formed by reaction of matrix constituents with argon in the plasma. For instance, high chloride concentrations can lead to the formation of ArCl, which interferes with the accurate measurement of arsenic (May and Wiedmeyer, 1998). Similarly, the formation of ArCe (May and Weidmeyer, 1998) prevents the accurate measurement of chromium. Sulfur, calcium, sodium, and phosphorus polyatomic species also interfere with a range of metals. Careful selection of the isotopes measured and correction equations can be used to compensate for most of these interferences (Wu et al., 1997). For freshwaters, most metals can be determined free of interference. In saline waters containing gram quantities of many cations (sodium, magnesium, etc.) and anions (chloride, sulfate, etc.), many severe polyatomic interferences exist. It is hard to generalize about metals that can be determined accurately in brackish water because this is a function of the metal concentration to polyatomic concentration ratio. Reducing the solvent load by desolvation can be used to reduce polyatomic interferences (Minnich and Houk, 1998). At present, routine analysis of estuarine and coastal waters requires a separation step using chelating agents or hydride generation (McLaren et al., 1985; Beauchemin et al., 1988; Halicz et al., 1996; Willie et al., 1998; Stroh and Vollkopf, 1993) to remove the analyte from the salt matrix. Alternatively, graphite furnace may be used to volatilize metals from the salt matrix prior to introduction into the ICP-MS (Chapple and Byrne, 1996). Recently, ICP-MS-MS instruments have become available commercially and allow the separation of polyatomic species from the analytes of interest and the direct analysis of seawater. Saline samples still need to be diluted because the high salt content decreases nebulization efficiency, changes the plasma chemistry, and blocks the inlet of the mass spectrometer. Nebulizer design is an important determinant of sensitivity and the sample volume required (Beres et al., 1994; Debrah et al., 1995).

The analysis of mercury by ICP-MS presents an additional problem. Mercury adsorbs to glass and plastic surfaces and, unless long wash times are used, will build up within the nebulizer/spray chamber system (U.S. EPA, 1998). The addition of gold(III) chloride to samples and the use of a low-volume nebulizer/spray chamber system will prevent this problem (U.S. EPA, 1998).

Vapor Generation Techniques

Arsenic and selenium display poor sensitivity when determined directly by atomic absorption spectromentry (AAS) and atomic emission spectrometry (AES) and are subject to interferences when using ICP-MS. For this reason, derivatization and introduction of the element as a gas to the atomization cell or ICP torch is used to improve sensitivity dramatically (Santosa et al., 1997). Hydride generation involves the reaction of various metalloids with a reducing reagent (usually sodium tetrahydroborate) to form a volatile hydride. The hydride is purged from solution, sometimes preconcentrated by cryogenic trapping, and then determined by some form of atomic spectrometry (usually atomic absorption or atomic fluorescence). This approach offers greater sensitivity owing to the preconcentration of the element in the gas phase and greater atomization efficiency. The main application is to the analysis of arsenic (and its organoarsenic acids) and selenium. Many transition elements will suppress hydride generation (Campbell, 1992), and a chelating agent such as cysteine or thioglycollic acid should be added to prevent this problem (Howard and Sabu, 1998; Le et al., 1994). Continuous-flow or flow-injection systems are available for hydride generation.

Natural waters contain low concentrations of arsenic and selenium (<1 μg/liter As; <0.2 μg/liter Se), and cryogenic trapping of the generated hydrides with liquid nitrogen

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has to be used to preconcentrate the hydrides before analysis (Apte et al., 1989; Santosa et al., 1997). Care must be exercised to ensure that quantitative generation of hydrides is achieved.

Mercury is present in natural waters at typically low nanogram per liter concentrations and usually is analyzed separately from other metals. Mercury is determined by generating mercury vapor from samples by reduction (usually stannous chloride), with detection as elemental mercury by atomic spectroscopy. Preconcentration onto gold foil or columns is required to enhance the sensitivity of the cold vapor technique (Fitzgerald and Gill, 1979). AAS has now been replaced by atomic fluorescence spectrometry (AFS), which offers greater sensitivity (Liang and Bloom, 1993; Cossa et al., 1995). Dedicated instrumentation normally is required to attain reliable routine performance.

Electrochemical Analysis

The most widely used electroanalytical techniques for the determination of trace metals in natural waters are anodic stripping voltammetry (ASV) and cathodic stripping voltammetry (CSV). A major advantage of these techniques is their applicability to saline matrices. With appropriate care, they are applicable to the analysis of a range of metals in open ocean waters (Grasshoff et al., 1999; Scarponi et al., 1995). They are comparatively low cost procedures and offer some simultaneous analysis capabilities. For example, ASV is able to analyze copper, lead, cadmium, and zinc in one voltamogram. Typical detection limits obtained with ASV and CSV are given in Table 6.1. Generally, electroanalytical methods are nonrobust and require a high degree of operator skill. They are used rarely for routine analysis.

ASV and CSV measure an electrochemically labile fraction that is determined by both thermodynamic and kinetic factors (Davison, 1978). To determine total metal concentrations, some form of pretreatment is required. Ultraviolet irradiation with or without the addition of hydrogen peroxide (Batley and Florence, 1976; Achterberg and van den Berg, 1994) is used for the digestion of filtered samples and unfiltered samples having a low turbidity.

Colorimetric Methods

Colorimetric methods are still used for some metals. These include aluminum, chromium, iron, and manganese (Hunt and Wilson, 1986; Grasshoff et al., 1999). Typical detection limits range between approximately 1 and 10 μg/liter. All these procedures are amenable to automation either using flow-injection or continuous-flow analysis.

ANALYTICAL QUALITY CONTROL

Whatever the analytical method employed, some form of QC is essential. Several comprehensive texts detailing analytical quality control in water laboratories are available (Hunt and Wilson, 1986; Cheeseman et al., 1989; Quevauviller, 1995). Appropriate QC procedures include frequent calibration, spike recovery tests (particularly important when analyzing new matrices), analysis of sample duplicates, and analysis of a certified reference material and in-house reference material (see Chapter 2). For large laboratories engaged in routine analysis, laboratory accreditation and participation in interlaboratory trials and external QC check-sample programs is also advisable. In a well-run laboratory, typically

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between 10 and 20 percent of total analytical effort is invested in QC. Certified reference waters are now available from a number of suppliers, such as the National Research Council of Canada (NRC), the European Bureau of Community Reference (BCR), and the International Atomic Energy Agency (IAEA). Care should be taken to choose reference waters that have similar matrices and metal concentrations to the samples being analyzed. This is not always possible, and in-house QC standards may be used as a substitute. These are used to check between-batch variability, although they are not generally a check for accuracy unless the metal concentrations have been determined by several independent laboratories. The use of reference standards that are prepared in deionized water confirm the accuracy of calibration but do not test the analytical method's ability to cope with matrix effects.

TRACE METALS SPECIATION PROCEDURES

As indicated previously, total metal concentrations are generally a poor indicator of metal bioavailability and toxicity to organisms (Luoma, 1983; Craig, 1986; Campbell, 1995). Measurements of chemical speciation are required. At present, no universally applicable technique for determining metal speciation exists. Nevertheless, a number of methods are available that measure a fraction of the filterable metal concentration that is more closely related to metal bioavailability (Table 6.2). Metal speciation methods are more complex than procedures used for measuring total metal concentrations. Extensive reviews of such techniques may be found in the books by Batley (1989) and Tessier and Turner (1995). A major problem confronting speciation studies is the lack of analytical methods that can determine the concentrations of specific inorganic species such as the free metal ion. Ion-selective electrodes determine free metal ion concentrations but generally are insensitive and prone to interferences (Batley, 1989). Their application largely has been limited to studies of copper speciation (Meador, 1991; De Marco, 1994). Electrochemical procedures such as anodic stripping voltammetry (ASV) and cathodic stripping voltammetry (CSV) measure labile metal concentrations (assumed to approximate the concentration of inorganic metal species and weakly bound organic complexes) and have been used to elucidate the extent of complexation by dissolved organic matter for a range of metals (Batley, 1989; Tessier and Turner, 1995). Size fractionation techniques such as dialysis and ultrafiltration also have been used (Apte et al., 1989; Buffle et al., 1992; Buffle, 1988), although these methods give an operationally defined split of metal species that is difficult to relate to actual chemical species.

For covalently bonded molecules (organometallic species) such as methylmercury and organoarsenic compounds, the favored approach involves derivatization (e.g., ethylation or hydride formation), cryogenic trapping, and chromatographic separation, followed by element-specific detection using atomic absorption, emission, or fluorescence spectrometry (Marshall and Momplasir, 1995; Apte et al., 1989; Howard, 1989). Derivatization normally is necessary prior to gas chromatography to form volatile species (Andreae, 1979; Bloom, 1989; Rapsomanakis and Craig, 1991).

The determination of oxidation states is important for elements such as As, Se, and Cr because toxicity and reactivity can vary with oxidation state (Cooper and Glover, 1974; Neff, 1997). This may be achieved by selective coprecipitation (Cranston and Murray, 1978), hydride generation (Andreae, 1977), electrochemical determination (Florence, 1986), or volatilization following species-selective derivatization (Marshall and Momplasir, 1995).

Sample storage is a critical issue confronting speciation analysis. Refrigeration at 4°C and storage in the dark generally are thought to be the best storage procedures because they slow chemical reactions and biological processes (Batley, 1989). Freezing generally is not

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TABLE 6.2 Summary of Speciation Techniques for Metals in Natural Waters

Metal	Technique	Species measured
Aluminum	CSV,[a] cation exchange resin, ligand competition, spectrophotometry, solvent extraction AAS[b]	Reactive aluminum, inorganic, noncomplexed monomeric
Arsenic	HPLC[c] or hydride GC-AAS (AFS)[d]	As(III), As(V) $CH_3AsCHOOH$, $(CH_3)_2AsCOOH_2$
Cadmium	ASV,[e] ligand competition	Labile Cd or Cd^{2+}
Chromium	Resin separations, spectrophotometry	Cr(III), Cr(VI)
Copper	ASV, CSV, ISE,[f] ligand competition	Labile Cu, Cu^{2+}
Lead	ASV, CSV, ligand competition	Labile Pb, Pb^{2+}
Mercury	GC-AFS	Hg(II), CH_3Hg^+
Nickel	Ligand competition, CSV	Labile Ni
Selenium	Hydride or hydride GC-AAS (AFS),[d] derivatization/GC, colorimetry	Se(IV), Se (VI), organoselenium species
Uranium	CSV, TRLFS,[g] UV-vis[h]	U(VI)
Vanadium	Capillary electrophoresis, IC[i]	V(IV), V(V)
Zinc	ASV, CSV, ligand competition	Labile Zn

[a]Cathodic stripping voltammetry.
[b]Atomic absorption spectrometry.
[c]High-performance liquid chromatography.
[d]Atomic fluorescence spectrometry.
[e]Anodic stripping voltammetry.
[f]Ion-selective electrode.
[g]Time-resolved laser-induced fluorescence spectroscopy.
[h]Ultraviolet visible spectrophotometry.
[i]Ion chromatography.

recommended because it can rupture cells and cause precipitation of some constituents (Batley, 1989). An alternative approach is the fixing of certain metal species by immobilization onto selective adsorbents in the field (Boussemart and van den Berg, 1994). This is probably the best approach for highly unstable species. Whichever storage procedure is adopted, it is highly recommended that rigorous tests are carried out to characterize the effects of storage on sample stability.

FUTURE DEVELOPMENTS

Improvements in water quality monitoring will be made by the measurement of metal species concentrations that are more meaningful to answering the questions posed (e.g., metal bioavailability). Increased spatial and temporal coverage and reduced time between sampling, analysis, and decision making are desirable. To achieve these goals, portable field analysis, in situ sensing, and real-time monitoring of metal concentrations will become increasingly important.

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CHAPTER 7
ANALYSIS OF ORGANIC SUBSTANCES IN NATURAL WATER

Andrew Revill

INTRODUCTION

Organic compounds are ubiquitous in natural waters either as natural products or as contaminants. For example, naturally occurring organic compounds from algae and bacteria include hydrocarbons, heterocyclic compounds, and a range of the so-called volatile organic compounds (VOCs), whereas water quality guidelines (ANZECC/ARMCANZ, 2000) identify some 220 organic compounds for monitoring. These include organic alcohols, chlorinated hydrocarbons, aromatic hydrocarbons, nitroaromatic hydrocarbons, pesticides, and nitrophenols. In addition to these, there will always be specific industrial discharges that require monitoring.

Natural sources of organic compounds such as algae and bacteria are in general diffuse sources, although inputs such as natural oil seeps can be a point source. The converse tends to be true for anthropogenic inputs in that these are generally point sources such as effluent discharge points, although some contaminants will enter waters via atmospheric deposition, which is a more diffuse source.

The intention of this chapter is to provide information on important factors to consider when sampling organic compounds and on the range of possible analytical techniques. However, given the large range of potential analytes, it is clear that no one method can be used to analyze for all compounds. In general, analytical protocols need to be developed for particular compound classes.

Sampling Strategy

The subject of sample strategy design is lengthy and complex and is not really appropriate for discussion in this chapter, but it is relevant to include some general points at this stage (for a more comprehensive review, see Chap. 2). Where and when to sample are issues that really can be determined only by the analytes in question and their source. For example, a survey designed to assess the distribution of a particular naturally occurring compound in a bay will require a very different sampling strategy from a monitoring program for an effluent discharge in an estuary. Issues to be considered include current direction and strength, water chemistry (e.g., fresh versus saline or estuarine mixing zones), frequency of discharge (e.g., continuous or pulsed), and whether to sample on the surface or at depth.

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Sample Collection

What to Sample? At this stage it is necessary to decide which components of the aquatic system are to be sampled. Organic compounds are often hydrophobic and thus are associated primarily with particulate material, although there will be a small dissolved/colloidal fraction, especially with the more polar compounds such as alcohols and fatty acids. Thus a common question is whether to collect a whole sample or to filter the sample and analyze a particulate and dissolved component. From the point of view of a monitoring program, a whole sample is the quickest and cheapest way to an assessment of concentrations of the analyte in question. If this provides a result below guidelines. then no further work needs to be undertaken. If concentrations are above guidelines, then a decision needs to be made as to whether a separate assessment of particulate bound or dissolved component needs to be made. There is often an assumption that the dissolved fraction is the bioavailable component, but this is not necessarily the case. For example, filter feeders probably will be exposed to greater quantities of particulate bound compounds, and once in the lipophilic environment of their digestive system, these compounds become available. This question really can only be answered by investigating the literature for the compounds in question.

Contamination Issues. Some general points about sampling equipment are as follows: All sampling equipment must be inert and precleaned and rinsed with an organic solvent such as dichloromethane (unless this is the analyte). For example, sample containers for waters to be analyzed for hydrocarbons would be glass, washed with a laboratory detergent, followed by an acid rinse to remove residues, and then rinsed with a solvent such as hexane. At all stages of the sampling process, the sample must not be allowed to come into contact with plastic because this may cause contamination with compounds such as phthalates, which are readily leached by water. A potential source of contamination often missed is sample container caps, which should be lined with foil or PTFE. Any tubing used should be PTFE tubing, again to prevent leaching of contaminants. During sampling, all collections must be carried out wearing inert gloves because contact with the skin can introduce a relatively high level of contamination with squalene, especially in hot locations.

Any equipment used in filtration or other techniques must be subjected to the same rigorous precleaning as described earlier. Filters, generally GF/F, should be precombusted at 450°C prior to use (e.g., Miller, 1999) and stored in precombusted foil until used. There are filters on the market that are encapsulated to provide greater rigidity. It is important that these are subjected to a rigorous assessment of potential contamination before use.

A lot of aquatic sampling is performed from boats, and it is essential that this cannot introduce contamination into the samples. The issues relating to sampling from small boats tend to be associated with possible contamination from engines, and therefore, wherever possible, the boat should be anchored and the engines turned off or the boat pointed upstream of the prevailing current and samples taken from in front of the engines. On larger ships, the sources of contamination become more numerous, e.g., engine exhaust, winch cables (oil and grease), and other products being used on the ship such as cleaning fluids.

How to Sample? Water samples can be collected in a variety of ways, from a simple weighted open bottle to a sophisticated programmable autosampler. Probably the most common water sampling device is the Niskin bottle. This is an open-ended bottle that can be lowered to a prescribed depth and the bottle closed by means of a messenger. More sophisticated setups use a rosette of 12 or 24 bottles, which allows each bottle to be closed independently for the collection of depth profiles. Niskin bottles tend to have a capacity of approximately 10 liters, so for compounds in very low concentrations it may be necessary either to collect multiple samples or to use an alternative method. One alternative is the use

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of pumping systems, where the inlet is lowered to a prescribed depth and the sample pumped into a collection vessel at the surface. It is important to note that with this type of system it is preferable to locate the collection vessel prior to the pump in order to minimize contamination.

If it becomes a requirement to analyze the particulate and dissolved fractions separately, then a decision has to be made how to do this. A common method is to filter, generally through a 0.45-μm filter; however, this may or may not be the optimal separation depending on the analyte in question. Other alternatives are centrifugation and membrane separation. However, it is important to remember that techniques such as membrane separation, where conditions are made more favorable for the analyte on one side of a membrane, can cause a shift in the sample equilibrium and may even lead to desorption of the analyte from particles, thus introducing a bias.

Other sampling devices include long-term integrating samplers, which may pump the water through a filter and then trap dissolved components on a resin. This type of sampling device is often self-contained and can be deployed at specific depths with the use of moorings (Ehrhardt and Burns, 1990). Some systems can include a pumping arrangement and a series of sample bottles on a carousel; controlled by a personal computer (PC), this type of system can collect samples at prescribed intervals. A basic form of this system is used in sediment traps that are designed to collect sinking oceanic particles. These are deployed at preset depths, either with a mooring or free floating, and basically collect particles into a container. The trap may have 12 containers, programmed to rotate each month.

More recent developments have been focused on passive samplers that can integrate (and therefore concentrate) contaminants over long periods. These generally involve the use of semipermeable membranes encasing a solvent into which contaminants will partition (Peterson et al., 1995).

Sample Extraction

Why Extract? Extraction of the sample is required basically for one reason, and this is to transfer the compounds of interest from the water/particulates to an organic solvent, which has the effect of both concentrating and making them more amenable to analysis. If we consider this section as the interface between the bulk sample and the actual analysis, then we have to consider the process of extraction and any appropriate fractionation into compound classes required. This is shown schematically in Fig. 7.1.

Methods Available for Extraction. The extraction process is basically a partition between the sample matrix (water or particulates) and an organic solvent. The most basic extraction is a liquid-liquid partition between water and a solvent. The choice of solvent depends on several factors, but first and foremost it must be immiscible with water. Thus the water sample is placed in a separating funnel, solvent is added, and the two are shaken together and allowed to separate, and the solvent is recovered. This is normally repeated at least once more, assuming the general principle that each extraction obtains approximately 80 percent of the analytes in the water. The solvent is then removed to concentrate the analytes prior to analysis. Other factors to consider when choosing a solvent are the analytes of interest, volatility, ease of separation from water, any subsequent separations, and the final analytical tool. For example, a general rule of thumb is that like dissolves like, which would suggest that for chlorinated compounds, a chlorinated solvent would work best, and this is probably true. However, if the final analytical tool is an electron capture detector, a chlorinated solvent may not be the most appropriate. This said, it is always possible to exchange solvents prior to analysis. Similarly, if the analytes in question are volatile, then

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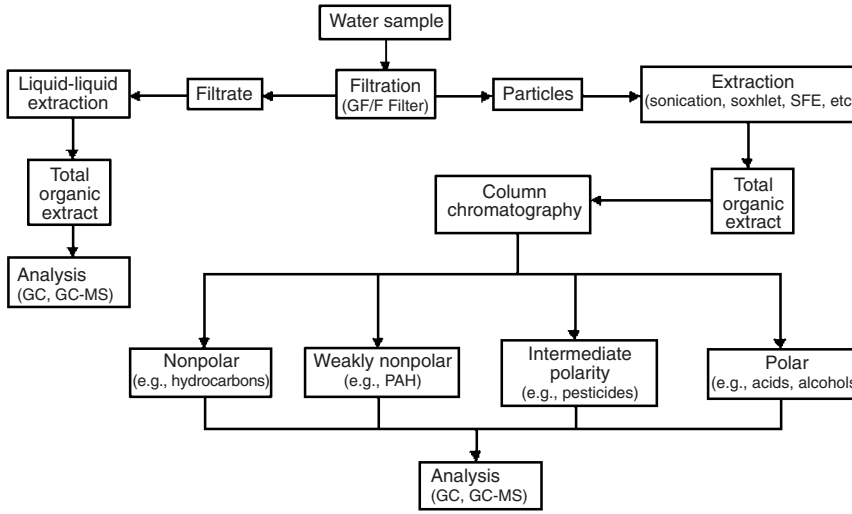

FIGURE 7.1 A schematic example of how a water sample may be analyzed for organic contaminants.

a more volatile solvent is preferred to increase the chances of solvent removal while minimizing analyte losses. Some solvents are more miscible with water than others, and this can be important when attempting to minimize water carry-over from the extraction. For example, in a liquid-liquid extraction solvents such as hexane will provide a clean interface with little carry-over of water, whereas dichloromethane may allow a small amount of water to be carried over.

Extraction of particulate samples on filters is a little more problematic in that the filters are the sample matrix, but there is inevitably some water also associated with the filter and particulates. Thus, if extraction is attempted solely with a hydrophobic solvent, a poor extraction efficiency will be obtained. It is necessary to use solvent mixtures to allow the solvent to come into close contact with the analytes. This can be achieved in two ways. The filters can be extracted sequentially, initially with a more polar solvent such as methanol, followed by a methanol-dichloromethane mix, and finally with dichloromethane only. The various solvent extracts are combined, and water is added to form a two-component mixture that is then treated as a liquid-liquid extraction. The alternative method is to use a three-component single-phase mixture such as chloroform-methanol-water to perform the extraction. The ratio of the solvents is then altered to break phase, and the resulting two-component system is treated as a liquid-liquid extraction.

Extraction of organic compounds from their matrix generally requires some form of energy input. For liquid-liquid extractions, this is generally in the form of shaking; however, for the extraction of particulates, the choices are more varied. The sample simply can be shaken with the solvent, or energy can be applied by different means. A classic approach is Soxhlet extraction, where the sample is placed in a thimble and solvent refluxed to sequentially extract the analytes. Another common approach is the use of ultrasound to agitate the sample in the solvent. More recently, attempts to reduce solvent use and speed up extractions have led to techniques such as supercritical fluid extraction (SFE) and enhanced solvent extraction (Heemken et al., 1997). Dissolved components initially trapped onto resins or solid-phase cartridges (Table 7.1) generally can be recovered by eluting the medium with a suitable solvent.

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TABLE 7.1 Examples of Resins Used in Solid-Phase Extraction of Water Samples

Type	Phase	Porosity (Å)*	Uses
C_{18}, C_8, C_2, C_1	$-Si(R)-$	60, 150, 500	Nonpolar: least selective and most common adsorbent; will retain most organic compounds. Degree to which nonpolar compounds can be eluted depends on the chain length of R.
	$R = C_nH_{2n+2}$		
	R = cyclohexyl		
Cyclic	or phenyl	60	Moderately nonpolar: used when the more common nonpolar adsorbents do not provide the desired selectivity.
CN	$-Si(C_3H_6CN)-$	60	Moderately nonpolar: used if nonpolar analytes irreversibly bonded to more common adsorbents.
NH_2	$-Si(C_3H_6NH_2)-$	60	Weak anion: rarely used, more for specialist applications such as the isolation of acids.

*The larger the pore size, the more macromolecular material will be retained.

Sample Fractionation. Depending on the type of sample and the amount of organic material extracted, it may be necessary to fractionate the sample into compound classes. This is generally performed to remove interferences from other compounds, enhancing the final analysis, and to prevent unnecessary deterioration in analytical equipment. The most common method of fractionation is column chromatography. In its most simple form, an adsorbent such as activated silica gel or alumina is packed in a glass column, the sample is applied to the top, and the components of interest are eluted with a variety of solvents. The important points to remember are

- Choose the most suitable adsorbent for a mixture.
- Do not overload the column (a 30:1 adsorbent-sample ratio is a good starting point).
- Use a suitable range of solvents for elution starting with the most apolar.

Alternatives to column chromatography include thin-layer chromatography (TLC) and high-performance liquid chromatography (HPLC). Like column chromatography, TLC is quite labor-intensive but has the added disadvantages of being more suited to smaller quantities of sample and is more restricted in terms of the number of solvents that can be used to elute the plate, so in general it finds less use in a preparative sense. HPLC is a similar technique to column chromatography, except that it is performed at higher pressure, which reduces the time required for separation. HPLC has the added advantage that it can be automated.

Once the appropriate fraction has been obtained, a choice of the most suitable analytical method can be made.

Sample Analysis

High-Performance Liquid Chromatography (HPLC). Although not used as commonly as gas chromatography in the analysis of organic compounds, HPLC can be used to analyze compounds with an adsorption and/or fluorescence characteristic, such as PAHs. The

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limited resolving power, compared with gas chromatography, and one-dimensional detectors such as adsorption and fluorescence detectors made this technique of limited use for mixtures. However, the advent of the photodiode array detector (HPLC-DAD) and the successful coupling of HPLC with mass spectrometry (HPLC-MS) have increased the usefulness of this technique in environmental applications. The diode array detector has the capability to simultaneously measure absorption in multiple wavelengths, thus building up a three-dimensional "picture" for each eluting peak. By applying absorption characteristics for known compounds, mixtures potentially can be deconvoluted. Similarly, HPLC-MS allows the mass spectrum of each eluting peak to be analyzed and individual components identified (Barcelo et al., 2001). The advantage of HPLC is that it can be used for the analysis of substances not readily amenable to gas chromatography, e.g., algal toxins (Metcalf et al., 2000).

By far the most common analytical technique in the analysis of organic compounds is gas chromatography (GC), which can be coupled with a variety of detectors. The art of GC is far too detailed to discuss here, but anyone interested is encouraged to read Jennings (1987). Suffice to say here that GC provides a final high resolution separation of compounds of interest. The important factors are the choice of GC column and the detector (Table 7.2).

GC Detectors. There are a wide variety of detectors available for GC, and discussion here will be restricted to the detectors used most commonly in organic analyses (see Table 7.2). One of the most common detectors is the flame ionization detector (FID). This is a general-

TABLE 7.2 Examples of GC Columns and Common Detectors

Column phase*	Polarity	Common applications
100% dimethylpolysiloxane	Nonpolar	Hydrocarbons, phenols, pesticides, PCBs
5% diphenyl + 95% dimethylpolysiloxane	Nonpolar	PAHs, fatty acid methyl esters
50% phenyl + 50% dimethylpolysiloxane	Intermediate	Steroids, pesticides
Polyethylene glycol	Polar	Free acids, alcohols

Detector	Uses
Flame ionization detector (FID)	Most common general-purpose detector
Electron capture detector (ECD)	Halogenated compounds
Nitrogen-phosphorous detector (NPD)	Nitrogen- and phosphorous-containing compounds
Flame photometric detector (FPD)	Sulfur-containing compounds. Can also be retuned for organotin compounds
Atomic emission detector (AED)	Metallated compounds
Mass spectrometer (MS)	General-purpose, potentially highly specific, and provides structural information

*There are a wide variety of phases that provide a more gradual change in polarity than those shown here.

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ANALYSIS OF ORGANIC SUBSTANCES IN NATURAL WATER

purpose detector that responds to carbon-hydrogen bonds in organic compounds, and its response is directly related to the CH content of the compounds of interest. Thus, while all organic compounds will cause a response on this detector, some will cause a larger response than others. This is an important factor if quantitation is to be used because response factors will be required. The nature of this detector makes it the first choice for some compounds, e.g., hydrocarbons, but the fact that all organic compounds will respond means that sample cleanup is very important or the resulting chromatograms will be "busy" and confusing.

Where the compounds of interest have some functionality, it may be possible to use a more selective detector. For example, the electron capture detector (ECD) can be used to detect compounds that contain an electronegative group, and only these compounds will cause a response. Probably the most common use for this detector is in the analysis of halogenated compounds such as pesticides. Other specific detectors include the flame photometric detector (FPD) for sulfur-containing compounds and the nitrogen phosphorus detector (NPD) for compounds containing nitrogen and phosphorous atoms. These detectors not only provide increased specificity but also can provide increased sensitivity. For example, the FID commonly will detect compounds in nanogram quantities at the detector, whereas the FPD will detect compounds such as dibenzothiophene ($C_{12}H_8S$) at picogram quantities at the detector (Berthou and Vignier, 1986).

An interesting development in GC has been the coupling of this basically organic analytical technique with those used more commonly in inorganic analytical chemistry. For example, GCs have been coupled with inductively coupled plasma instruments (Kim et al., 1992) and atomic emission detectors (AEDs) (Andersson and Schmid, 1993). These developments have allowed for more selective analysis of metallated organic compounds, e.g., porphorins. The interest in these detectors has been twofold. They have allowed investigators to analyze the range of metals complexed by organic compounds, but they also allow investigators to selectively detect compounds containing a specific metal, e.g., copper or magnesium.

While a lot of information about a sample can be obtained from GC, especially when coupled with a selective detector, compound identification relies very heavily on the analysis of known standards to obtain retention times, and these must be analyzed frequently to ensure that changing column conditions and so on are not causing changes. Given this limitation, there will always be compounds present in a chromatogram that are unknown.

Gas Chromatography–Mass Spectrometry. The greatest advance in GC probably has been the coupling of GC with mass spectrometry (GC-MS). This has allowed thousands of compounds to be identified and a degree of selectivity to be applied to organic analyses not previously possible. The basic principles of GC-MS are that the chromatographic peak is bombarded with electrons, and this results in compounds losing electrons, they fragment, and the resulting positive ions are detected. These ions can then be reconstructed like a jigsaw to reveal the compound's identity. This is basically three-dimensional information in that a chromatogram is obtained that looks very similar to that from a conventional GC, but behind every peak is the mass spectrum.

The advantages of this technique from an analytical point of view are several. First, any unknown peaks in the chromatogram potentially can be identified. Second, the distinguishing fragmentation patterns of certain compounds can be used to identify similar compounds within a chromatogram, e.g., a homologous series, and third, this distinctive fragmentation can be used to filter out unwanted information so that the mass spectrometer will detect only the ions of interest. This is particularly useful when the compounds of interest are relatively minor components and cannot be separated by any sample pretreatment. This type of analysis is often referred to as *selected ion monitoring* (SIM), and an example of how this technique is used in oil fingerprinting in shown in Fig. 7.2. In this

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example, relatively minor but diagnostically important compounds have been highlighted within a hydrocarbon analysis by using specific fragmentations associated with these compounds. A further enhancement on this technique is GC-MS-MS, where compounds of a very predictable fragmentation can be analyzed and identified. This generally involves the use of the first mass spectrometer to isolate an ion of interest and the second mass spectrometer to fragment this ion and determine its structure.

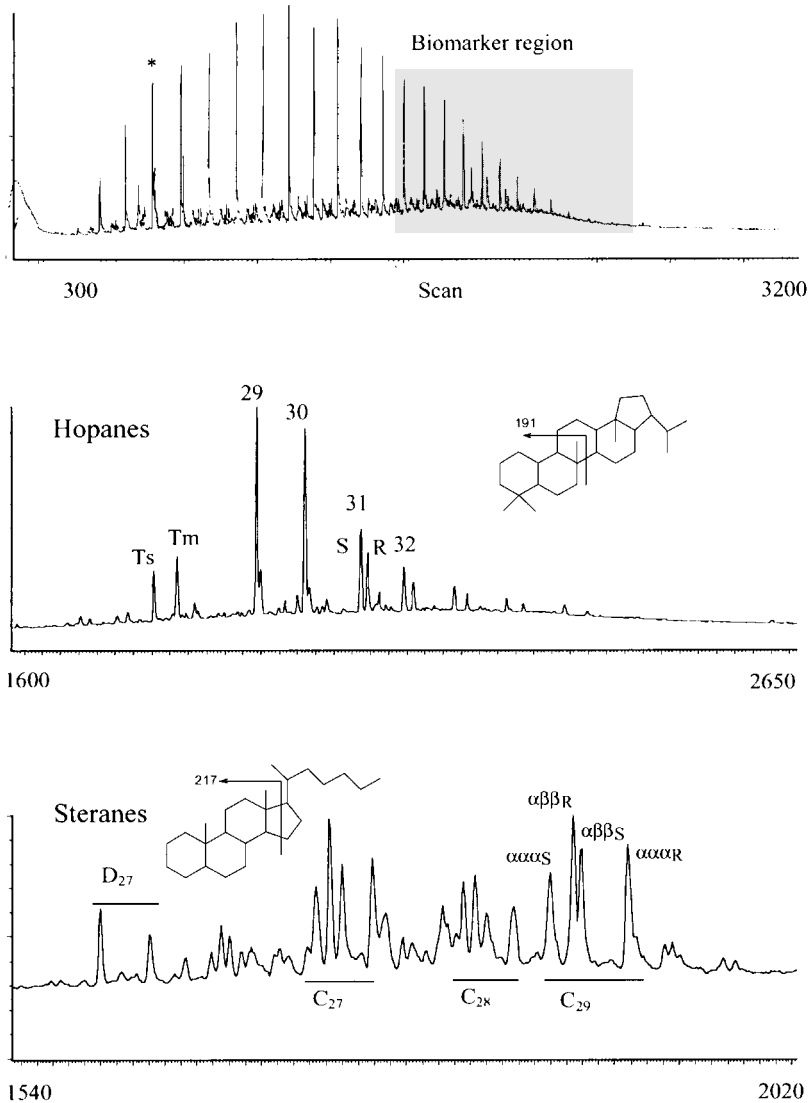

FIGURE 7.2 An example of how minor components in a complex mixture may be highlighted using GC-MS in SIM.

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Initially, GC-MS instruments relied on the use of large magnetic sector instruments, but in recent years advances in instrumentation have seen the mass spectrometer shrink from an instrument that filled a room to one that will sit comfortably on a bench top. This has resulted in a dramatic increase in the number of laboratories using GC-MS. Initially, bench-top instruments used a so-called quadrupole geometry and were capable of the basic GC-MS functions, including SIM. However, recent years has seen the development of bench-top instruments that use ion-trap technology. These instruments also perform the basic functions but are also capable of GC-MS-MS techniques.

While techniques such as SIM and GC-MS-MS provide a high degree of selectivity to analyses, this has now been advanced further by a technique called *negative ion chemical ionization.* Chemical ionization is a technique commonly used in MS to "softly" ionize a compound so as to induce little or no fragmentation to calculate its molecular mass. Ideally, the technique simply dislodges a single electron using a collision gas at low kinetic energy that fails to induce fragmentation, allowing the resulting positively charged molecular ion to be detected. Recently, advances have been made to allow the polarity of the mass spectrometer ion source (that part which carries out the ionization) to be basically reversed. Thus, instead of expelling positive ions, it now expels negative ions. Therefore, any compound that can be induced to gain an electron instead of losing one can be selectively analyzed. This is now the ECD of mass spectrometry and is used for all the same compound types. The advantage, though, is that when used in an ion-trap GC-MS system, the negative ion can be isolated and then fragmented (GC-MS-MS) to provide selectivity and structural information, making it a very powerful technique.

The ability to selectively analyze for compounds of interest has been and still is very useful in monitoring the inputs and fates of these compounds in aquatic systems. However, there is still one aspect of the cycling of these compounds that is unknown, and this is their source. For example, we can measure what is there and how much is there, but we also need to know where it came from (and possibly how long has it been there). In some situations, this question can be answered relatively easily because there may only be one possible source, but in reality, there are often multiple potential sources for organic compounds in aquatic systems, ranging from natural to anthropogenic sources. The greatest advance in this area has been the development of compound specific isotope analysis (CSIA), which involves the coupling of GC with a stable isotope ratio mass spectrometer (GC-IRMS).

All organic compounds, by definition, contain carbon, which occurs as ^{12}C and to a much lesser extent (approximately 1 percent) ^{13}C. Any process that involves chemical kinetics will lead to a fractionation away from this normal $^{12}C/^{13}C$ ratio (Hayes, 1993). This includes natural processes such as diffusion of CO_2 and photosynthesis through synthetic manipulation such as pharmaceutical production. Thus, if the same compound is produced by two different processes, the ratio of the degree of fractionation may be different.

This ratio is measured by the GC eluent being directed into a microcombustion furnace (as opposed to a detector) that quantitatively produces CO_2. This CO_2 is then swept into a magnetic sector MS measuring the masses 44 ($^{12}C^{16}O_2$), 45 ($^{13}CO_2$ + $^{12}C^{16}O^{17}O$), and 46 ($^{12}C^{16}O^{18}O$ + $^{13}C^{17}O^{16}O$ + $^{12}C^{17}O_2$). All measurements are calibrated against an international standard (Pee Dee Belemnite, PDB) and expressed as a delta per mil ($\delta‰$) notation:

$$\delta^{13}C = \left\{ \frac{R_{\text{sample}}}{R_{\text{standard}}} - 1 \right\} \times 1000$$

where $R = {}^{13}C^{12}C$.

This technique now provides analysts with a potential source indicator for compounds with potential multiple sources and is already being applied to such areas as PAH contamination in rivers (O'Malley et al., 1994).

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FUTURE DEVELOPMENTS

The area most likely to see a rapid increase in both application and development is that of compound-specific stable and possible radioactive isotope analyses. Already there are instruments entering the market that offer compound-specific deuterium (^{2}H) and compound-specific nitrogen (^{15}N) capability. Other functional groups with stable isotopes (such as chlorine) are certain to receive attention from instrument developers. In addition, work is underway involving the isolation of specific compounds and then subjecting these to ^{14}C analysis, which of course provides a potential age signature (Eglinton et al., 1996). At present, this technique requires painstaking isolation of compounds by preparative GC followed by analysis using an accelerator mass spectrometer (AMS), which is capable of measuring the small amounts of ^{14}C present. However, this is also destined to receive attention in the future.

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CHAPTER 8
ENVIRONMENTAL MONITORING OF NUTRIENTS

Grady Hanrahan, Paulo Gardolinski, Martha Gledhill, and Paul Worsfold

INTRODUCTION

This chapter describes the biogeochemistry of nutrients (nitrogen, phosphorus, and silicon), methods of sampling and storage, and techniques for their determination in aquatic environments. It also considers the validation of nutrient data, which is important for intercomparison purposes, particularly in view of the range of analytical techniques used and the different physicochemical forms of nutrient elements that can exist in natural waters. The need for accurate and precise data is also driven by water quality issues (e.g., eutrophication) and legislation. A glossary of key terms is provided at the end of this chapter.

BIOGEOCHEMISTRY OF NUTRIENTS

Role of Nutrients

Nutrients are essential elements for biochemical reactions and the growth and maintenance of biomass, with nitrogen, phosphorus, and silicon being the most important and commonly determined nutrients in aquatic ecosystems. This chapter therefore focuses on these three macronutrients, but it should be noted that a number of other elements also act as micronutrients.

The cumulative effect of enrichment of water by nutrients, particularly nitrogen and phosphorus, leads to eutrophication with an accompanying increase in biomass and natural productivity within a given aquatic community structure and deterioration of the quality of the water concerned (Wilson et al., 1993; Moss, 1996; Young et al., 1999). This can cause major ecological changes, e.g., production of algal blooms, reduction in species diversity, and major changes in community structure. Thus, assessing nutrient concentrations on a regular basis is of paramount importance for providing an insight into the relative health of aqueous environments.

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ENVIRONMENTAL MONITORING OF NUTRIENTS

CHEMICAL SPECIATION

Nitrogen

The elemental gas dinitrogen (N_2) is the most abundant but least reactive form of nitrogen in the global environment. However, many biochemical transformations can convert dinitrogen into dissolved inorganic species, e.g., nitrate (NO_3^-), nitrite (NO_2^-), ammonium (NH_4^+), and organic nitrogen compounds in both dissolved and particulate forms. Nitrogen speciation can be defined operationally as total particulate nitrogen (TPN), total dissolved nitrogen (TDN), dissolved organic nitrogen (DON) and dissolved inorganic nitrogen (DIN) (Robards et al., 1994). See the Glossary at the end of this chapter for definitions. Figure 8.1 illustrates the aquatic nitrogen cycle, including biochemical transformations. Three of the processes, i.e., fixation, nitrification, and ammonification, convert gaseous nitrogen into bioavailable chemical forms. The fourth, denitrification, converts fixed nitrogen back into gaseous species.

The global distribution of nitrogen is shown in Table 8.1. The atmosphere is the principal nitrogen reservoir, with over 99 percent of the total in the form of N_2. Nitrogen in terrestrial systems occurs mainly as soil organic matter, with litter and soil inorganic nitrogen accounting for the majority (97 percent). N_2 in dissolved form is the most abundant form in the world's oceans. Nitrogen also occurs in various inorganic forms, e.g., nitrate, nitrite, ammonia, hydrazine, nitrous oxide, and nitrogen dioxide, and organic forms, e.g., amino acids, amines, and amides. However, the organic fraction is not well characterized.

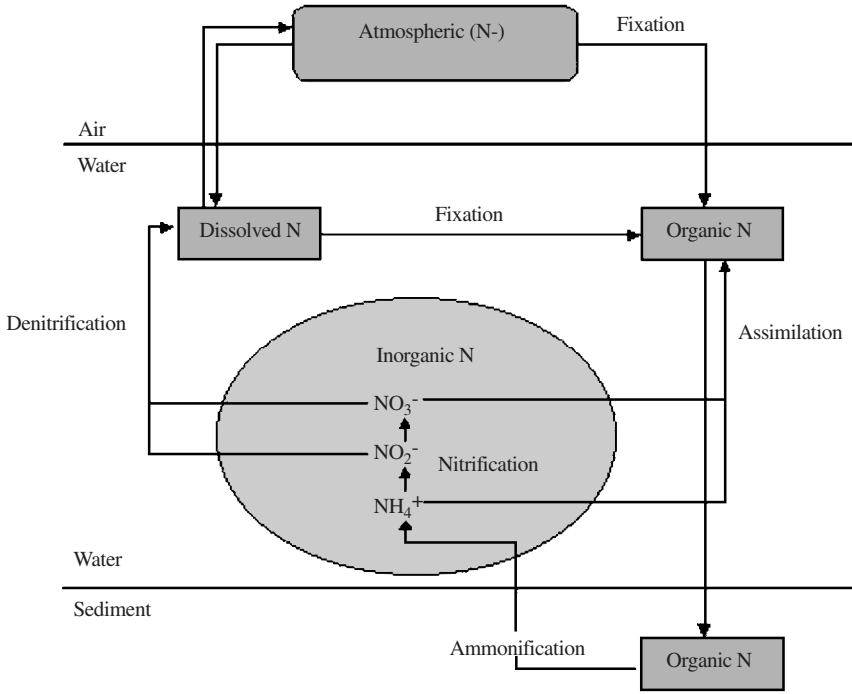

FIGURE 8.1 The aquatic nitrogen cycle.

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TABLE 8.1 The Major Global Reservoirs and Fluxes of Nitrogen

Reservoir	10^{15} g N
Lithosphere	190,000,000
Atmosphere	3,900,000
Oceanic	23,000
Terrestrial	500
Flux	10^{15} g N yr^{-1}
Dry and wet deposition (terrestrial + oceanic)	0.160–0.450
Denitrification (terrestrial)	0.043–0.390
Denitrification (oceanic)	0.10–0.330
Biological nitrogen fixation (terrestrial)	0.044–0.200
Biological nitrogen fixation (terrestrial)	0.001–0.130
River runoff (terrestrial + oceanic)	0.013–0.040

Source: Adapted from Bolin and Cook (1983).

Phosphorus

Phosphorus occurs in aquatic systems in both particulate and dissolved forms and can be defined operationally as total phosphorus (TP), total reactive phosphorus (TRP), filterable reactive phosphorus (FRP), and total filterable phosphorus (TFP). See the Glossary for definitions.

The distribution and transformation of phosphorus in aquatic systems are shown in Fig. 8.2. Unlike nitrogen, the phosphorus cycle does not have a significant atmospheric component. A chemical distribution of phosphorus between aquatic and particulate components occurs via, e.g., adsorption and precipitation processes. The major reservoirs and fluxes of phosphorus are shown in Table 8.2. Other bulk sources include marine sediments and crustal rocks and soil.

Silicon

Globally, silicon (Si) is found primarily as a constituent of various silicate minerals, often combined with iron, magnesium, and calcium. Free silica occurs in rocks as quartz $(SiO_2)_x$ and is relatively insoluble. In solution, SiO_2 is present as silicic acid, which is moderately soluble and readily undergoes polymerization to form silica: $xH_4SiO_4 \rightarrow (SiO_2)_x + 2xH_2O$. The silicon cycle consists of relatively few forms, with the main sources coming from the weathering of Si-containing minerals in catchments and its subsequent transport to the oceans (Fig. 8.3).

Anthropogenic Sources of Nutrients in Aquatic Environments

Anthropogenic supply of nutrients to the aquatic environment can be via point or diffuse sources. Stormwater runoff is the primary component of diffuse-source pollution, with the water quality of the discharge being determined by the dominant land use of the catchment area. Nutrient contamination can originate from runoff of fertilizers from agricultural and residential lands and from livestock and human wastes. Point sources are distinct sources

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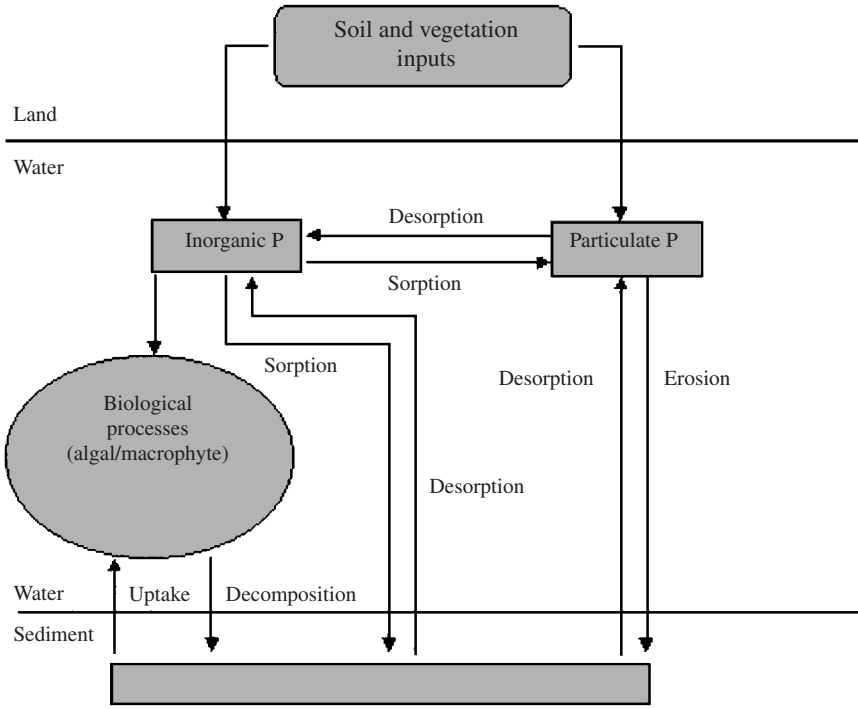

FIGURE 8.2 The aquatic phosphorus cycle.

TABLE 8.2 The Major Global Reservoirs and Fluxes of Phosphorus

Reservoir	Tg P
Marine sediments	840,000,000
Soil	96,000–160,000
Crustal rock	19,000
Biota	2,600
Flux	**Tg P yr^{-1}**
Marine dissolved → marine biota	600–1,000
Terrestrial biota → soils	200
Crustal rock → soils (weathering)	14
Marine detritus → marine sediment	2–13

Source: Adapted from Bolin and Cook (1983).

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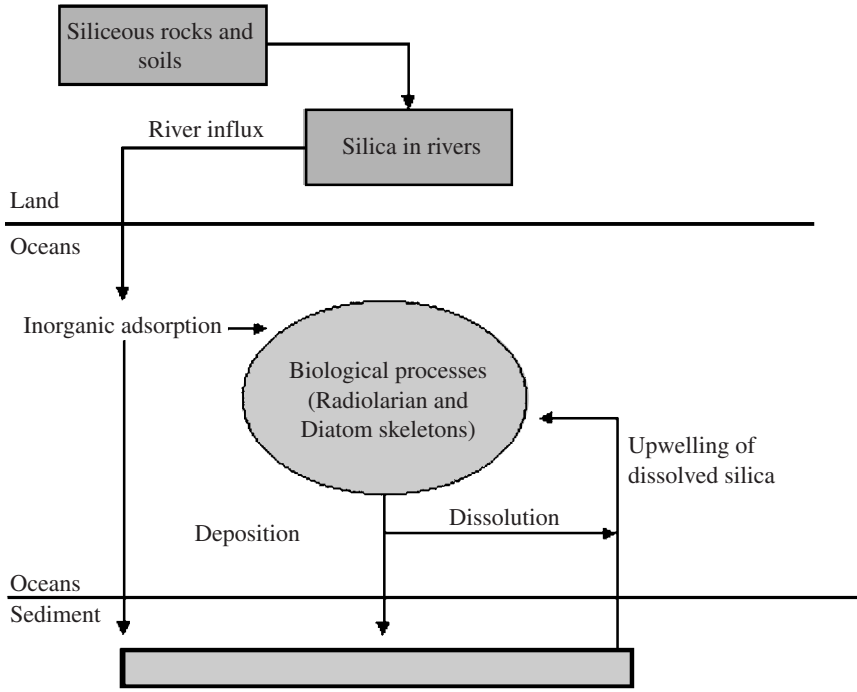

FIGURE 8.3 The global silicon cycle.

of contamination, i.e., those coming from a concentrated point and flowing directly into water bodies at a discrete point (e.g., industrial discharges, municipal sewage-treatment facilities, and agricultural animal production facilities).

Legislation Relating to Nutrients in Aquatic Environments

Concerns regarding the environmental impact of elevated nutrient concentrations are reflected in recent legislation enacted in many parts of the world. For example, the main European Union (EU) directives relating to the quality of surface and seawaters, with special consideration for nitrogen and phosphorus, are as follows (Council of the European Communities, 1975, 1980, 1991a, 1991b):

Directive 75/440: Abstraction of Drinking Water in Member States. Surface waters abstracted for drinking water purposes are grouped in three classes, A1, A2, and A3, based on the type and degree of treatment, with A3 being the most advanced. The mandatory value for nitrate is 11.3 mg/liter NO_3-N for all classes. For phosphates, compliance values are 0.17 mg/liter PO_4-P for A1 and 0.31 mg/liter PO_4-P for A2 and A3.

Directive 80/778: Quality of Water Intended for Human Consumption. This covers all water intended for human consumption, treated or untreated, regardless of origin. Both guide levels (G) and maximum admissible concentrations (MAC) are listed for most parameters. For nitrates, values of 5.35 mg/liter NO_3-N (G) and 11.3 mg/liter NO_3-N (MAC) are reported. Values for phosphate are 0.17 mg/liter PO_4-P (G) and 2.18 mg/liter PO_4-P (MAC).

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Directive 91/271: Urban Wastewater Treatment. This concerns the determination of the required treatment of urban wastewater prior to discharge into a given body of water, which is based on the receiving water characteristics and sensitivity to eutrophication. In the case of sensitive areas, the aim is to reduce nitrogen and phosphorus concentration levels below 10 mg/liter NO_3-N and 1 mg/liter PO_4-P, respectively.

Directive 91/676: Protection of Waters from Nitrates from Agricultural Sources. This prescribes surveys for the identification of sensitive surface waters with respect to nitrogen inputs, especially of an agricultural origin. It aims to promote sound agricultural practices in order to reduce pollution caused by nitrogen inputs.

As a general comment, limits for protection and maintenance of sensitive aquatic ecosystems are much lower than for water intended for human consumption or waters receiving urban wastewater.

SAMPLING AND STORAGE

Sampling Strategy

The fundamental requirement of any sampling procedure is that the sample taken is representative of the bulk material, i.e., a body of water. Most aquatic systems are dynamic in nature, changing randomly and/or systematically over time and space. Through the seasons, nutrient levels will fluctuate with changes in water temperature, biological activity, and the status of other water quality parameters, e.g., pH and sediment upwelling (Casey, 1992). Therefore, a well-organized sampling strategy should retain the original chemical composition of the sample and take account of temporal and spatial variations, site locations and access, seasonal trends, and most important, cost.

Site Selection

Selecting representative sampling sites is one of the most important factors in any nutrient monitoring program. The number and location of potential sites should be determined in the initial phase of the sampling campaign and will depend on the problem that needs to be addressed. If the purpose of the program is to monitor the impact of point sources, monitoring sites should be clustered where nutrients are likely to enter the water body. To help ensure scientific validity, sites upstream and downstream from the pollutant inflow, as well as the point of entry, should be monitored to provide comparative data and to monitor dispersal/dilution. Other considerations include avoiding boundary areas (e.g., confluence of streams or rivers), convenience, and overall accessibility (Lambert et al., 1992).

Frequency and Cost

Nutrient concentrations fluctuate with changes in physicochemical conditions and biological activity on a diurnal and seasonal basis. The rate and transport of nutrients in surface waters vary depending on sources, pathways, interactions with particulate matter, and the inherent biology of the water body. Other factors include in-stream velocity (flow rate), the proportion of surface runoff, and the blending of water from tributaries of different quality. Effective monitoring therefore involves sampling at adequately frequent intervals that the data set spans the inherent changes. However, continuous sampling is not always a viable

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option. Most sampling programs are a compromise in that information is obtained in the most cost-effective way.

Sample Collection and Storage

Sample collection should be simple and avoid the possibility of contamination or interference from foreign substances. Today, there are several types of automatic sampler that can be programed to take samples at specific time intervals or locations. Individual grab samples also can be taken at specific times and locations. Whatever method is chosen, it is important that it minimizes contamination of or alteration to the sample. All sample bottles should be clean and rinsed at least twice with the water of interest prior to analysis. Care must be taken to avoid the surface film, which can be enriched with nutrients. The sample should be collected halfway between the surface and the bottom and upstream of where you are standing (if collecting grab samples) to avoid disturbing underlying sediments.

For nutrients, preliminary treatment often involves filtration. This process differentiates between the dissolved phase, operationally defined as that fraction which passes through a 0.45-μm filter (Hurd and Spencer, 1991). Nuclepore material filters and cellulose acetate membrane filters are reported to be best for dissolved constituents in natural waters (Hall et al., 1996). High concentrations of suspended solids can cause analytical interference, e.g., scattering of light in spectrophotometry. Filtering also removes the majority of bacteria and plankton that may alter nutrient concentrations during storage but may not eliminate colloidal particulate matter that can remove or release nutrients (Horowitz et al., 1992).

Both physical (i.e., refrigeration, freezing, and deep-freezing) and chemical (i.e., addition of chloroform, mercuric chloride, and acidification) preservation techniques are used to maintain the original nutrient concentration of a sample. The effectiveness of preservation methods depends on various factors, including filtration technique, composition of sample, container type and size, temperature, type of chemical addition, irradiation of sample, and pasteurization (Kirkwood, 1992; Brezonik and Lee, 1996; Dore et al., 1996; Zhang and Ortner, 1998). It is also important to consider what actually happens during the storage process. Biological activity does not cease when samples are collected and stored because bacteria and microplankton continue to digest and excrete nutrient species. Walls of bottles and containers are excellent substrates for bacteria, often enhancing bacterial growth, and therefore rigorous cleaning of all laboratory ware is necessary. This is usually done by washing with nutrient-free detergent, soaking in 10% HCl overnight, and then final rinsing with ultrapure water such as Milli-Q.

Breakdown of organic compounds and changes in the speciation of inorganic constituents also may alter measured nutrient concentrations. For example, it has been shown that both organic phosphorus compounds and inorganic polyphosphates are hydrolyzed in acidic conditions such as those used in the molybdate colorimetric method shown below (Clesceri and Lee, 1965; Tarapchak, 1983). Other considerations include adsorption of nutrients to container walls, contamination from sampling/transfer procedures, and sample matrix characteristics.

Table 8.3 is a modified and abbreviated table from Maher and Woo (1998) that shows the methods of storage and maximum storage time for the dissolved fraction obtained using a 0.45-μm filter. Freezing (to $-20°C$) is the chosen method for storing samples over several weeks or even months. However, silicate is likely to polymerize during the freezing process, especially low-salinity and low-silicate samples (Alvarez and Sparks, 1985). Refrigeration is a possible but less likely choice for samples stored for limited time periods (<2 weeks). The addition of preservatives often is used to combat nutrient loss in stored samples. Sulfuric acid, chloroform, and mercury(II) ions are used most commonly to remove biological effects.

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TABLE 8.3 Storage Protocols for the Determination of Dissolved Nutrients in Filtered Waters

Authors	Nutrient species	Matrix	Method of storage	Maximum storage time	Comments
Ryder et al. (1972)	FRP	Distilled, tap, and lake water	Refrigerator (4°C)	1 day	Polypropylene and polycarbonate containers were suitable for storage. Glass containers sorbed phosphorus within 1–6 h.
Skjemstad and Reeve (1978)	FRP	Standards added to rain water	Room temperature with $HgCl_2$ (0–50 mg/liter)	3 days	$HgCl_2$ interfered with the molybdenum blue method when ascorbic acid was used as reducing agent.
Pichet and Jamati (1979)	FRP	River water	−10, 4, and 20°C with or without thymol (0.01%), KF (0.01%), TBT (0.001%), H_2SO_4 (0.05 *M*) or $CHCl_3$ (5 ml//liter)	14 days	Samples showed no decrease in FRP if chloroform was added and samples were stored at 4°C.
Morse et al. (1982)	FRP and TP	Open ocean water	Frozen (quick and slow), cooled (2°C) with or without $HgCl_2$ (120 mg/liter), phenol (4 mg/liter), and acid (pH 5)	60 days	No significant change in TP concentration when samples frozen with or without acid.
MacDonald and McLaughlin (1982)	FRP	Coastal and estuarine waters	−10°C, slow and quick freezing	365 days	Small change in FRP when samples were frozen. Quick freezing reduced losses.
Vesely (1990)	NH_4 and NO_3	Precipitation and lake waters	Refrigerator (4°C)	19 days	Significant changes in concentration were observed after 1 day.
Clemenston and Wayte (1992)	FRP and NO_3	Seawater	Frozen at −40°C initially, then stored at −20°C	147–210 days	FRP concentration decreased in samples stored longer than 4 months.

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Lambert et al. (1992)	TP, TDP, FRP, and TRP	Lake water	Refrigerator (4°C)	180 days	No change in TP in samples for up to 6 months.
Avanzino and Kennedy (1993)	FRP	Stream water	Frozen at −16°C	4–8 years	No significant change in FRP concentration.
Haygarth et al. (1995)	FRP	Soil leachates	Room temperature (5–19°C), refrigeration (4°C), frozen (−20°C) with or without $HgCl_2$ (40–400 mg/liter) and H_2SO_4	1–2 days	Changes occurred within 2 days for all samples, with smallest changes in samples stored at room temperature or 4°C.
Dore et al. (1996)	TON, FRP, and FRSi	Oligotrophic seawater	Frozen at −20°C	360 days	Concentrations were adequately maintained for several months if frozen immediately and stored at −20°C in HDPE bottles.
Aminot and Kerouel (1997)	TON, NH_4, and FRP	Seawater	Pasteurization and stored at room temperature	18 months	TON and FRP remained constant for 1 year. NH_4 losses after 3 days.

Source: Modified from Maher, W. and Woo, L. (1998). Procedures for the storage and digestion of natural waters for the determination of filterable reactive phosphorus, total filterable phosphorus and total phosphorus. *Anal. Chim. Acta*. **375:**5-47.

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ANALYTICAL TECHNIQUES

In order to better understand nutrient utilization and transport in aquatic systems, there is a need to develop sensitive and robust analytical measurement technologies. Monitoring techniques must be able to provide the necessary detection limit and linear range to meet all environmental situations. Typical ranges for nitrogen, phosphorus, and silicon in surface waters are given in Table 8.4. The need to measure low levels of analytes has, in many cases, contributed to problems of poor precision and reduced accuracy (Kirkwood et al., 1991). It is therefore necessary to adopt an analytical method that meets all the preceding requirements.

Nitrogen Determination

The cadmium reduction procedure is used widely in both batch and automated (continuous-flow) spectrophotometric methods for nitrate determination (Margeson et al., 1980; Koupparis et al. 1982; Skicko and Tawfik, 1988; Van Staden, 1982). Nitrate is reduced to nitrite, which is then determined by diazotization with sulfanilamide and coupling with NED to form an intensely pink-colored azo dye. Other methods of nitrogen determination include ion chromatography (IC), ion-selective electrodes (ISEs), and flow injection analysis (FIA). FIA is an automated technique that allows rapid and in situ spectrophotometric determination of nutrients (Clinch and Worsfold, 1987; Andrew et al., 1994; McKelvie et al., 1994). It is robust, portable,

TABLE 8.4 Typical Nutrient Concentrations in Surface Waters

Nutrient	Concentration (mg/liter)
Nitrogen (NO_3-N)	0.1–10
Nitrogen (NO_2-N)	0.001–1.0
Phosphorus (PO_4-P)	0.005–0.020
Silica (SiO_s-Si)	1–30

Source: From Chapman (1996).

TABLE 8.5 Overview of Techniques for Nitrogen Determination

Species	Matrix	Method*	Range (mg/liter)
Nitrate	River water	Automated FIA; diazotization using sulfanilamide and NED	0.03–12
Nitrite, TON	Seawater	FIA; diazotization using sulfanilamide and NED	0.08–0.8
Nitrate	Natural waters	Nitrate-selective electrode	1–1000
Nitrite	Drinking water	Ion-exclusion chromatography	10^{-4}–1
Nitrite	River water	Diazotization using 3-nitroaniline and NED	10^{-2}–0.8
Nitrate, nitrite	Seawater	CFA; diazotization using sulfanilamide and NED	3×10^{-5}–1×10^{-3}

*FIA, flow-injection analysis.

Source: Adapted from Robards et al. (1994).

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has low power and reagent consumption, and reduces the probability of sample contamination and loss of stability by analyzing directly in the field. Table 8.5 summarizes the most popular techniques for nitrogen determination in water.

Phosphorus Determination

Most methods of phosphorus determination are based on the reaction of phosphate with an acidified molybdate reagent to yield phosphomolybdate heteropolyacid, which is then reduced to an intensely colored blue compound and determined spectrophotometrically at 840 nm (McKelvie et al., 1995).

$$PO_4^{3-} + 12MoO_4^{2-} + 27H^+ \rightarrow H_3PO_4\,(MoO_3)_{12} + 12\,H_2O$$

$$H_3PO_4\,(MoO_3)_{12} \rightarrow \text{phosphomolybdenum blue Mo(V)}$$

Reduction is achieved by the addition of ascorbic acid or tin(II) chloride, with the main potential interferences being silicate and arsenate. The phosphorus determined is defined as molybdate-reactive or soluble reactive phosphorus (SRP). Other phosphorus-containing organic compounds and condensed phosphates can be determined using the molybdate reaction following chemical, photochemical, thermal, or microwave digestion (Goossen and Kloosterboen, 1978; Cembella et al., 1986; Johnes and Heathwaite, 1992). As for nitrogen, various phosphorus species can be determined by FIA. Table 8.6 summarizes the most popular techniques for the determination of SRP.

Silicon Determination

Dissolved silica in natural waters usually is determined as silicate by reaction with molybdate to form yellow molybdosilicate heteropoly acid ($H_4SiMo_{12}O_{40}$), which is then reduced to intensely colored silicomolybdenum blue and measured spectrophotometrically at 810 nm (Fanning and Pilson, 1973). Oxalic acid is added to minimize interference from phosphate. Other methods for silicate determination include gravimetry and atomic spectroscopy. It is important to avoid the use of glassware to minimize contamination.

TABLE 8.6 Overview of Techniques for Phosphate Determination as SRP

Matrix	Method	Detection	Range (μg/liter)
Seawater and natural water	FIA, (reagent injection, field system)	Spectrophotometry	3.1–31; 0–2000
Natural waters	FIA	Spectrophotometry	0–4000
Effluents	Batch	Spectrophotometry	0.30–600
Seawater	FIA	Spectrophotometry (reagent injection)	0.2–130
Natural waters	Ion chromatography	Spectrophotometry post-column reactor	100–2000
Natural waters	Batch, FIA	Gel-phase absorptiometry	Various

*FIA, flow-injection analysis.
Source: Adapted from Robards et al. (1994).

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VALIDATION OF NUTRIENT DATA

A large number of sample storage and preservation techniques, pretreatment procedures, and analytical methods are used to determine nutrients. It is therefore essential that protocols are in place to ensure that consistently high-quality data (accurate and precise) are obtained both within and between laboratories.

Controls

In-house quality control samples provide a day-to-day check of variability due to various factors, e.g., storage effects, different operators, blanks, instrumental effects, and environmental effects (Clementson and Wayte, 1992). Synthetic samples can be prepared to represent the sample of interest as closely as possible in terms of nutrient concentrations and matrix composition. These synthetic samples can then be analyzed by the in-house method and percentage recovery determined. Any contamination by foreign substances or loss due to removal processes (e.g., biological uptake) can then be assessed.

Interlaboratory Comparisons

Interlaboratory comparisons are an essential feature of method development and validation and also play a major part in certified reference material (CRM) programs, which depend on collaborative certification (Maier, 1991). These exercises are studies in which several laboratories analyze one or more homogeneous and stable materials under designated conditions, the results of which are compiled, compared, and put into a single report. The main objectives of interlaboratory exercises are

- To determine the precision and accuracy of results between laboratories for the same analytical method as well as those for different analytical methods
- To provide an impartial evaluation of in-house quality control procedures
- To identify best practice and support training needs
- To provide a valuable database of analytical information

Such comparisons are vital for improving the quality and performance of a given laboratory using specific analytical techniques. Many surveys aimed at nutrient monitoring make use of such data and participate in intercomparison exercises. In practice, such comparisons provide the structure of a strong analytical method.

Certified Reference Materials (CRMs)

A CRM is a reference material with one or more component values certified by a technically valid procedure, accompanied by or traceable to a certificate or other documentation that is issued by a certifying body (ISO Guide, 1981). CRMs are products of high added value and play a number of important roles in helping produce reliable results:

- Calibration and verification of measurement processes
- Quality control

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- Verification of standardized methods
- Development and validation of new methods

By using CRMs to calibrate and validate measurement systems, analytical chemists can be confident that their measurements will be comparable and traceable. Certification is based on the analysis of subsamples from a homogeneous and stable bulk sample containing the analytes (nutrients) in the required sample matrix. This is done using independent methods (at least three) and a large number of expert laboratories (normally more than 10) and is governed by accuracy, stability, and physical form requirements (Taylor, 1985). The major suppliers of CRMs for environmental matrices, especially including nutrients, are listed in Table 8.7.

CONCLUSIONS

Nutrients are essential to biochemical structure and function and are found in varying proportions in aquatic ecosystems. The availability of some nutrients, particularly nitrogen and phosphorus, is often limited, and the concentrations of these control the rate of primary production. However, an excess of nutrient loading can lead to eutrophication, which ultimately may lead to a deterioration of water quality. An increased public awareness based on environmental, economic, and sociopolitical concerns has led to the development of water quality monitoring programs.

Ideally, the chemical composition of the water being analyzed should be measured in situ. However, this is not always possible and requires the adoption of appropriate sampling, collection, and storage techniques. Currently, numerous sampling and storage procedures are available. However, waters vary considerably in composition, and what is suitable for preserving nutrient concentrations in one system may not apply to others. It is therefore recommended that laboratories carry out their own experiments and set appropriate procedures.

Monitoring programs are contingent on good laboratory practices and analytical protocol, and the precision and accuracy of measurements must reflect the level of confidence placed on the measurements. Numerous types of procedures are available to measure nutrients in aquatic systems. However, the measuring systems should be determined by the objectives of the monitoring program and meet specified objectives. Most laboratories institute strict quality assurance and quality control methods to ensure consistently reliable results. Methods employed include controls, intercomparison exercises, and certified reference materials.

TABLE 8.7 Suppliers of Environmental CRMs

Supplier	Country of origin	Web site
BCR, European Union	EU	*http://www.irmm.jrc.be/mrm.htm*
Laboratory of the Government Chemists (LGC)	UK	*http://www.lgc.co.uk*
National Institute of Standards and Technology (NIST)	USA	*http://www.nist.gov/*
National Research Council (NRC)	Canada	*http://www.nrc.ca/*
National Water Research Institute (NWRI)	Canada	*http://www.cciw.ca*

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GLOSSARY

CFA Continuous flow analysis. This term applies to any analytical procedure in which the analyte concentration is measured without stopping the flow of a liquid stream.

DIN Dissolved inorganic nitrogen. The inorganic forms of nitrogen (principally nitrate, nitrite, and ammonia) that pass through a 0.45-μm membrane filter.

DO Dissolved oxygen. A major indicator of water quality.

DON Dissolved organic nitrogen. The organic forms of nitrogen (principally urea, peptides, proteins, and nucleic acids) that pass through a 0.45-μm membrane filter.

FIA Flow injection analysis. A type of CFA in which the liquid flow is segmented by air bubbles. The samples are injected, and chemical equilibrium is not attained in the reaction manifold.

FRP Filterable reactive phosphorus. The amount of phosphorus present in the filtrate of a water sample passed through a 0.45-μm membrane filter.

FRSi Filterable reactive silicate. The amount of silicate present in the filtrate of a water sample passed through a 0.45-μm membrane filter.

G Guide level. Concentration of a substance that should be used as a target to aim for under European Union directives.

MAC Maximum admissible concentration. The maximum concentration of a substance permitted in drinking water under European Union directives.

NEDN *N*−(1-naphthyl)ethylendiammonium chloride.

SFA Segmented flow analysis. A type of CFA in which the liquid flow is segmented by bubbles. The samples are aspirated sequentially, and chemical equilibrium is attained within the reaction manifold.

TDN Total dissolved nitrogen. The total amount of nitrogen (inorganic plus organic) passing through a 0.45-μm membrane filter.

TFP Total filterable phosphorus. The amount of phosphorus present in the filtrate of a digested water sample passed through a 0.45-μm membrane filter after digestion.

TP Total phosphorus. The total concentration of all forms of phosphorus in an unfiltered sample.

TPN Total particulate nitrogen. The amount of nitrogen retained on a 0.45-μm membrane filter.

TRP Total reactive phosphorus. The amount of phosphorus present in an unfiltered, nondigested water sample.

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CHAPTER 9

BIOMARKER APPROACHES FOR ECOTOXICOLOGICAL BIOMONITORING AT DIFFERENT LEVELS OF BIOLOGICAL ORGANIZATION

Richard Handy, Awadhesh Jha, and Michael Depledge

INTRODUCTION

The purpose of biological monitoring (*biomonitoring*) is to detect environmental hazard (Lynch and Wiseman, 1998). This information on detected hazards may then be used in the decision-making process by environmental managers. Traditionally, environmental managers have employed biological monitoring to detect new threats to ecosystems and their components, as well as ensuring that procedures put in place to limit the impacts of known pollutants have been effective. The concept of using biological monitoring to detect otherwise unknown or intermittent pollutants that may be missed during routine water sampling is well established (e.g., Hellawell, 1977). Researchers in the early 1980s recognized the value of early warning systems to detect new hazards (Cairns and Schalie, 1980; Morgan and Küln, 1984) and the need to collect ecologically relevant data (Cairns, 1981), with data interpretation in terms of ecosystem function (Matthews et al., 1982; Boudou and Ribeyre, 1989). Despite this early recognition of the importance of ecosystem function, monitoring efforts largely have been devoted to measuring contaminant concentrations in water, sediment, or the tissues of biota (e.g., Schmitt and Brumbaugh, 1990). This was based on the rationale that organisms should be prevented from being exposed to concentrations of chemicals that had been shown to cause (or might cause) adverse effects. This approach has now been revised to integrate chemical data, bioavailability, and taxa diversity with body-burden data (e.g., metals; see Birge et al., 2000).

In the 1990s it became clear that environmental biomonitoring needed to be robust, simple, cheap, reproducible, and diagnose the health of an ecosystem at the individual, population, and/or community levels (e.g., Lynch and Wiseman, 1998). A number of methods are now being developed for biomonitoring at different levels of biological organization (e.g., Salanki et al., 1994; Depledge and Hopkin, 1995; Linthurst et al., 1995; Carlisle and Clements, 1999; Kedwards et al., 1999). These include ecological survey procedures for identifying changes in the abundance and diversity of species comprising communities and

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chemical and biomonitoring procedures for determining the concentrations and bioavailability of anthropogenic contaminants. These methods also include biochemical, physiological, and behavioral biomarkers that signal exposure to and in some cases adverse effects from pollution [see Depledge (1994) for a review of biomarkers]. The development of rapid assessment techniques also enables prompt environmental management of emerging hazards (see below).

It is with levels of biological organization in mind that we subdivide this chapter to review the merits of biomonitoring approaches starting at the molecular level and working toward integrated responses of the organism (e.g., animal behavior) that may reflect change at the population level. In the final sections of this chapter we recognize the need for a pragmatic framework of assays that works well in the field and enables environmental managers to logically integrate biological and chemical data in the decision-making process.

BIOMONITORING USING BIOMARKERS OF GENOTOXICITY

The biomonitoring of genotoxicity in aquatic organisms is important for several reasons. First, from the ecological perspective, the protection of genetic diversity in natural populations is important for population survival, and avoiding contaminant-induced mutations that skew genetic diversity is desirable (Wurgler and Kramers, 1992; Anderson et al., 1994; Depledge, 1998; Jha, 1998). Second, the detection of carcinogenic effects in aquatic organisms is needed to assess the health of aquatic organisms, as well as to prevent carcinogens from entering the food chain to humans (Mix, 1986; DeFlora et al., 1991). This section outlines the approaches for the direct measurement of genetic damage in aquatic organisms.

Recently, bacterial or in vitro tests (e.g., Ames test, SOS chromotest, Umu test) have been applied to environmental samples for monitoring purposes (Houk, 1992; White et al., 1996; Claxton et al., 1998). These in vitro approaches are not reviewed here (see Oda et al., 1985; White et al., 1996), and the focus remains the measurement of genotoxic activity in intact organisms in ecologically relevant situations where the toxic response is affected by the route of exposure, metabolism, and DNA repair efficiency (Jha et al., 2000). In general, methodologies developed for mammalian or human tissues are more established but may be adapted for use with aquatic organisms. These methodologies divide broadly into two classes: (1) biochemical and molecular approaches, which include analysis of DNA adducts and strand breaks, and (2) cytogenetic approaches, which include analyses of sister chromatid exchanges (SCEs), of micronuclei, and of chromosomal aberrations. Most of these methods require collection of cells in the field, e.g., hemocytes from invertebrate hemolymph samples, red blood cells or lymphocytes from fish (see below for a discussion of blood sampling), and cells isolated from tissues (e.g., gill biopsy) or derived from gametes (e.g., oyster larvae). Some examples of biomonitoring for genotoxicity are summarized in Table 9.1.

Analysis of DNA Adducts

This approach takes advantage of the fact that some chemicals react with DNA to form covalent bonds, and these DNA adducts may be differentiated from normal fragments of DNA by size (e.g., using high-performance liquid chromatography, or HPLC). Any chemical capable of forming a DNA adduct should be considered a potential mutagen, carcinogen, or teratogen (Randerath et al., 1985). The methodology involves isolation of DNA from the cells (e.g., by phenol extraction), lysing the DNA into nucleosides (by incubation

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TABLE 9.1 Examples of Genotoxicity Biomarkers Used for Biomonitoring

Genotoxic end point/approach	Species	Toxic substance	Type of response	Authors
DNA adducts	Various marine fish	Various contaminated sites	Elevation of DNA adducts and hepatic lesions	Reichert et al. (1998)
DNA adducts	Intertidal teleost (*Lipophrys pholis*)	*Sea Empress* oil spill	Increased incidence of DNA adducts	Lyons et al. (1997)
DNA adducts	Fish (*L. pholis, Pleuronectes platessa,* and *Limanda liminda*)	Recovery from *Sea Empress* oil spill	No detectable DNA adducts in invertebrates; DNA adducts still present in fish after 17 months; immediate impact less severe than expected	Harvey et al. (1999)
DNA strand breaks, alkaline elution technique	Invertebrates (*Halichondria pancea* and Mytilus edulis) Mussels (*Mytilus galloprovincialis*)	PAH-contaminated sites	Higher incidence of strand breaks in gill cells at contaminated sites	Bolognesi et al. (1996)
DNA strand breaks, alkaline elution technique	Redbreast Sunfish (*Lepomis auritus*)	Various contaminated sites	Increase incidents of strand breaks at contaminated sites	Everaarts et al. (1993)
DNA strand breaks, comet assay	Bullhead fish (*Amerirurus nebulosus*) and carp (*Cyprinus carpio*)	Biomonitoring of the Great Lakes, Canada	Higher levels in strand breaks from erythrocytes associated with contaminated sites	Pandrangi et al. (1995)
DNA strand breaks, comet assay	Tadpoles (*Rana clamitans* and *Bufo americanus*)	Pesticide-contaminated sites	Increased strand breaks at contaminated sites	Ralph et al. (1996)
Sister chromatid exchange	Mussel (*Mytilus edulis*) larvae	Sediments containing toxic metals and PAHs	SCE (and chromosomal aberrations) increase with exposure dose	Jha et al. (2000)

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with nucleases), and separation of the fragments by HPLC/chromatography, followed by autoradiograph after radiolabeling (see Randerath et al., 1985). Sensitive techniques have been developed and modified to detect a large number of chemicals of diverse structure, even with low DNA binding activities. Such methods have been shown to be capable of detecting extremely low binding of the order of a single adduct per diploid mammalian genome of about 1.2×10^{10} DNA nucleotides (Randerath et al., 1985).

It is important to validate methodology in the laboratory for species, age/life stage, sex, and cell-type differences prior to application in the field. Once validated, this technique has many applications in environmental monitoring. For example, field and laboratory studies have shown that DNA adducts are effective molecular dosimeters of genotoxic contaminant exposure in marine fish. DNA adduct formation is associated with the incidence of hepatic lesions, including neoplasms, in fish at contaminated sites (Reichert et al., 1998). There is now strong evidence of a cause-and-effect relationship between exposure to genotoxins in sediment and water and neoplasm epizootics in wild fish populations (see Baumann, 1998). DNA adducts were induced in intertidal fishes but, interestingly, not appreciably in invertebrates following the *Sea Empress* oil spill in February 1996 (Lyons et al., 1997; Harvey et al., 1999).

Analysis of DNA Strand Breaks

It is well established that physical and chemical genotoxins can influence the integrity of the genetic material, and the appearance of DNA strand breaks is a sensitive indicator of genetic damage. Induction of DNA strand breaks, if unrepaired or misrepaired, could lead to production of chromosomal aberrations, which as discussed below are considered to be an important biological end point in genotoxicity. DNA strand breaks also have been correlated with the mutagenic and carcinogenic potential of genotoxins (Sina et al., 1983). There are two main approaches to measuring DNA strand breaks: (1) the alkaline elution method, which involves lysis of cells on to a fine millipore filter and then treatment with high-alkaline conditions to unwind their DNA; alkaline washes are then carried out, and the proportion of DNA retained by the filter is measured microfluorometrically (Ahnstrom and Erixon, 1973; Kohn et al., 1976), and (2) the comet assay, which involves single-cell gel electrophoresis (SCGE) and has the advantage of identifying damage in individual cells or nuclei (Ostling and Johanson, 1984; Singh et al., 1988).

Several applications of the alkaline elution technique are reported (see Table 9.1). Vukmirovic et al. (1994) found high levels of DNA damage in the hemolymph of mussels collected from the northern Adriatic coast. Bolognesi et al. (1996) applied similar approaches to the gill cells of mussels. However, incidences of DNA strand breaks are not always correlated with contamination gradients (Everaarts et al., 1994). Alternatively, the comet assay also has been applied to the detection of DNA breaks in aquatic organisms (see Table 9.1). In an interesting study, significant increases in the frequency of cells with damaged DNA were found in mussels with exposure to contaminants in the San Diego Bay, California (Steinert et al., 1998). This study also demonstrated that sperm, egg, and somatic cells could be distinguished from one another in the comet assay on the basis of nuclear diameter and, in the case of eggs, by their unique crescent appearance. The damage also was consistently higher in sperm cells than in somatic cells.

The comet assay promises a rapid, sensitive, and economical technique to evaluate the induction of genetic damage in aquatic organisms for biomonitoring purposes, which as a prerequisite requires a single-cell suspension of the target cells. It is important to recognize, however, that DNA strand breaks are repairable damage and that this damage may occur via mechanisms not related to direct genotoxicity of chemicals. The activation of different endogenous enzymes and reactants could induce strand breaks. Despite these limitations,

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BIOMARKER APPROACHES FOR ECOTOXICOLOGICAL BIOMONITORING AT DIFFERENT LEVELS OF BIOLOGICAL ORGANIZATION

the comet assay offers considerable advantages over many other assays and, with suitable controls, may be considered a useful assay for environmental monitoring using different cell types and a variety of organisms.

Analysis of Sister Chromatid Exchanges

Crossover, which involves the exchange of homologous segments between nonsister chromatids at meiosis or sister chromatids at mitosis, normally occurs in diploid organisms. Sister chromatid exchanges (SCEs) are the cytological manifestation of these interchanges between DNA replication products at apparently homologous loci. The technique involves cytological examination of chromatids after incubation with a thymidine (base present in DNA) analogue, bromodeoxyridine (BrdU), for two DNA replication cycles. This technique has been applied successfully to a wide variety of aquatic organisms, including fish (Kligerman, 1979; Alink et al., 1980; Zakour et al., 1984; Maddock et al., 1986; Pacheco et al., 1993), bivalve molluscs (Harrison and Jones, 1982; Dixon and Clarke, 1982; Jha et al., 2000), and polychete worms (Pesch et al., 1981; Jha et al., 1996). These studies have demonstrated a dose-response relationship for a wide variety of chemicals and contaminants. Since this technique requires incubation with BrdU, application of this assay under field situations is difficult. Given this problem, Dixon and Pascoe (1994) suggested that it was possible to detect an increased level of SCEs in the chromosomes of two-cell-stage mussel embryos originating from field-exposed animals. It is difficult to conceive of the idea of analysis of SCEs at the two-cell stage, however, given the fact that at least two cell divisions (leading to production of four cells) are required in the presence of BrdU to elucidate sister chromatid differential staining. In addition, the failure to obtain complete metaphases during slide preparation at this early stage of the development poses a problem for the applicability of this technique. Data on SCEs should be interpreted with caution because apparently nongenotoxic compounds induce SCEs (Galloway et al., 1987). In addition, the exact mechanism of production of SCEs is still not clear, and SCEs show limited persistence and accumulation under in vivo conditions (reflecting DNA repair/cell turnover). Despite these limitations, SCE assays are used widely in mammalian toxicology and can be used for aquatic organisms in laboratory conditions for hazard assessment.

Analysis of Micronuclei

Micronuclei (MN) normally are formed by broken parts of the chromosomes lacking a centromere or the whole chromosomes from daughter nuclei at mitosis and exist separately from the main nuclei of the cell. MN are induced by physical and chemical agents and can be scored during the interphase stage of the eukaryotic cell cycle. Compared with other cytogenetic methods, MN assay is considered to be relatively simple and fast and could be applied to a wide range of different species without any requirement for a detailed knowledge of the chromosome complements (karyotype).

This assay has been applied widely to aquatic organisms. Al-Sabti and Metcalfe (1995) have reviewed the studies pertaining to MN assay in the erythrocytes and other cells (e.g., gills, kidneys, and liver) of teleosts under both laboratory and field conditions. A number of studies have been carried out using MN assay in bivalves in both marine and freshwater environments (Mersch and Beauvis, 1997; Brunetti et al., 1988; Wrisberg and Van der Gaag, 1992; Burgeot et al., 1995; Weis et al., 1995). These studies mainly have used the gill and blood cells of the bivalves. MN assay also has been applied to echinoderm larvae under laboratory conditions (Hose and Puffer, 1983). In most of the studies using aquatic organisms, the MN assay has been reported to be sensitive and reproducible. In the case of

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fishes, however, a very low level of MN induction and lack of adequate information about the rate of hematopoiesis (of blood cells) and replacement make the system a little insensitive. The hemocytes of bivalves in comparison appear to be more sensitive and reproducible.

Analysis of Chromosomal Aberrations

Analysis of chromosomal aberrations is considered to be the most important genetic end point because they are associated with the initiation and progression of malignancies, congenital abnormalities, and reproductive wastage (Natarajan et al., 1992; Tucker and Preston, 1996). However, use of this assay for aquatic biomonitoring in the field has severe limitations because actively dividing cells are required to obtain sufficient metaphase spreads for the analysis. The chromosomes of aquatic organisms are often small and occur in large numbers, making the analysis tedious. In addition, unlike mammalian systems (e.g. bone marrow cells, peripheral blood lymphocytes), attempts to harvest the growing cells at metaphase stage from aquatic organisms in the field have not given satisfactory results. Under laboratory conditions, however, this assay has been applied successfully to evaluate the genotoxic potential of environmental contaminants using different life stages of the organisms. For example, several studies have been performed to show the suitability of gill cells of different fish species exposed under in vivo conditions to reference and environmental contaminants (Kligerman et al., 1975; Hooftman, 1981; Krishnaaja and Rege, 1982; Al-Sabti, 1985). Among the invertebrates, the gill cells of bivalve mussels also have been explored to analyze chromosomal aberrations with some limited success (Dixon and Flavell, 1986). In contrast to adult invertebrates, the early life stages (which contain large numbers of differentiating dividing cells) have been used quite successfully for the chromosomal aberration assay, in particular for polychete worms (Pesch et al., 1981; Jha et al., 1996, 1997) and for bivalve molluscs (Jha et al., 2000).

In addition to metaphase chromosomal aberrations (which as a prerequisite require exposure to colchicine), several authors also have attempted to analyze the aberrations at the anaphase-telophase stage. Since this assay is independent of the chromosome complement of species, it has an advantage over classic metaphase analyses. In addition to chromosomal damage, this assay also analyzes the lagging chromosomes (aneugenic effects). This assay has been employed for biomonitoring purposes using several species, including fish (Hose and Brown, 1998) and mussels (Dixon, 1982), and also has been shown to have some promises with sea urchins (Anderson et al., 1994) and polychete worms (Dixon et al., 1999).

BIOMONITORING USING BIOCHEMICAL BIOMARKERS

Biochemical changes associated with pollutant exposure might include: (1) the inhibition or induction of enzymes, (2) modulation of cellular defenses involved in chemical chelation/storage of contaminants, (3) induction of specific enzymes involved in the metabolism of pollutants and the appearance of associated metabolites, and (4) structural changes in proteins or lipids and the appearance of protein adducts. Examples of biochemical approaches are shown in Table 9.2. Probably the most widely used of these biomarkers are induction of the cytochrome P450 system, hepatic metallothionein, and more recently, stress proteins. These topics have been reviewed individually recently (see references in Table 9.2), and here we focus on general aspects of methodology and the rationale for

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TABLE 9.2 Examples of Biochemical Biomarkers That May Be Used for Ecotoxicological Monitoring

Organism/biological material	Biomarker	Pollutants identified	Reference
Fish blood, hemolymph of decapod crustaceans	Elevated plasma glucose	General response to stress	McDonald and Milligan (1997); Fingerman et al. (1998).
Fish blood	Elevated plasma cortisol	General response to stress	Whitehead and Brown (1989); Pottinger et al. (1992); Brown (1993).
Fish and invertebrates, homogenates of various tissues	Induction of stress proteins (heat shock proteins)	General, induced by many environmental stresses	Lewis et al. (1999)
Liver homogenates from fish, whole-body homogenates from invertebrates	Elevation of malondialdehyde (TBARS)*	Lipid peroxidation by prooxidants (organics and oxidizing metals)	Baker et al. (1998); Narbonne et al. (1999); Cossu et al. (2000).
Liver homogenates from fish, whole-body homogenates from invertebrates	Increased activity of superoxide dismutase (SOD), catalase, or glutathione transferase	Presence of oxygen radicals, probably generated from organics and oxidizing metals	Choi et al. (2000). Stephensen et al. (2000)
Liver homogenates or whole blood from fish, whole-body homogenates from invertebrates	Glutathione depletion	Presence of prooxidants (organics or oxidizing metals)	Cossu et al. (2000).
Gill, gut, or liver homogenates from fish/crustacea and whole-body homogenates from smaller invertebrates	Induction of metallothionein	Toxic metals	Hogstand and Haux (1991); Olsson (1996); Viarengo et al. (1997; 1999).
Fish livers, invertebrate tissue homogenates	Induction of the cytochrome P450 (CYP) system	Organic pollutants	Jorgensen and Wolkers (1999); Flammarion et al. (1999); Machala et al. (2000)
Whole blood from fish	δ-Aminolevulinic acid dehydratase (ALAD)	Lead exposure	Hodson et al. (1978).
Excreta from invertebrates	Change in porphyrin composition	Polyaromatic hydrocarbons	Fossi et al. (2000).
Homogenates of brain tissue from fish or invertebrates, red blood cells	Inhibition of esterase activity	Carbamates and organophosphate insecticides	Thompson (1999); Fossi et al. (2000).

*TBARS, thiobarbituric acid reactive substances.

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selection of biochemical assays from the many biochemical biomarkers available. Integration of these assays with other approaches is discussed later in this chapter. Given this potential complexity and the logistics of field work, the following issues should be considered before selecting biochemical assays for monitoring.

Type of Sampling

The collection of tissue may involve sacrificing the animal (destructive sampling) or may occur via biopsy from live animals (nondestructive sampling). The former may apply where there are large numbers of specimens available (e.g., fish or invertebrate populations) but is clearly inappropriate with small populations/protected species (Fossi and Marsili, 1997). Nondestructive sampling usually is restricted to tissues that are easily accessible (blood, skin, hair, feces, urine), whereas biopsies of internal organs require specialist veterinary skills and appropriate sterile conditions (difficult to achieve in the field).

Sample Collection, Storage, and Viability in the Field

Appropriate collection of tissue samples is paramount, and for blood, at least some generalizations can be made. Blood chemistry is influenced by animal handling procedures (Waring et al., 1992), the use of anesthesia and anticoagulants (Korcock et al., 1988; Iwama et al., 1989), and the type and duration of sample storage prior to chemical analysis (Jayaram and Beamish, 1992). Houston (1990) discusses the general consideration for blood sampling in detail. In the field, stunning of fish followed by immediate collection of caudal or cardiac blood into previously heparinized tubes that are placed immediately in an ice box offers a good chance of collecting a representative blood sample. Some assays on blood or tissues may have particular storage requirements for the specimens (e.g., use of $-80°C$ freezing, a narrow osmotic pressure or pH range, specialist storage buffers), and these should be established and tested prior to validation of the monitoring program. Multiple freezing and thawing of samples are generally best avoided. If samples are usually reported relative to tissue protein (e.g., enzyme activities) or lipid content (e.g., residues of persistent organic pollutants), then sample volumes and storage should reflect this need for protein/lipid assays.

Target Tissues

The tissue collected should be a known target tissue for the pollutant, where the biochemical change must be related causally to the contaminant exposure or effect (e.g., Levine and Oris, 1999).

Monitoring for Exposure or Effect?

Potentially any target organ may be selected to confirm exposure, but biological effects will be manifest via target organs involved in the toxic mode of action or adaptation to exposure. For example, monitoring organophosphate pesticide exposure via inhibition of blood acetylcholine esterase may indicate exposure but often does not correlate with acetylcholine esterase inhibition in the brain (origin of the neurological effect) because of temporal differences in toxic effects in the two compartments (e.g., Dikshith et al., 1975; Thompson, 1999). Tissues involved in long-term storage/chelation (e.g., body fat for persistent organics), by definition, are also not good markers of biological effect at the organism/population level.

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BIOMARKER APPROACHES FOR ECOTOXICOLOGICAL BIOMONITORING AT DIFFERENT LEVELS OF BIOLOGICAL ORGANIZATION

Monitoring for General Pollution or Specific Contaminants?

A tiered approach using general biomarkers of stress, then those for major groups of contaminants (e.g., metals or organics), and finally, those for specific groups of substances or individual contaminants may be employed during hazard identification (see Table 9.2). For example, elevation of the plasma glucose level may indicate general stress (McDonald and Milligan, 1997), whereas induction of hepatic metallothionein (MT; e.g., Hogstrand and Haux, 1991) or the cytochrome P450 system (e.g., Spies et al., 1996; Flammarion et al., 1999) might indicate exposure to metals or organics, respectively, the final tier being more specific e.g., blood δ-aminolevulinic acid dehydratase (ALAD) for lead exposure (Haux et al., 1986) or acetylcholine esterase for exposure to organophosphate pesticides (Thompson, 1999).

Confounding Factors

Interpretation of biochemical data may depend on animal age, sex, nutritional status, season, genotype of the population studied, previous exposure history, and latent effects of pollutant exposure (e.g., Hylland et al., 1998; Jorgensen and Wolkers, 1999; Van Cleef et al., 2000). Some of these factors, in theory, can be fixed when designing sampling protocols, but necessary deviations from standard protocols can arise in the field (e.g., due to a temporal lack of specimens at very polluted sites). Some examples of confounding factors for particular biomarkers follow. For example, antioxidant defences (SOD, catalase, glutathione levels) may show age-dependent trends due to the natural accumulation of oxidative stress that partly defines the ageing process (Accomando et al., 1999; Demaree et al., 1999). For metallothionein (MT), aged-dependent changes in induction occur during early development and sexual maturation but are further confounded by seasonal effects induced by water temperature and/or day length (Olsson, 1996). For some biomarkers, sex differences are evident. For example, female fish tend to have lower CYP1A activity than males (Flammarion et al., 1999), but this sex difference and basal enzyme activity itself vary with season (Leaver, 1996).

Data Reporting

Since many biochemical assays are referenced against tissue protein or lipid levels, apparent population differences in biochemistry may be attributed to differences in body proximate composition. Data from animals with very different proximate compositions should be interpreted with caution (e.g., for stress proteins) (Lewis et al., 1999). Many biomonitoring studies also report absolute levels of biochemical biomarkers (e.g., Holdway et al., 1995; Adams et al., 1996; Spies et al., 1996). This approach may not take into account latent biochemical change and/or acclimation of the response (Handy, 1994). However, if the capacity for biomarker induction is tested by transplanting animals from the field to the laboratory for a controlled exposure, site differences can be more pronounced (e.g., cytochrome P4501A induction in fish) (Flammarion et al., 1999).

Personnel, Specialist Expertise, and Overall Cost

Economic cost and staff training are important issues, regardless of the type of monitoring program. For the biochemical approaches, assays that can be performed using diagnostic kits and rapid colorimetry of small sample volumes (e.g., using microtiter plate readers) offer a time advantage. Simple extraction steps prior to assay procedures may increase sensitivity or the range of biological materials that may be assayed.

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BIOMONITORING USING HISTOLOGICAL BIOMARKERS

This approach has been applied largely to fish (Table 9.3), although the general principles probably also apply to aquatic invertebrates. Some data are available on histopathology in marine mammals in ecosystems of known concern (e.g., St. Lawrence River beluga population) (Deguise et al., 1994). Published histological data relating lesions to pollutant exposure in aquatic birds and mammals generally are sparse compared with the literature for fish. Measurement of histological change offers several advantages over other approaches for detecting environmental stress (for review, see Hinton and Laurén, 1990):

1. Target organs, target cells, and sometimes organelles can be identified in vivo.
2. Sample collection and storage are relatively simple in the field.
3. Both short- and long-term toxic effects may be identified.
4. Histochemical methods may indicate routes of exposure (e.g., Husøy et al., 1996).

Similar to biochemical or physiological monitoring approaches, seasonal change (Haaparanta et al., 1997), sex differences (Cooke and Hinton, 1999), nutritional status (Frischknecht et al., 1994), general limnology, and the incidence of infection (Schwaiger et al., 1997) may be compounding factors in data interpretation. Many of these factors can be differentiated firmly from direct effects of pollutants using the histological approach. For example, glycogen deposition patterns in the liver may indicate nutritional status, whereas pathologies associated with infection often are distinct from those associated with contaminants (e.g., renal injury associated with proliferative kidney disease) (Schwaiger et al., 1997). The main disadvantage of the histological approach is the observational skill needed to score microscope slides. However, image-analysis techniques offer an automated approach to scoring slides (Schwaiger et al., 1997; Couillard et al., 1999) that may be performed by less specialist staff.

A number of histological approaches and their uses in the field are described for fish (see Table 9.3). The traditional approach to histology consisted of a nonquantitative description of lesions. This approach is now redundant, and most researchers devise a semiquantitative system for scoring the frequency, type, or severity of lesions (see Table 9.3). Quantitative approaches include direct stereoscopic measurements (e.g., gill dimensions) (Speare et al., 1997) or the application of image analysis to measure relative tissue area, size, or staining intensity within organs (Schwaiger et al., 1997; Couillard et al., 1999). The methodology should include at least triplicate measurements from each organ (from three serial sections), and each measurement for the triplicate may comprise several fields of view from each slide (e.g., Handy et al., 1999). However, the unit of replication in the experimental design remains the individual animal, and usually 10 or more animals are needed at each site/sampling interval. It is also vital to have reference material. Complete and detailed histological atlases of most aquatic species are not available, perhaps with the exception of salmonids (Yasutake and Wales, 1983), although reference texts illustrating selected species and pollutant-induced pathologies are available (e.g., Ribelin and Migaki, 1975). It is therefore prudent to generate a reference collection of slides from healthy animals held in the laboratory along with appropriate morphometrics (e.g., Hinton et al., 1985) and perhaps "positive controls" from animals exposed to known contaminants/effluents in the laboratory. However, laboratory-reared fish are not the same as wild fish. The latter may carry lesions from infection/local variation in water quality not associated with pollution (e.g., glycogen depletion in the liver, hepatic fatty change, or presence of ectoparasites) (Schmidt et al., 1997; Schwaiger et al., 1997; Teh et al., 1997). It is therefore vital to consider the background incidence of lesions in animals from relatively uncontaminated reference sites in the field.

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TABLE 9.3 Examples of Histological Biomarkers That May Be Used for Ecotoxicological Monitoring

Histological approach/ target organ	Species	Toxic substance	Type of response	Authors
Relative abundance score of ectoparasites on gill, skin, and gut epithelium	Brown trout (*Salmo trutta*) and rainbow trout (*Oncorhynchus mykiss*)	Diluted sewage effluents	*Gyrodactylus* load on the skin increased from <20 to 50–60 percent	Schmidt et al. (1999)
Wax sections (H&E, PAS) of many internal organs; pathology scored according to reaction pattern and extent.	Brown trout (*salmo trutta*) and rainbow trout (*Oncorhynchus mykiss*)	Diluted sewage effluents	Total indices summed from all organs show a temporal elevation in brown trout; gill and liver pathology indices increased compared with controls	Schmidt et al. (1999)
Resin sections (H&E) of liver; defined tumor scoring system for type and prevalence	Medaka (*Oryzias latipes*)	24-h aqueous carcinogen exposure (diethylnitrosamine), followed by chronic dietary exposure to xenoestrogens	Following carcinogen exposure, 10 ppm 17β-estadiol or 100 ppm β-hexachlorocyclohexane caused about a 20% or 10% increase in tumor incidence, respectively. Sex differences in pathology observed	Cooke and Hinton (1999)
Wax sections (H&E) and immunohistochemical staining for P-glycoprotein transporter; hepatoblastomas (early liver cell tumor) described, nonquantitative approach	Mummichog (*Fundulus heteroclitus*)	Fish sampled from a river contaminated with creosote	From the few fish examined, tumors were present, but P-glycoprotein labeling was not always coincident with the tumors; details of field sampling not reported	Vogelbein et al. (1999)
Percent prevalence of skin lesions	Pacific rockfish (*Sebastes* spp.)	Open-ocean site in proximity to historic toxic/radioactive waste dump site	Prevalence of lesions increasing in some species since 1985 but decreasing in others	Okihiro et al. (1992).
Progression of cytological change in liver tumors	*Cyprinodon variegatus* and *Oryzias latipes*	*N*-nitrosodiethylamine (DENA)	Histochemical change preceded tinctorial and morphologic alterations leading to foci/tumors	Hinton et al. (1988)

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TABLE 9.3 Examples of Histological Biomarkers That May Be Used for Ecotoxicological Monitoring (*Continued*)

Histological approach/ target organ	Species	Toxic substance	Type of response	Authors
CYP1A immunohistochemistry in various organs; semiquantitative evaluation of intensity/ frequency of staining	Atlantic cod (*Gadus morhua*) and European flounder (*Platichthys flesus*)	Caged fish in a PAH-, PCB-, and metal-contaminated fjord, Norway	Strong CYP1A induction after caging in the liver and nonhepatic tissue (e.g., intestine) suggesting exposure via sediment/food	Husøy et al. (1996)
Wax sections (H&E) of many organs; absolute number of fish with lesions	Rainbow trout (*Oncorhynchus mykiss*)	Bleached Kraft mill effluent	Incidence/type of lesions not clearly correlated with exposure	Hall et al. (1992)
Wax and resin sections of gills, with intensity of change on an arbitrary scale; percent of total fish with lesions counted	Perch (*Perca fluviatilis*) and roach (*Rutilus rutilus*)	Interconnected lakes downstream of pulp mill effluent discharge	Incidence of lesions and cell proliferation were generally higher at the "control" site; seasonal variation exceeds intersite variation	Haaparanta et al. (1997)
Liver lesion frequency and type correlated with sediment chemistry using multivariate analysis	Winter flounder (*Pleuronectes americanus*)	Ten coastal sites in United States, clean and polluted (various contaminants)	Many PAHs associated with neoplastic change/inflammation; some pesticides correlate with neoplasia but not necrosis; various metals associated with inflammation, necrosis, or neoplasia	Chang et al. (1998)

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Wax sections (H&E and others) in spleen, liver, and pancreas; percent incidence of lesions, semiquantitative grading of vacuolation, and image analysis of spleen area used; health indices measured	Atlantic tomcod (*Microgadus tomcod*)	Estuary with pulp/ paper mill effluent	Multifocal granulomatous lesions in the spleen and vacuolation in the pancreas associated with contaminanted sites; other pathologies observed not related to pollution (probably infection)	Couillard et al. (1999)
Wax sections (H&E) and electron microscopy, gills and liver; water quality/tissue contaminant levels reported	Threespot tilapia (*Oreochromis andersonii*)	Caged fish on the Kafue River, Zambia (copper mine and agricultural runoffs)	Branchial mucus production, edema, and epithelial sloughing after 2 weeks; a dense precipitate appears in liver cells	Norrgren et al. (2000)
Wax sections (H&E) of internal organs; morphometric data obtained by image analysis	Brown trout (*Salmo trutta*) and loach (*Barbatula barbatula*)	Diverted water from polluted streams (various contaminants)	Various lesions observed, with trout more sensitive to pollution than loach; organ lesions also associated with general limnology and infection	Schwaiger et al. (1997)

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Histological methods clearly enable clean and contaminated sites to be differentiated (see Table 9.3), and if data on ecosystem characteristics are integrated with a suite of histological investigations, it is possible to identify the main categories of pollutants present (Teh et al., 1997). Histochemical methods may be especially useful because local enzymatic alterations in tissues usually occur before structural change during the progression of injury (Hinton et al., 1988). Conversely, cytological damage can be absent while biochemical disturbance remains during recovery from exposure (Blom et al., 1998). Histology also aids interpretation of biochemical data (Schwaiger et al., 1997), and it is recommended that histology is integrated with health indices and biochemical data to give an overview of the toxic effect or biological response. This is particularly important for the latter because both histological and biochemical change may be an adaptive biological response to exposure (e.g., Handy et al., 1999) rather than an adverse toxic effect.

BIOMONITORING USING PHYSIOLOGICAL BIOMARKERS

Physiological responses offer a major advantage for biomonitoring because the effects of pollutants usually are rapid. Thus physiological responses offer a real-time measurement of exposure or toxic effect. In addition, continuous monitoring is possible, sometimes at levels below chemical detection limits, for pollutants (Handy, 1994). However, the body system used for ecotoxicological monitoring must be carefully selected. Pollutants can cause a variety of respiratory, cardiovascular, osmoregulatory, neurological, and/or endocrine disturbances (Wendelaar Bonga and Lock, 1992; Wood, 1992; Randall et al., 1996; Bamber and Depledge, 1997; Arcand-Hoy and Benson, 1998; Handy and Depledge, 1999). The cardiovascular system might be used for generic biomonitoring where potential pollutants of concern are not identified because this body system responds to a variety of organic and inorganic pollutants (Table 9.4). Alternatively, if, for example, pesticides (or other neurotoxins) are a major concern, then a neurologically based biomonitor may be more appropriate.

Major pollution incidents may cause acute and often fatal physiological disturbances that manifest as respiratory distress, vomiting, diarrhea, loss of locomotor ability, and/or unusual behaviors in fish. However, in such circumstances, the cause of pollution is often identified quickly by water quality measurements. Such extreme physiological responses have little value as a biomonitor because death is an insensitive end point from an ecosystem perspective and the maximum dose-response gives little information about environmental contamination, except that the lethal dose has been exceeded. Instead, physiological assays attempt to measure responses within the normal physiological scope of the organism and correlate these with pollutant exposure or effect. A number of respiratory, cardiovascular, osmoregulatory, or neurological assays have been developed (see Handy and Depledge, 1999). Table 9.4 illustrates some of the species and toxic substances that have been evaluated in terms of physiological responses that may be used in biomonitoring or as a biomarker of exposure. Physiological assays are especially useful for monitoring fluctuating exposures or acting as early warning systems for acute events because the toxic response is usually instantaneous and/or sensitive to low exposure concentrations (Handy, 1994).

Most physiological assays are based on recording the resting response of the organism and then quantifying changes in the physiological parameter with exposure. The normal resting response must be established in defined environmental conditions (i.e., temperature, pH, photoperiod, salinity, hardness, fed/unfed animals) prior to validation of the assay. Interanimal variability in physiological measurements is considerable (e.g., Förlin et al., 1986), and thus it is usual to report a normal resting range rather than a single mean value. In practical terms, the response to the pollutant must be at least twice the normal range to

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TABLE 9.4 Some Examples of Aquatic Animals where Physiological Biomarkers Have Been Used to Assess or Monitor Toxic Responses

Physiologic biomarker	Species	Toxic substance	Type of response	Authors
Heart rate monitor	Freshwater crayfish (*Pacifastacus leniusculus*)	Landfill leachate lagoon and ammonia	Stimulation of heart rate, correlated with exposure; note, using a fully automated field-based monitoring unit	Bloxham et al. (1999)
Heart rate monitor	Rock crabs (*Hemigrapsus edwardsi*)	Polluted harbor (many substances)	15–20% decrease in median heart rate along pollution gradient and increased variability in response at the most contaminated sites	Depledge and Lundebye (1996)
Body Na and Ca loss	Brook charr (*Salvelinus fontinalis*)	Coal mine–polluted streams	Loss of whole-body Na and Ca, correlated with changes in stream acidity and [Ni]	Grippo and Dunson (1996)
Ion flux measurements	Freshwater fish	Acid and toxic metals	Various changes in net salt balance during exposure reviewed	Wood (1992)
Hematology	Whitefish (*Coregonus* spp.)	Lead-contaminated field sites	Decreases in plasma Na by 17 mmol/liter; hemoglobin shows both increases and decreases relative to control site; about 80% decrease in δ-aminolevulinic acid dehydratase in the blood of animals at contaminated sites	Haux et al. (1986)
Hematology	Rainbow trout (*Oncorhynchus mykiss*)	Pulp mill effluent	43% increase in hemoglobin content of the blood due to a decrease in plasma volume after 10 days' exposure	Oikari et al. (1985)
Respiratory and cardiovascular	Rainbow trout (*Oncorhynchus mykiss*)	Monochloramine	Gradual decrease in ventilation rate from about 90 to 75 breaths/min and a 10-fold increase in cough frequency during repeated exposure to a peak concentration of 0.4 mg/liter monochloramine	Travis and Heath (1981)

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TABLE 9.4 Some Examples of Aquatic Animals where Physiological Biomarkers Have Been Used to Assess or Monitor Toxic Responses (*Continued*)

Physiological biomarker	Species	Toxic substance	Type of response	Authors
Swimming speed	Rainbow trout (*Oncorhynchus mykiss*)	Various agrochemicals	Reductions in swimming speed observed, often at concentrations lower than the 96-h LC_{50}	Little and Finger (1990)
Respiratory and cardiovascular response syndromes	Rainbow trout (*Oncorhynchus mykiss*)	Various insecticides	For example, chloropyrifos exposure caused up to a 78% increase in ventilation volume and 18% decrease in heart rate; changes in hematology, blood gases, heart rate, and ventilation used to statistically define response syndromes to insecticides	Bradbury et al. (1991)
Respiratory and locomotor activity	Rainbow trout (*Oncorhynchus mykiss*)	Cu (oral exposure)	Three months' exposure to 500 mg Cu per kg of food caused a 35% reduction in time spent swimming but a 12% rise in mean swimming speed when swimming occurred; no changes in oxygen consumption or ventilation observed	Handy et al. (1999)
Electrocardiogram	Carp (*Cyprinus carpio*)	Sewage and wastewater	Initially a shortening of atrioventricular conduction time and systole duration, gradually extending during exposure; an initial rise in heart rate and ventilation rate decreases below normal as exposure progresses	Kakuta and Murachi (1997)
Respiration and locomotor activity	*Gammarus pulex*	Cu- and Pb-polluted stream water	Monitoring system based on impedance conversion technology; initially metal exposure increased ventilation and locomotor activity, with the latter declining after several days of exposure	Gerhardt (1995)
Respiration and locomotor activity	Rainbow trout *mykiss*) (*Oncorhynchus mykiss*)	Mine effluent	Decreased locomotor activity and increased ventilation volume and frequency within the first 2 h of exposure at effluent concentrations greater than or equal to the 96-h LC_{50} for a 10% dilution of effluent	Gerhardt (1998)

Source: Modified from Handy and Depledge (1999).

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be detected, or many test animals should be monitored simultaneously to statistically define the limits of the normal resting response. The latter is now a good proposition with modern multichannel recording apparatus (Aagaard et al., 1991). Physiological responses that are not related to toxicant exposure (e.g., changes in respiration rate due to exercise) and gradual alteration of the normal range attributed to acclimation during chronic exposures (e.g., Wilson, 1996) may be quantified, if not eliminated, by incorporating design features that correct for these effects, preferably by experimental calibration in the laboratory before application in the field (e.g., Okland et al., 1997).

Full methodological details of how to make physiological measurements are described by Handy and Depledge (1999). These are discussed in the following subsections.

Online Cardiovascular Monitoring

This uses a noninvasive optical transducer for recording heart rate in crustaceans and bivalves. Originally developed by Depledge and Andersen (1990) and then Aagaard et al., (1991), this assay has been applied successfully in the field (e.g., Depledge and Lundebye, 1996).

Respiratory Responses

Respiratory responses have been used to monitor pollutant stress in invertebrates and fishes. These are rapid and therefore useful for identifying short pollution events. Oxygen consumption rate is mainly used because it shows a clear dose-response in many organisms and for many chemicals and is also a surrogate for metabolic rate (McKim and Erickson, 1991; Randall et al., 1996).

Ion Flux Measurements

Pollutants are well known for their effects on salt and water balance in aquatic animals. For many aquatic species, the gills are an important osmoregulatory organ and the route of entry for waterborne contaminants. Consequently, altered ion flux across the gills arises during pollutant exposure (Wendelaar Bonga and Lock, 1992; Wood, 1992). Ion flux measurements provide a very sensitive and noninvasive approach that may be applied in the field (for review, see Wood, 1992).

Hematology

These methods are well established (e.g., hemoglobin assay, hematocrit, blood cell counts), but the use of blood parameters to identify pollutant exposure in the field is relatively new to ecotoxicology and is best done in conjunction with histopathology and physicochemical data from the site (Handy and Depledge, 1999).

ANIMAL BEHAVIOR

A number of animal behaviors have potential as biomonitors of exposure, including avoidance of the pollution gradient, changes in feeding activity, predator avoidance, and

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reproductive and swimming behaviors (Little et al., 1985; Schreck, 1990; Little and Finger, 1990). Behavioral biomarkers offer important advantages over other biomonitoring approaches: (1) the behavioral response is often an integrated effect of the underlying biochemical and physiological disturbances and so may reflect a series of toxic effects and compensatory responses, (2) behavioral responses are usually more sensitive indicators of exposure than chemistry, biochemistry, or physiology, and (3) some behavioral responses can be linked on an energetic basis to population survival, e.g., locomotor activity (Priede, 1977; Handy et al., 1999).

Ecotoxicological studies on fish behavior in the laboratory have studied both metals and organic pollutants (Little et al., 1985), but generally have focused on relatively short-term acute effects lasting a few hours or days (e.g., Scarfe et al., 1982; Little and Finger, 1990; Rice et al., 1997). Most studies have focused on exposure via the gills, where disturbances to respiration and osmoregulation may limit locomotion and so the behavioral repertoire of the animal. Behavioral measurements during oral toxicity studies (intact gills) are rare (e.g., Handy et al., 1999). Thus the scientific background on behavioral effects is largely restricted to acute aqueous events, whereas the more realistic field situation of chronic and/or intermittent exposure via either the food and/or water have not been addressed adequately to develop meaningful biomonitoring systems.

However, telemetry devices exist for measuring animal behavior in the wild. For example, passive integrated transponders (PITs) that emit a radio signal at a predetermined frequency may be used to monitor fish movements within rivers (e.g., Gerlier and Roche, 1998). If the radio signal detector stations are linked to a satellite, it is possible to track fish over very mountainous terrain and in severe weather without the need to have researchers in the field in such conditions (Eiler, 1995). Modular acoustic tags with advance coding techniques have enabled a high level of precision in localizing fish in both space and time, as well as simultaneously recording from many fish (Cote et al., 1998). Acoustic approaches can provide detailed spatial and temporal maps of fish movements in ecosystems, even in open ocean (Ogura and Ishida, 1992). If fish location devices are combined with physiological telemetry, it is possible to measure metabolic rate in relation to activity patterns (Lucas et al., 1993). Physiological telemetry devices can record heart rate as a surrogate measure of metabolic rate (Lucas, 1994; Armstrong, 1998), provided that the heart rate response has been calibrated under realistic swimming speed, water quality, and thermal conditions in the laboratory (Thorarensen et al., 1996). Electromyograms of axial skeletal muscle can provide similar information relating activity and metabolic rate (Briggs and Post, 1997). Insertion of physiological telemetry into the body cavity requires the use of large fish and good surgical technique (Knights and Lasee, 1996; Baras and Jeandrain, 1998). The trend in electronics toward smaller and more powerful devices will no doubt eliminate the problems associated with fish size and expand the use of telemetry to smaller species (Clough and Beaumont, 1998).

PRAGMATIC APPROACHES TO BIOMONITORING: RAPID ASSESSMENT TECHNIQUES

The preceding discussion shows that there are many procedures for detecting the impacts of pollutants, ranging from molecular- to community-level approaches. However, some of the preceding methodologies require specialist expertise or equipment. In developing countries, these staff and equipment resources are extremely limited. In contrast, developed countries have competing demands for limited public funds that therefore constrain resources available for environmental protection and may hamper efforts directed toward detecting pollution threats in situ. However, monitoring multiple stressors at multiple

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scales and levels of biological organization is still a priority (Linthurst et al., 2000). A tiered series of economic, technically simple, and rapid hazard-detection procedures therefore is needed to help prioritize remedial action among field sites so that resources can be expended efficiently and effectively.

This issue is currently addressed through the development of rapid assessment procedures. For example, immunoassay-based tests (ELISAs) provide an inexpensive, rapid, and highly selective means of measuring specific chemical compounds and have been used to diagnose medical conditions for many years. Recently, the technology has been directed toward environmental contaminants in water, food, and soil samples. The method involves using antibodies that have been raised to specific types of chemical pollutants. Test kits are designed so that the intensity of a color reaction diminishes when the antibody and chemical combine. The intensity of the color is used to estimate the concentration of the pollutant in samples. The analyses can be run by relatively unskilled personnel in the field using simple equipment and provide obvious advantages for environmental scientists in developing countries. Limited trials have proved of great interest, and some environmental agencies are discussing incorporation of the techniques into screening programs. Comparisons of immunoassay techniques have been made with more traditional chromatographic–mass spectrometric techniques and show a high level of consistency (Fillman et al., 2000). The choice of determinants amenable to detection by the rapid chemical analysis procedures is broad, and thus the most relevant contaminants can be selected following surveys and discussions with scientists in the study region. Polyaromatic hydrocarbons (PAHs), PCBs, dioxins, organochlorine and organophosphorus pesticides, and selected herbicides and fungicides appear to be common environmental contaminants/pollutants of relevance. Water and sediment samples can provide information regarding the distribution and environmental concentrations of contaminants. In addition, immunoassays also can be performed on tissue extracts, hemolymph, and urine samples to determine the concentrations of chemicals in organisms. These can then be related to biological effects (see below).

The biomarker approach has been adopted to measure biological effect. For example, general toxicity is reflected in the onset of cellular pathology, which can be detected using the neutral red lysosomal assay (Lowe et al., 1995). This involves incubating blood cells from molluscs or crustaceans with a neutral red dye. The dye becomes incorporated within vesicles (lysosomes) within the cells. The time taken for the dye to leak out of the lysosomes reflects the health of the cells (and the organism from which they were taken); the shorter the time, the more stressed is the organism.

Currently, biological responses to and effects of pollutants are being explored in a United Nations pilot program, Rapid Assessment of Marine Pollution (RAMP), in which the following procedures are being applied to a range of estuarine or marine invertebrates and fish:

1. *Exposure and effects of organophosphorus and carbamate pesticides.* A simple colorimetric assay of cholinesterase inhibition in crustaceans and molluscs (Lundebye et al., 1997).
2. *Exposure to polyaromatic hydrocarbons.* A fluorescence assay to detect pyrenes and other PAHs and metabolites in fish bile and the urine and hemolymph of selected invertebrates (Aas et al., 1998).
3. *Exposure and effects of organotin compounds.* Assessment of the imposition of imposex or intersex in gastropod molluscs (Matthiessen and Gibbs, 1998; Oehlmann, 1998).
4. *Exposure to selected trace metals.* A colorimetric assay of metal-binding protein induction (metallothionein and metallothionein-like compounds) (Pedersen et al., 1997).
5. *Exposure and effects of genotoxins: Induction of micronucleii.* The method involves scoring cells with one or several cytoplasmic micronucleii of reduced size associated

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with the main cellular nucleus. These micronucleii are formed at the end of cell division and provide evidence of DNA breakage and spindle dysfunction during cell division resulting from exposure to genotoxic agents (Mersch and Beauvais, 1997).

6. *Detection of microbial pathogens: Colilert and Enterolert.* Rapid test kits for the detection of coliform bacteria and enterococci.
7. *Detection of sewage pollution.* Rapid, spectrophotometric measurements of ammonia.

In addition, three simple biomarkers of the general condition of invertebrate sentinel species have been used:

1. Cardiac activity in bivalve molluscs and decapod crustaceans (Depledge and Anderson, 1990).
2. Lysosomal neutral red dye retention in the hemocytes of bivalve molluscs (Lowe et al., 1995).
3. Apoptosis assay, also known as programmed cell death. Apoptosis refers to the morphological and biochemical alterations that occur in dying cells. In organisms exposed to toxicants and pathogens causing disease, the occurrence of apototic cells increases. The assay involves using three fluorescent dyes that bind to plasma membranes and nuclear membranes. On examination, normal cells appear green, apoptotic cells blue, and dead cells red (Piechotta et al., 1999).

These later three procedures provide a rapid indication of the well-being of organisms at a given locality.

New statistical procedures developed in Plymouth (the PRIMER package) will allow the data collected from a given site to be input into a multidimensional scaling statistical program to facilitate detection of pollution gradients and identification of sites with similar characteristics (Astley et al., 1999).

These procedures have been selected primarily with regard to their ease of use, low cost, and relevance to known environmental problems. In some cases, more robust procedures are available and might provide more accurate information on the nature and extent of pollution at a particular site. However, such procedures are more expensive and more time-consuming and require more highly trained personnel and high-quality analytical facilities than are generally available. They are thus impractical to include in a rapid assessment program. The approach just described has been applied in modified form in different circumstances, e.g., in the Venice lagoons (Lowe et al., 1995), Otago Harbor, New Zealand, and the Black Sea mussel watch program (UNEP).

INTEGRATING BIOMARKER BIOMONITORING WITH CHEMICAL MONITORING

The process of ecological risk assessment is used as part of a framework to identify and eventually prioritize environmental problems in a particular ecosystem. This process starts by identifying the pollution problem(s), then characterizes pollutant exposure and biological effects, and finally estimates the probable risk to the health of the ecosystem. The latter step may be used to plan a protection program or prioritize remedial tasks to protect the ecosystem. Biological monitoring should be used to evaluate exposure and/or biological effect, but not in isolation. Rather, it should be integrated into the risk-assessment process along with biodiversity survey programs and local hydrology, water quality, and sediment quality data. The assays described herein for biomonitoring should be implemented after a

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logical screening program to identify pollutants of concern. Some of the biomaker assays used for biomonitoring also can be applied to the initial screening of environmental samples (Fig. 9.1). The rapid assessment techniques for general health (e.g., neutral red assay, apoptosis assay) may be used in combination with fish health assessment/simple histological approaches (see Table 9.3) to prioritize field sites of concern. Environmental samples (water, sediment, serum, tissue homogenates, and even air samples extracted to a liquid phase) may then be screened for toxicity (see Fig. 9.1). This process starts with a nonspecific but rapid screen that may be applied to many different types of environmental sample (e.g., microtox assay) (Ringwood et al., 1997). Those samples showing toxicity may then be subjected to solvent extraction to separate organic contaminants, and additions of chelators (Hockett and Mount, 1996) may be used to study toxicity of the aqueous (metals) fraction. More specific bioassays may then be applied to identify families of compounds (e.g., PAHs, organophosphate pesticides, heavy metals) in the organic and aqueous fractions. This also may include further fractionation of the environmental sample for specific subgroups of contaminants or preferably the application of contaminant-specific biomarker assays (as earlier for rapid assessment).

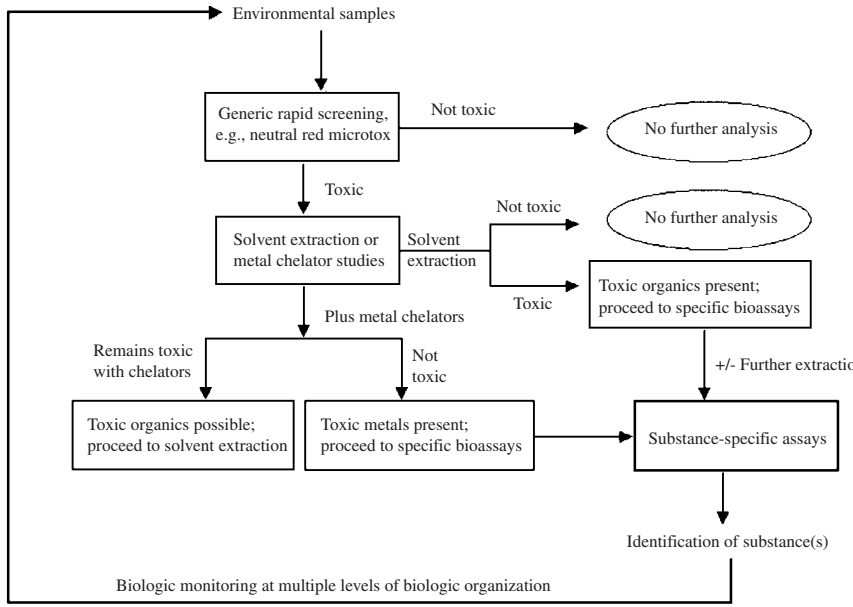

FIGURE 9.1 Scheme for ecotoxicological screening of environmental samples and subsequent biomonitoring. Environmental samples (e.g., water, sediment extracts) can be screened initially for general toxicity to decide whether or not the sample is likely to be hazardous. Rapid general-purpose toxicity assays can be applied such as the neutral red assay or the microtox assay. If the sample is toxic, then potential organic contaminants may be solvent extracted for further testing. Alternatively, metal chelators may be added to the sample and toxicity reassessed to test for the presence/absence of metals. A decrease in toxicity in the presence of metal chelators will indicate bioavailable toxic metals in the original sample. If metal chelators do not change toxicity, then organic contaminants are more likely to be the problem. Once the major groups (metals or organics) are identified, then substance-specific assays may be used to identify subgroups of pollutants, e.g., esterase inhibition for organophosphate pesticides/carbamates, fluorescence assays for hydrocarbons or specific metals, as described for the rapid assessment program. Once the groups of contaminants are identified, the various biological monitoring techniques described in this chapter may be used to monitor environmental contamination or the effectiveness of remedial action in the ecosystem.

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CONCLUSIONS

It is evident that ecotoxicological monitoring can provide extremely valuable information on which to base environmental management decisions. By detecting pollutant effects at different levels of biological organization, ecotoxicological monitoring can provide greater insight into the mechanisms by which chemicals, mixtures of chemicals, and biotic and abiotic factors bring about adverse effects on cellular systems, organizmal physiology and behavior, population dynamics, and community structure. The heirarchical approaches described here illustrate how the integrated use of chemical and biological (biomarkers) markers can be used to prioritize areas for study and inform environmental managers about which types of in-depth analyses should be undertaken at sites of concern. The potential for incorporating ecotoxicological monitoring procedures into bioremediation efforts is enormous because this will provide a means of verifying the effectiveness of management actions.

GLOSSARY

Ames test A screening test for the mutagenicity of chemicals that uses special strains of the bacteria *Salmonella typhimurium* that carry a mutation for the requirement of the amino acid histidine in the culture medium.

Apoptosis The normal process of removing dead or injured cells from a tissue, sometimes called *programmed cell death.*

Carcinogen A substance that may cause cancer.

Chromatid A strand of DNA that contains one DNA double helix. Note that after replication, each chromosome may contain two chromatids held together at a point called the *centromere.*

Chromosomal aberration Damage, such as breaks, deletions, and abnormal reordering or switching of parts, of a chromosome.

Chromosomes Threadlike structure of DNA and associated proteins found in the nucleus of a cell.

Comet assay A method of detecting DNA strand breaks in single cells that employs electrophoresis to separate the DNA fragments from the cell.

CYP1A A subclass of enzymes in the cytochrome P450 system.

Cytochrome P450 system A group of cellular enzymes usually found in the endoplasmic reticulum inside the cell and involved in catalyzing the chemical breakdown (metabolism) of organic chemicals. These enzymes belong to a group of proteins called *cytochromes* that have characteristic spectral properties at 450 nm, hence the term P450.

DNA adduct A fragment of DNA that has reacted with a chemical (pollutant) to form a covalently bound product.

DNA strand breaks A break in one or more DNA strands or a missing portion of a DNA strand, perhaps due to effects of toxic substances.

Edema The osmotic swelling of a tissue, perhaps due to mechanical injury or toxic effects, causing abnormal fluid balance or poor control of electrolyte concentrations in and around the tissue.

Genotoxin A substance that produces adverse or abnormal change in the genetic material within cells.

Hematology The study of blood and blood cells.

Karyotype A complete description of the chromatid pairs possessed by a given cell type, usually observed during cell division.

Metallothionein A peptide found in the cytoplasm of some cells that has metal-binding properties; functions include to chelate excess free metal ions in the cytoplasm, thus protecting the cell from metal toxicity.

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Metaphase The stage in cell division where the nuclear membrane has broken down and chromosomes are clearly visible in an ordered array across the midline of the cell.

Micronuclei (MN) Small spherical packages of darkly staining genetic material found in the cells, usually at the periphery of the nucleus.

Multifocal granulomatous lesions An injury to a tissue characterized by the appearance of abnormal granular material in the cells as observed using a light microscope. When these injuries occur in small patches in different places across the tissue, they are described as multifocal.

Necrosis Cell death, often abnormal or premature, that is not part of the normal cell cycle.

Neoplasia The occurrence of a group of abnormal and rapidly dividing cells forming the early stages of a tumor.

Neoplasm epizootics Organisms on the exterior surfaces of the host that may initiate neoplasms in epithelia, e.g., pathogenic bacteria in the mucus layers of the gut.

Neoplasm An abnormal, rapidly dividing cell that eventually may lead to tumor formation.

Neutral red assay A method to assess the toxicity of substances to the cell that exploits the fact that cells under toxic stress may accumulate the dye neutral red from the cell culture medium. Dye retention is scored as a measure of relative toxicity compared with resting control cells.

PAHs A group of organic chemicals called *polyaromatic hydrocarbons,* well known for their induction of the cytochrome P450 system during their metabolism.

Sister chromatid exchange (SCE) The exchange of homologous segments between two homologous chromatids at mitosis. This can be induced in rapidly dividing cell cultures by genotoxic substances.

Sister chromatid Replicated pair of DNA structures derived from a chromosome during cell division.

SOS chromotest An assay for mutagenicity that exploits the *son of sevenless* (SOS) gene in *Drosphila* that encodes for a mediator protein (tyrosine kinase receptor) involved in light transduction in cells.

Stress protein A group of low-molecular-weight proteins that are synthesized in the cell during stress. These proteins were first demonstrated during thermal stress and are often also called *heat shock proteins.* They are, however, induced by many stresses, including a wide variety of environmental contaminants.

Umu test A mutagencity assay that, like the Ames test, uses the bacteria *Salmonella typhimurium.* The mutant used in this test contains the gene *umUc* and may be combined with elements of the SOS assay.

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CHAPTER 10
INORGANIC NONMETALLIC SUBSTANCES

Ian D. McKelvie

INTRODUCTION

This chapter contains an outline of the sampling, storage, and analysis procedures required for a number of important nonmetallic inorganic species frequently found in either natural, drinking, or treated water. This chapter is not aimed at providing a detailed description of methods for these parameters but rather at giving the reader an introduction to the scope of methods available and drawing attention to the strengths and weaknesses of commonly used methods. Detailed method descriptions may be found in *Standard Methods* (APHA/AWWA/WEF, 1998) or in the methods published by the U.S. Environmental Protection Agency (EPA).

The inorganic species discussed in this chapter include dissolved carbon dioxide species (e.g., carbonic acid, bicarbonate, and carbonate), halides and related compounds (e.g., chloride, free chlorine, chlorine dioxide, and fluoride), sulfur compounds (e.g., sulfate, hydrogen sulfide, monohydrogen sulfide, and thiosulfate), and cyanides (e.g., cyanide and hydrogen cyanide, cyanate, and isocyanate). Some of these species (e.g., chloride, sulfate, and bicarbonate) are present as major constituents in natural waters as a result of weathering, groundwater, atmospheric, and biogeochemical processes, whereas others (e.g., free chlorine) occur as a product of water treatment or industrial pollution (e.g., cyanide).

Measurement of these species is often performed as a means of monitoring drinking water quality or the environmental quality of discharged domestic and industrial wastes. The methods of analysis described for the various parameters are all designed to be performed in the laboratory using standard analytical equipment. However, with the advent of portable test kits and flow and sequential injection analysis systems, it is feasible and often desirable to perform many of these analyses in situ.

DISSOLVED CARBON DIOXIDE SPECIES

Significance

Inorganic carbon, in the form of dissolved CO_2 and its equilibrium products, plays an essential part in many mineral weathering sequences, is required for photosynthetic production, and is central to the pH regulation of natural waters. CO_2 is present in the atmosphere at approximately 0.033 percent (v/v), and when it partitions across the air-water interface,

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CO_2 produces dissolved CO_2 and carbonic acid (H_2CO_3)[1], which ionizes to form bicarbonate and carbonate.

Consumption of organic matter by heterotrophic bacteria also leads to the production of carbon dioxide. This can be an important source of dissolved CO_2, especially in soil waters, where the dissolved CO_2 content may be as much as 30 times that normally found in surface waters (Drever, 1982).

The amount of dissolved carbon dioxide species present in water is quantified by the alkalinity *A,* which is defined as the hypothetical amount of base (HCO_3^-, CO_3^{2-}, and OH^-) that must be titrated with acid in order to reach a pH corresponding to a solution of only H_2CO_3*; i.e., for a simple system of CO_2, H_2O, and some base (say, NaOH),

$$A = [HCO_3^-] + 2\,[CO_3^{2-}] + [OH^-] - [H_3O^+]$$

Alkalinity is an important parameter because it is the principal control of buffer capacity of the water. A buffer is a solution that resists a change in pH following the addition of acid or base. The range over which a buffer operates is dictated by the ionization constant of the weak acid–conjugate base system and the relative concentrations of these species. For example, the buffering *range* for water buffered by carbonic acid and bicarbonate is given by:

$$\text{pH} = \text{p}K_1 + \log \frac{[HCO_3^-]}{[H_2CO_3^*]}$$

Fresh waters typically are buffered by dissolved carbon dioxide species in the range of pH 6.5 to 7.5, whereas marine waters contain dissolved boric acid salts, and these shift the buffering of seawater to a higher pH of approximately 8.2 (Butler, 1982).

The buffer capacity β is a measure of the resistance of a buffer to pH shift and is related to the alkalinity by the relationship

$$\beta = \left(\frac{\delta A}{\delta \text{pH}}\right)_{P_{CO_2}}$$

under conditions of constant partial pressure of carbon dioxide. Thus the higher the alkalinity, the greater is the ability of the water to withstand a pH change. Physicochemical conditions leading to pH change were discussed in Chap. 3.

Measurement of Alkalinity

Titration. Alkalinity is determined by titrating a water sample with standardized 0.01 *M* H_2SO_4. Phenolphthalein is first added to the sample to detect if carbonates and hydroxides are present. If they are, the sample is titrated until the pink color disappears at about pH 8.3; this is the *phenolphthalein alkalinity P.* Titration of the same sample is then continued until an end point is reached at pH 4.5 using a bromocresol green–methyl red mixed indicator. This gives the *total alkalinity.* By appropriate calculation, the individual concentrations of bicarbonate, carbonate, and hydroxide can be determined (Fig. 10.1).

Instrumental Methods. Alkalinity or its constituent parts also can be determined by instrumental techniques, including ion chromatography and flow injection analysis (Canata et al., 1987; Turner et al., 1987).

[1]The sum of dissolved CO_2 and H_2CO_3 is designated H_2CO_3*.

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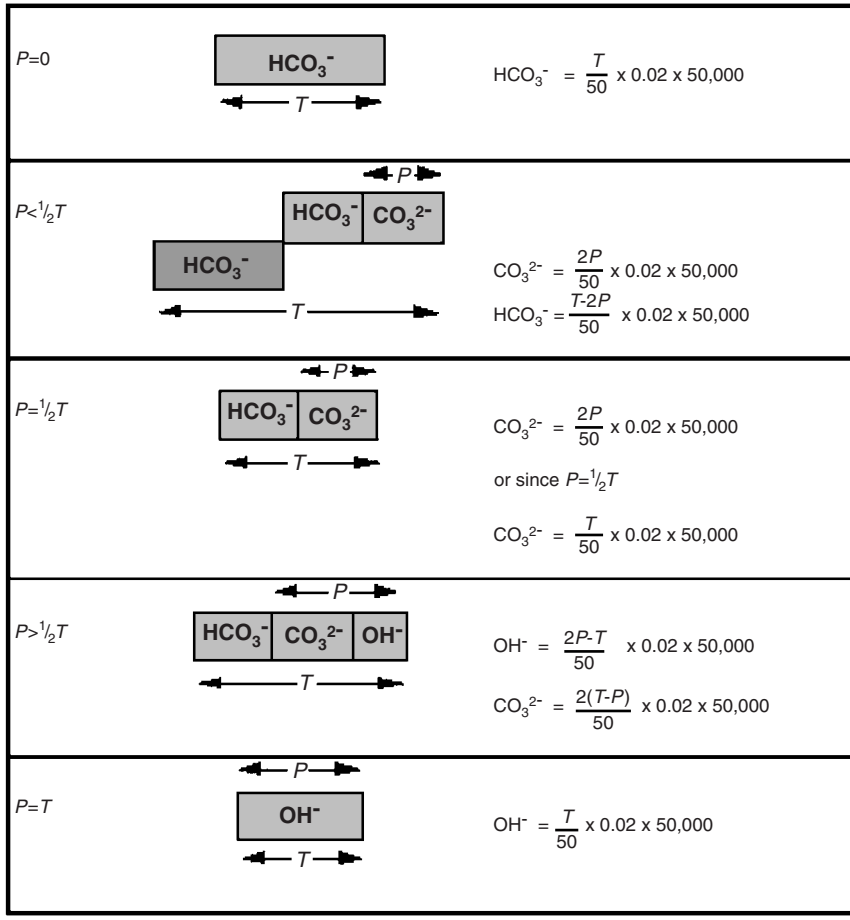

FIGURE 10.1 Alkalinity titration relationships. *P* refers to the titration volume against a phenolphthalein end point at pH 8.3, whereas *T* is the total titration value for a sample titrated against a mixed indicator to a pH of 4.5 using a mixed bromocresol green–methyl red indicator. The calculations are based on a 50-ml sample titrated with 0.01 *M* sulfuric acid. All carbonate, bicarbonate, and hydroxide concentrations are reported as equivalent mg $CaCO_3$ per liter. Equivalent weight of $CaCO_3$ = 50 g/equivalent or 50,000 mg/equivalent.

HALIDES AND RELATED CONSTITUENTS: CHLORIDE, CHLORINE, CHLORINE DIOXIDE, AND FLUORIDE

Significance

Chloride (Cl^-) is a major constituent of natural freshwaters and seawaters. Coastal freshwaters may contain relatively high concentrations of seawater because of the deposition of chloride-rich marine aerosols in precipitation (Hart and McKelvie, 1986). The average seawater chloride concentration is 19,320 mg/liter (0.545 *M*) (Morel, 1983), and estuarine

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waters will contain lower chloride concentrations through mixing and dilution of seawater. Chloride behaves conservatively in the aquatic environment and often is used as a conservative index of mixing in estuaries. Industrial and domestic wastewaters also may contain higher concentrations of chloride. Elevated chloride levels cause metal corrosion, are damaging to pipes and metal-reinforced structures, and are damaging to vegetation (Bartram and Ballance, 1996).

Chlorine in the form of hypochlorous acid (HOCl) is a very effective disinfecting agent and often is used for this purpose in drinking waters and wastewaters. Large-scale chlorination is performed by dissolving chlorine gas in water to form hypochlorous acid:

$$Cl_2\,(g) + H_2O\,(aq) \rightarrow HOCl\,(aq) + Cl^-$$

If pH is allowed to become too high, ionization of HOCl occurs, and disinfection is diminished because hypochlorite is less effective at penetrating the bacterial cells than the acid form (Baird, 1995). Small-scale chlorination of drinking and recreational waters and domestic wastewater treatment plants is often performed by addition of solid calcium hypochlorite or as aqueous sodium hypochlorite with careful pH control used to ensure that the active concentration of hypochlorous acid is maximized.

Chlorination of wastewaters and industrial effluents can involve reaction of chlorine with ammonia or organic substances to form chloramines and organochlorine compounds (termed *combined* chlorine). For example, during the disinfection of drinking water, HOCl is known to react with dissolved organic matter to form trichloromethane (chloroform), which is a suspected carcinogen. The determination of free chlorine in receiving waters is therefore of environmental interest in monitoring the formation of potentially harmful organochlorine substances, and in this assessment it is useful to be able to operationally distinguish between free and combined chlorine.

Chlorine dioxide (ClO_2) exists as a peroxy free-radical species and is an oxidizing agent that is used widely for disinfection and as a bleach in the paper and pulp industries. Because chlorine dioxide oxidizes rather than chlorinates dissolved organic matter, little or no trihalomethane or chloramine is formed, and in some countries, there is a preference to use chlorine dioxide or ozone as an alternative to chlorine. The recommended permissible amount in drinking waters is between 0.3 and 1 mg/liter (Nagy and Nagy, 2000).

Fluoride occurs in natural waters from the weathering of fluoroapatite [$Ca(PO_4)_3F$] and may occur at concentrations of as much as 10 mg/liter, although the average U.S. river water concentration is closer to 0.1 mg/liter (Baird, 1995). Fluoride is also added to some potable waters to a concentration of approximately 1 mg/liter as a protective measure against dental caries in children.

Methods of Analysis for Chloride

Argentometric Titration. Chloride is determined by titration with silver nitrate (0.0141 *M*) standardized against 0.0141 *M* NaCl using potassium chromate as an indicator. The end point of the titration is indicated by the formation of a yellowish pink precipitate of Ag_2CrO_4. Other potential interferences include high color, which should be removed by flocculation with aluminum hydroxide, or sulfide, sulfite, or thiosulfate, which can be removed by oxidation with a small amount of H_2O_2. The pH of the sample also should be adjusted to the range of 7 to 10 with sulfuric acid or sodium hydroxide.

Phosphate also interferes at concentrations of greater than 25 mg/liter by causing precipitation of silver phosphate, and iron at more than 10 mg/liter masks the end point (APHA/AWWA/WEF, 1998). These interferences may be minimized by judicious dilution in some cases.

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Potentiometric Titration. This method is more appropriate for samples containing turbidity or color. A sample is titrated with standardized silver nitrate in a beaker that is continuously mixed with a magnetic stirring bar, and the progress of the titration is followed with an Ag/AgCl electrode referenced against either a glass (APHA/AWWA/WEF, 1998), mercuric sulfate, calomel, or Ag/AgCl reference electrodes (Golterman et al., 1978). Where calomel or Ag/AgCl reference electrodes are used, they must be separated from the sample by an ammonium nitrate or potassium nitrate agar bridge or double-junction electrode system to avoid contamination from the KCl electrolyte filling solution that is used. Titrant is added in relatively large portions to begin with, e.g., 1/5, 2/5, 3/5, and 4/5 of the expected equivalence point, and the potential difference is measured from the millivoltmeter. As the equivalence point is approached, much smaller additions are made, and the potential is recorded after each. The equivalence point is the point of inflection in a plot of the measured potential versus the volume of titrant added (Fig 10.2*a*). Larger titrant volumes are added after the equivalence point is passed. Better visualization of the equivalence point can be achieved by plotting a first derivative plot of $\Delta E/\Delta V$ versus the volume of titrant added (Fig. 10.2*b*).

Direct Potentiometric Measurement. A chloride ion–selective electrode can be used to measure the chloride concentration directly. This consists of a sensing membrane of, e.g., silver chloride and silver sulfide, the potential of which is measured against an appropriate reference electrode system.

The ion-selective electrode is calibrated using a series of chloride standards, and these data are used to plot a calibration plot of measured potential versus $-\log [Cl^-]$. The sample concentration may then be determined using the measured potential and this calibration plot. Both samples and standards must be adjusted to the same ionic strength, and it is common to dilute both samples and standards 1:1 with 2 *M* potassium nitrate for this purpose (Nagy and Nagy, 2000). For wastewaters containing complex chemical matrices, it is preferable to use a standard addition technique rather than the calibration method (Skoog et al., 1998). A successful method has been described for removal of sulfide by addition of H_2O_2 in the flow potentiometric determination of chloride (Altunbulduk et al., 1995).

In all the preceding methods, bromide, iodide, and cyanide also react with silver ions. If these anions are present in appreciable amounts, a more selective alternative technique, such as ion chromatography, should be employed.

Methods of Analysis for Chlorine and Chlorine Dioxide

Titrimetric Measurement of Chlorine. Free chlorine at pH $\leq$ 8 reacts with potassium iodide to produce free iodine that is titrated with standard sodium thiosulfate under acidic conditions (pH 3–4); the end point may be detected by the use of a starch indicator. This method is suitable for quantification of chlorine at greater than 1 mg/liter. Interferences include oxidizing agents and oxidized forms of manganese. For more sensitive detection, an amperometric titration may be used. This involves the direct titration of free or total chlorine with standardized phenylarsine oxide solution, with the end point being detected using a polarographic detection cell with a Pt working electrode. By suitable manipulation of pH and reagent conditions, the free chlorine, total chlorine, monochloramine, and dichloramine fractions can all be estimated (APHA/AWWA/WEF, 1998).

Spectrophotometric Measurement of Chlorine

Diethyl-p-*phenylenediamine (DPD) Method.* Reactive chlorine (free + some combined chlorine) reacts with DPD to produce a red-colored product that has an absorbance maximum at 515 nm. For convenience, potassium permanganate solutions are used as a chlorine

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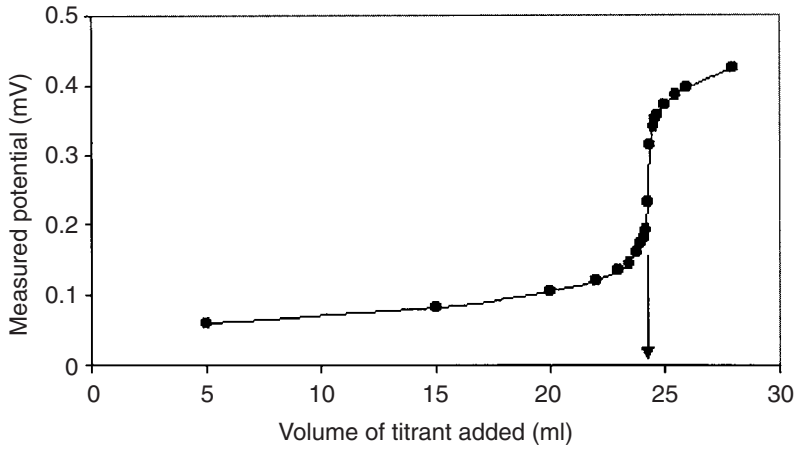
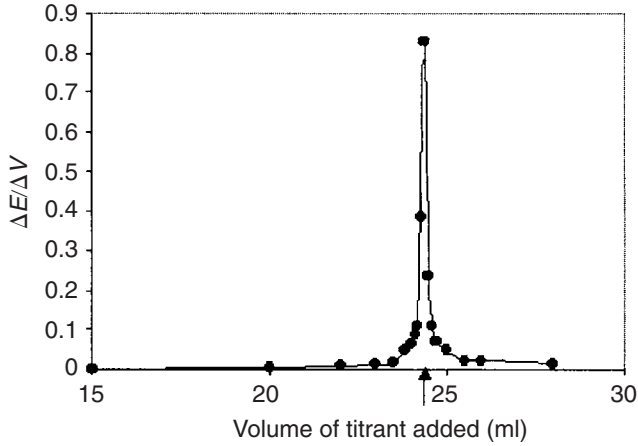


(a)



(b)

FIGURE 10.2 Determination of equivalence point (arrow) from potentiometric titration data from plots of (*a*) potential versus volume titrant added and (*b*) first derivative (ΔE/ΔV) versus volume titrant added.

equivalent to produce a calibration curve for DPD. The DPD method can be used for determination of chlorine in the range of 0.05 to 4 mg/liter (APHA/AWWA/WEF, 1998) and by adjustment of reagent conditions and reaction time also can be used to distinguish between free and total chlorine. The time required to form product is very short and critical in distinguishing between free and combined forms of chlorine.

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Syringaldazine Method (Also Called the FACTS[2] Method). Syringaldazine (3,5-dimethyoxy-4-hydroxybenzaldazine) in 2-propanol is oxidized by chlorine on a 1:1 stoichiometric basis, giving a product that absorbs strongly at 530 nm at pH 6.7. The method is sensitive to concentrations of less than 0.1 mg/liter and has the advantage that it is not as prone to interference from substances such as mono- and dichloramines, oxidized manganese and iron, or nitrate or nitrite as are other methods for chlorine determination (APHA/AWWA/WEF, 1998).

Spectrophotometric Measurement of Chlorine Dioxide. Chlorine dioxide can be determined by reaction with *o*-tolidine at pH 1.9 producing a yellow-colored product that has an absorbance maximum at 420 nm. Free chlorine is a potential interference in this determination, and its effect can be masked by the addition of malonic acid. Chlorite also interferes, but this effect is not amenable to masking with malonic acid.

Methods of Analysis for Fluoride

Ion-Selective Electrode Fluoride Method. Fluoride can be determined by potentiomentry using an ion-selective electrode that contains a membrane made from europium-dosed lathanum fluoride crystals. The potential of this electrode with respect to a reference electrode is related to the fluoride activity by the Nernst equation at 25°C:

$$E = E^\circ - \frac{RT}{F} \text{ in } \alpha_{F^-} = E^\circ - 0.0592 \log \alpha_{F^-}$$

where E is the electrode potential measured using a high input impedance pH/millivoltmeter, E° is the standard electrode potential, R is the gas constant (8.3143 $J \cdot K^{-1} \cdot mol^{-1}$), F is Faraday's constant (96,487 $J \cdot V^{-1} \cdot mol^{-1}$), and T is the temperature (K).

The fluoride electrode also responds to hydroxide ions, and measurements normally are performed at pH < 8 to avoid this problem. Because the activity of fluoride ions will be affected by varying ionic strength, a high concentration of background electrolyte is added. This electrolyte, termed the *total ionic strength adjusting buffer* (TISAB), as well as containing a high concentration of electrolyte, also includes a buffer to maintain the pH at 5 to 5.5 and a complexing agent such as cyclohexylenediaminetetraacetic acid (CDTA), the purpose of which is to complex interfering cations such as aluminum and release free fluoride ions (APHA/AWWA/WEF, 1998).

Using the fluoride ion–selective electrode, the fluoride concentration can be determined either by measuring the electrode potential and comparing it against a calibration plot of E versus $-\log [F^-]$ or by the use of standard addition. In both cases, the electrode with reference electrode is dipped into a stirred sample, and the equilibrium potential is obtained after several minutes. Simple automated electrode-dipping, sample-changing systems are marketed for this purpose. However, very rapid and reliable potential measurements also can be obtained when the fluoride electrode is housed in a flow-through cell and used in either the flow-injection or continuous-flow modes (Davey et al., 1986; Wang et al., 1995; APHA/AWWA/WEF, 1998).

Spectrophotometric Methods for Fluoride. A commonly used spectrophotometric method is the so-called SPADNS[3] method that involves the reaction between F^- and a

[2]FACTS, *f*ree *a*vailable *c*hlorine *t*otal *s*yringaldazine.
[3]*S*odium 2-(*pa*rasulfophenylazo)-1,8-*di*hydroxy-3,6-*n*aphthalene di*s*ulfonate (SPADNS).

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strongly colored zirconium-SPADNS complex. Fluoride forms the colorless ZrF_6^{2-} complex, and the absorbance of the zirconium-SPADNS complex measured at 570 nm decreases as the fluoride concentration increases. Potential interferences in this method include high alkalinity, aluminum, iron, and phosphate. In some cases it may be necessary to separate fluoride from the interfering matrix by distillation of hydrofluoric or fluorosilicic acid before analysis (Bartram and Ballance, 1996).

In order to avoid this time-consuming step, automated flow-injection methods have been described that involve separation of fluoride in a volatile form from interferences across a hydrophobic gas-permeable membrane, followed by spectrophotometric detection using a zirconium–Alizarin red S complex (Cardwell et al., 1994). This approach has the advantage that the gas diffusion membrane also can be used to perform preconcentration of fluoride.

CYANIDE SPECIES

Significance

The term *cyanides* encompasses all CN-containing substances in water that are determined as CN^- by common methods of analysis such as spectrophotometry and potentiometry. Cyanide commonly exists as the acid form, HCN, at the pH of natural water, and in this state it is extremely toxic to fish and other aquatic organisms. Cyanides occur in the environment as a result of industrial discharges from such industries as gold extraction, electroplating, plastics manufacture, and coal coking. Chlorination of some cyanide-containing wastes produces the toxic volatile gas CNCl, which hydrolyzes fairly rapidly (hours) to cyanate (CNO^-). Further oxidation of CNO^- with chlorine under neutral conditions produces a mixture of carbon dioxide and nitrogen gas. Under acidic conditions, NaCNO is converted to a mixture of ammonium sulfate and sodium bicarbonate. Not all metallocyanides undergo these reactions, and it is useful to distinguish between different operationally defined cyanide species, as shown in Table 10.1.

Interferences

Cyanide is often separated from a sample matrix by distillation and purging with a flowing airstream. The sample is acidified, and HCN is evolved and distilled into a collecting solution of sodium hydroxide, which is subsequently analyzed by titration or spectrophotometry. Distillation is a most effective means of separating cyanide as HCN from many of the potential interferences that may occur in the detection stage. However, some substances, such as oxidizing agents, sulfides, and fatty acids, may interfere in the distillation process itself and must be controlled as part of the sample pretreatment or preservation protocol. Oxidizing agents such as chlorine will oxidize cyanide, and sodium arsenite or sodium thiosulfate should be added to suppress this effect. Sulfide and other sulfur compounds may codistill with HCN, and lead carbonate can be added to either the sample or distillate to allow removal of this material as a sulfide precipitate. Fatty acids can distill across with the cyanide and form soaps in the alkaline receiving solution that interfere with the detection chemistry; fatty acids should be removed by solvent extraction prior to distillation. Nitrite may react with organic substances during distillation to form HCN, and sulfamic acid is added to suppress this effect of nitrite. For a comprehensive description of measures to control interferences, the reader is referred to 4500-CN^- B of *Standard Methods* (APHA/AWWA/WEF, 1998).

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TABLE 10.1 Sample Pretreatment Options for Determination of Different Operationally Defined Cyanide Forms

Cyanide form	Comprised of	Sample preparation techniques required
Cyanides, total	Free cyanide + most forms of metal-cyanide complexes	Sample acidified, distilled, and air purged; Pb carbonate absorber used to remove sulfides
Cyanides, amenable to chlorination (*with* distillation)	Free cyanide + cyanide complexes amenable to chlorination	Cyanides are chlorinated with calcium hypochlorite, and the sample is distilled; cyanides amenable to chlorination are calculated by the difference between total cyanide and the residual cyanide after chlorination
Cyanides, amenable to chlorination (*without* distillation)	Free cyanide + cyanide complexes amenable to chlorination + thiocyanates + cyanogen chloride	Sample heated cyanides converted to CNCl with chloramine-T
Cyanides, weak acid dissociable	Free cyanide + weakly complexed cyanide	Sample is acidified to pH 4.5–6.0 and distilled; zinc salts added to precipitate iron cyanides during reflux

Detection of Cyanide

After distillation, the collected cyanide must be quantified. Several techniques can be used, the simplest of which is titration with standard $AgNO_3$ to a colorimetric end point. This method is suitable for concentrations of as little as 1 mg/liter of CN^-. At lower concentrations, spectrophotometry or poteniometry should be used.

Spectrophotometric Method for Cyanide. Following preliminary distillation, cyanide absorbed in sodium hydroxide is treated with chloramine-T to produce cyanogen chloride (CNCl). Addition of pyridine–barbituric acid to CNCl produces a red-blue product with an absorbance maximum at 575 to 582 nm (APHA/AWWA/WEF, 1998). This method is suitable for determination of concentrations between 5 and 200 μg/liter of CN^-. An alternative colorimetric method involves the reaction of CNCl with chloramine-T, pyridine-pyrazolone, and a phosphate buffer to produce a blue product with $\lambda_{max} = 620$ nm. This method has similar sensitivity and linearity to the pyridine–barbituric acid method described earlier (Ikebukuro et al., 2000). The functional detection range using these techniques is of the order of 10 to 200 μg/liter of CN^-.

Ion-Selective Electrode Measurement of Cyanide. A cyanide ISE that uses a membrane electrode based on AgI with a double junction reference electrode system may be used to quantify the $[CN^-]$ in samples by measurement of the cell potential with a high-impedance pH/millivoltmeter. Standards in the range of 25 to 2500 μg/liter of CN^- are prepared and the potential measured. A plot of cell potential versus log $[CN^-]$ should yield a straight line with a Nernstian slope of 59 mV at 25°C. A sample of cyanide distillate is measured in an identical manner, and the concentration is calculated using the calibration equation.

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SULFUR SPECIES (SULFATE, SULFITE, SULFIDE)

Significance

Sulfate occurs widely in nature and is a major ion in natural and marine waters. The average concentration of sulfate in seawater is 2709 mg/liter (Morel, 1983), whereas in world average freshwater it is 18 mg/liter (Hart and McKelvie, 1986). Sulfate in water may originate from the weathering of sulfate minerals or as a result of pyrite oxidation, Sulfates also may be present in natural waters as a result of marine aerosol input or from dry fallout of dust, smoke, and fly ash. In this context, acid mine drainage may contribute large amounts of sulfate. The recommended sulfate concentration in drinking waters is 250 mg/liter (Karmarkar and Tabatai, 2000).

Sulfite is seldom found in natural waters but may be found in industrial wastewaters, in waste from food processing involving use of SO_2 as a preservative, or in boiler waters that have been treated with thiosulfate.

Sulfides in the form of H_2S, HS^-, or S^{2-} occur in waters and sediment pore waters under anaerobic conditions as a result of bacterial reduction of sulfate. For example, the anoxic hypolimnion of a stratified lake typically could have concentrations of several milligrams per liter of HS^- or H_2S. Waters receiving sewage or tannery, paper milling, oil refining, and gas manufacturing operations may contain elevated concentrations of reduced sulfur species. H_2S is toxic to aquatic organisms and also imparts a nuisance odor to water when the concentration reaches a threshold in the range of 0.025 to 0.25 μg/liter (APHA/AWWA/WEF, 1998). The speciation of sulfide species in waters is quite pH-dependent, with lower-pH waters favoring the free H_2S form.

Methods of Analysis for Sulfate

Sulfate analysis traditionally has been based on gravimetric analysis of precipitated barium sulfate after reaction with barium chloride. However, this method is time-consuming and susceptible to interference from suspended particulate matter, silica, nitrate, and sulfite. Alternative approaches based on turbidimetry or automated methods based on flow injection or segmented flow analysis or ion chromatography are now favored.

Turbidimetric Method. Sulfate is precipitated with barium chloride in an acetic acid medium under conditions of constant stirring, typically for a period of 60 s. The absorbance or turbidity of the barium sulfate suspension that is formed is related to the sulfate concentration, which is determined by a calibration method. The method is suitable for detection of sulfate at 1 mg/liter or more.

Automated Methylthymol Blue Methods for Sulfate. Both flow injection and segmented flow analysis systems have been described for the determination of sulfate. In the flow injection method (Madsen and Murphy, 1981), sample containing sulfate is injected into a carrier stream containing a low background of sulfate that merges with another stream containing an ethanolic mixture of Ba–methylthymol blue (MTB) complex at pH 2.5. The sulfate ions present in the sample react with the Ba-MTB at low pH to form a fine precipitate of $BaSO_4$. Adjustment of the pH to 13 with NaOH ensures that the Ba-MTB is in the form of a strong blue-colored complex. Reaction of the SO_4^{2-} ions causes a reduction in the absorbance of the Ba-MTB complex, which has a λ_{max} at 608 nm. Alternately, the absorbance of gray-colored uncomplexed MTB can be measured at 460 nm (APHA/AWWA/WEF, 1998). Because calcium and magnesium ions also may complex with MTB, they must be removed from the sample. This is achieved by pumping the sam-

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ple through a cation exchange resin column in the H^+ form prior to injection. This method has a method detection limit of approximately 2 mg/liter of sulfate. The same detection chemistry is used for sulfate detection with segmented flow technique, details of which are described in method 4500-SO_4^{2-} F of *Standard Methods* (APHA/AWWA/WEF, 1998).

Methods of Analysis for Sulfite

Sulfite may be determined by iodometric titration with a standardized iodide-iodate reagent. Free iodine produced when the iodide-iodate reagent reacts with sulfite, and in the presence of a starch indicator, the first excess produces a blue color that signals the end point. Interferences in this method may arise from the presence of other oxidizable substances such as sulfide, Fe_2^+, and thiosulfate that lead to overestimation of sulfite or from the presence of ions such as Cu^{2+} that catalyze the conversion of sulfite to sulfate if the sample is exposed to air before analysis (APHA/AWWA/WEF, 1998). A more sensitive spectrophotometric technique is also used. This involves the purging of SO_2 from an acidified sample with nitrogen gas for about 1 hour. The SO_2 is trapped in a solution of Fe^{3+} and 1,10-phenanthroline. Fe^{2+} produced by reaction with SO_2 is detected at 510 nm after removing excess Fe^{3+} with ammonium bifluoride (APHA/AWWA/WEF, 1998).

Methods of Analysis for Sulfide

Higher concentrations of sulfide, e.g., in wastewaters, may be measured by backtitration of iodine with standard sodium thiosulfate. The role of the added iodine is to oxidize sulfide under acidic conditions. This method is suitable only for waste and hot spring waters containing higher sulfide concentrations.

Spectrophotometric Methylene Blue Method for Sulfide Determination. This method involves the reaction of sulfide, ferric chloride, and dimethyl-*p*-phenylenediamine to produce methylene blue, which has an absorbance maximum at 660 nm. Residual ferric chloride will interfere in this measurement, and therefore, ammonium phosphate is added after color development to mask this effect. The effect of other interferences, such as reducing agents and thiosulfate, may be minimized if an automated gas diffusion separation step is employed. Sulfides are converted to volatile H_2S, which diffuses through a gas-permeable hydrophobic membrane, leaving interfering species such as thiosulfate in the donor stream (Schulze et al., 1988). The isolated H_2S is then determined as sulfide by formation of methylene, free from interferences.

Ion-Selective Electrode Measurement of Sulfide. A silver sulfide solid-state ion-selective electrode can be used to determine sulfide in the range of 0.032 to 100 mg/liter. To obtain reliable potential readings, the oxidation of sulfide by dissolved oxygen in the sample must be prevented, and the ionic strength must be adjusted. An *alkaline antioxidant reagent* consisting of NaOH, ascorbic acid, and EDTA is used for this purpose. An AgS ISE should exhibit an approximately half Nernstian slope of 28 ± 2 mV for each decade of sulfide concentration change, i.e.,

$$E = E^\circ + \frac{0.0592}{2} \log [S^{2-}]$$

at 25°C. That is, plot potential versus log $[S^{2-}]$ produces a linear plot.

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Dissolved organic matter may interfere with AgS ISE measurements, and standard addition should be used instead of a calibration method in this instance or when matrix interference is likely, e.g., in wastewaters.

AUTOMATED AND MULTIPARAMETER TECHNIQUES

Flow Injection Analysis (FIA) and Segmented Continuous Flow Analysis (SCFA)

Both these techniques involve the injection or merging of sample into a carrier stream that subsequently mixes with one or more reagent streams. In FIA, the sample zone is dispersed due to convection and radial and axial dispersion during the rapid transport of the zone through the flow manifold. Consequently, product formation may not be complete, but the transient signal measurement is very reproducible because of the highly controlled and reproducible dispersion conditions (Ruzicka and Hansen, 1988; McKelvie, 1999). Detection of product may be performed using a variety of flow-through detectors such as spectrophotometry, fluorescence, chemiluminescence, refractometry, FTIR, atomic absorption, potentiometry, voltammetry, and mass spectrometry (Fig. 10.3).

In SCFA, the sample is segmented into packets by the injection of air bubbles to minimize dispersion. Within each packet, complete mixing of sample and reagents occurs, and the signal that is measured is a steady-state one (Valcárcel and Luque de Castro, 1988).

Both techniques can be used in multichannel mode for the determination of several species, and both techniques are used widely in water analysis. Some typical applications for inorganic ion analysis are shown in Table 10.2.

Ion Chromatography

Separation and quantitation of inorganic anions is performed most commonly by ion chromatography (IC). Separation usually is performed using stationary phases of low ion-exchange capacity. Eluting anions are detected most frequently by measuring a change in electrical conductivity, although ultraviolet (UV) direct and indirect detection, electrochemical, and postcolumn methods also have been used. When conductivity detection is used, IC may be performed in either the suppressed or unsuppressed modes. *Suppression* refers to the use of a second column or membrane exchange device that converts eluent ions (e.g., carbonate, bicarbonate, and hydroxide) into their weakly conducting conjugate acids in order that the conductivity of eluting anions will not be swamped by the high background conductivity of the eluent. In the unsuppressed mode, eluents of lower conductivity tend to be used in conjunction with low capacity exchange resins. Discrimination of the conductivity of eluting anions from that of the eluent requires that the conductivity detector have a large zero offset so that the background conductivity can be set to zero. Unsuppressed IC tends to be less sensitive than suppressed IC (Skoog et al., 1998). IC offers a versatile and selective approach to anion analysis that is readily applicable for drinking, rain, and stream waters. However, for samples such as seawater that contain a high ionic strength, dilution may be necessary. Samples containing high dissolved organic carbon may require cleanup, e.g., using solid-phase extraction. For additional information on IC, refer to Haddad and Jackson (1990). Selected examples of the use of IC for inorganic anion analysis are shown in Table 10.3.

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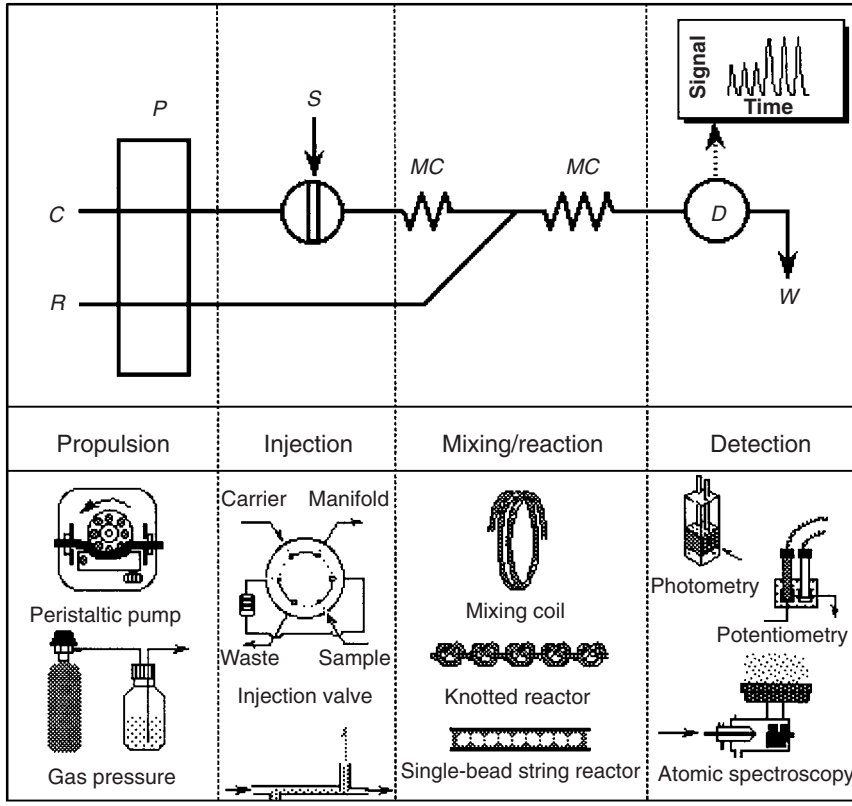

FIGURE 10.3 Schematic diagram of a typical flow injection analysis manifold (*top*). *P* is a pump, *C* and *R* are carrier and reagent lines, respectively, *S* is sample injection, *MC*s are mixing coils, *D* is a flow-through detector, and *W* is the waste line. The lower portion of the diagram indicates some typical instrumental options available for reagent and carrier propulsion, sample injection, sample-reagent mixing, and various detection modes.

TABLE 10.2 Selected Flow Injection Methods for Determination of Nonmetallic Inorganic Species

Parameter	Details of method	Reference
Chloride	Potentiometry with tubular silver electrodes	Van Staden (1986); Frenzel (1989); Altunbulduk et al. (1995)
Chloride	Photometry; indirect formation of iron thiocyanate	Ruzicka et al. (1976); Hansen and Ruzicka (1979)
Chlorine	Chemiluminescence with luminol	Qin et al. (1997)
	Ultraviolet (UV) photometric detection, gas diffusion separation	Aoki and Munemori (1983)

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TABLE 10.2 Selected Flow Injection Methods for Determination of Nonmetallic Inorganic Species (*Continued*)

Parameter	Details of method	Reference
Chlorine dioxide	Photometric detection, gas diffusion separation	Hollowell et al. (1985); Chen et al. (1999)
Cyanide, weak acid dissociable	Amperometric detection, with pre-evaporation separation	Sulistyarti et al. (1999)
Cyanide, weak acid dissociable	Photometric detection, gas diffusion separation	Sulistyarti et al. (1997)
Cyanide, total	Amperometric detection, UV photooxidation, gas diffusion separation	Solujic et al. (1999)
Cyanide, free, total, iron-cyanide complexes, thiocyanate	Photometric detection	Meeussen et al. (1989)
Cyanide, free and total	Potentiometric detection with Ag electrode or cyanide ISE electrodes	Frenzel et al. (1990); Marin et al. (1999)
Fluoride	Phorometric detection, online gas diffusion	Cardwell et al. (1988); Cardwell et al. (1994)
Fluoride	Potentiometry	Davey et al. (1986); Frenzel and Braetter (1986a); Frenzel and Braetter (1986b); Frenzel and Braetter (1986c); Davey et al. (1992)
Sulfate	Inverse photometric detection based on reaction between Ba–methylthymol blue and SO_4^{2-}	Madsen and Murphy (1981)
Sulfate	Inverse photometric detection based on reaction between Ba–dimethylsulfonazo III and SO_4^{2-}	Aono (1994)
Sulfate	Turbidimetric detection	Van Staden (1982)
Sulfite	Photometric detection based on reaction with 4,4'-dithiodipyridine, gas diffusion separation	Frenzel and Hillmann (1994)
Sulfide	Photometric detection based on nitroprusside or methylene blue, gas diffusion separation	Leggett et al. (1981); Kubán et al. (1992); Cassella and Santelli (1995)
Sulfide	Potentiometric detection technique	Brunt (1984); Van Staden (1988)

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TABLE 10.3 Ion Chromatography Methods for Inorganic Anion Determinations in Water

Parameter	Details of method	Reference
Chloride, bicarbonate, sulfate	KH phthalate eluent, refractive index detection	Schweizer and Schwedt (1985)
Chloride, carbonate, cyanide, phosphate, and sulfate	DMEA, HCHO, TTHA eluent, unsupressed conductivity detection; detection limit for cyanide of 50–μg/liter	Fujimura et al. (1994)
Chloride, nitrate, sulfate	Removal Ca and Mg with cation exchange precolumn, indirect UV detection	Hayakawa et al. (1991)
Free cyanide and metal-cyanide complexes	Preoxidation of CN^- to cyanate, conductimetric detection	Nonomura (1987)
Sulfide and cyanide	Pore water measurement, electrochemical detection to < 1 ng/g	Steinmann and Shotyk (1995)
Cyanide, cyanogen chloride	Postcolumn colorimetry with 4-pyridinecarboxylic acid–pyrazolone; detection limits of 0.25 and 0.19 ppb for cyanide, cyanogen chloride	Kumagai et al. (1993)

Capillary Electrophoresis

Capillary electrophoresis (CE) is a nonchromatographic technique that is capable of very rapid high-efficiency separations. A zone of sample is introduced into a 25- to 100-μm-diameter silica capillary filled with a UV-absorbent buffer solution that is connected at either end to a high-voltage supply. When a high-voltage electrical field is applied (15–30 kV) along the capillary, electro-osmotic flow (EOF) is initiated, and buffer moves from the cathode toward the anode. EOF in this instance is toward the anode, and in order to achieve this, the buffer must contain an electro-osmotic flow modifier. Modifiers such as cetyltrimethylammonium bromide alter the surface charge of the capillary such that the normal buffer migration toward the cathode is either slowed or even reversed. A small zone of sample is introduce into the cathode end of the capillary, either under pressure (hydrodynamic injection) or by electro-osmotic flow. Under the influence of the electrical field, different ions within the injected zone will separate on the basis of their relative electrophoretic mobility, with anions migrating toward the anode, neutral species remaining stationary within the zone, and cations tending to move backwards toward the cathode. As the ions within the zone separate, they are transported toward the detector by EOF. As the various anions pass through the flow-through UV detector, they displace UV-absorbing buffer ions, and a signal is registered. A number of other modes of operation of CE exist, some of which permit on-capillary preconcentration, whereas others involve chromatographic stationary-phase filled capillaries (Kuhn and Hoffstetter-Kuhn, 1993). While CE provides a very rapid means of determining anions such as fluoride, chloride, bromide, nitrate, nitrite, orthophosphate, and sulfate (Table 10.4), the sensitivity of this technique tends to be less than that which can be achieved using IC or FIA.

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TABLE 10.4 Selected Reported CE Methods for Anions

Parameter	Sample type	Notes	Reference
Chloride, sulfate, carbonate	Water, condensed steam from hydrothermal springs	UV (254 nm)	Santoyo et al. (2001)
Chloride, sulfate	Snow water	UV (diode array), μg/liter concentrations	Fernandez-Gutierrez et al. (2000)
Chloride, sulfate, fluoride	Groundwaters	UV (indirect), quantification limits 0.01–0.1 mg/liter	Hiissa et al. (1999)
Chloride, sulfate, fluoride	Drinking water	2–100 mg/liter range	Demay et al. (1999)
Chloride, bromide, carbonate, fluoride, sulfate	Surface waters	UV (indirect, 214 and 260 nm)	Morin et al. (1994)
Chloride, fluoride, bromide, sulfate, thiosulfate	Drinking water	UV (indirect), detection limits 1–3 mg/liter	Rhemrev-Boom (1994)
Chloride, sulfate	Rainwater	Conductivity (unsupressed)	Valsecchi et al. (1997)
Chloride, sulfate	Snow water	Sample stacking to improve sensitivity	Yang et al. (1999)
Chloride, carbonate, sulfate fluoride	Surface waters	Electromigration, on-capillary sample enrichment	Jackson and Haddad (1993)

SAMPLING AND PRESERVATION

There is no generic sample preservation and storage protocol that could encompass all types of samples or analytes that might be encountered. However, there are some guiding principles, and these are discussed briefly here.

When collecting samples, suitable sample containers and techniques should be used. Amber glass or dark bottles should be used to minimize photochemical reactions. Bottles for collection of samples containing volatile components, e.g., for dissolved CO_2, should be totally filled to avoid a dead space, which results in loss of volatile analyte when the bottle cap is removed.

Where possible, analyses should be performed on site to minimize potential changes in sample or analyte integrity. If this is not possible, samples should be preserved and transported appropriately, as shown by the guidlelines in Table 10.5. However, preservation and subsequent storage, even under deep freezing, does not guarantee perpetual stabilization of sample, as a number of studies have shown (Clementson and Wayte, 1992; Haygarth et al., 1995).

Some principal sources of analyte loss include adsorption to container walls, hydrolysis, or oxidation changes of analyte species. Refrigeration, freezing, addition of bactericide, and filtration through a 0.2-μm filter (and combinations of these) all have been used as a means to minimize or avoid biological activity that may consume the analyte or change its oxidation state.

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INORGANIC NONMETALLIC SUBSTANCES

TABLE 10.5 Suggested Sample Collection, Preservation, and Storage Protocols for Different Inorganic Species

Parameter	Container type	Preservation	Recommended longest storage
Alkalinity	Polyethylene, glass	Immediate analysis preferable; alternately, fill bottle and refrigerate (4°C)	24 h*
Chloride	Polyethylene, glass	None	7 d†
Chlorine (total)	Polyethylene, glass	Immediate analysis	Minutes*
Chlorine dioxide	Polyethylene, glass	Immediate analysis	Minutes*
Cyanide (total)	Polyethylene, borosilicate glass	Adjust to pH 12 with NaOH; refrigerate (4°C) in dark	24 h*
Cyanide (amenable to chlorination)	Polyethylene, borosilicate glass	If free chlorine present, add 0.6 g/liter ascorbic acid; refrigerate (4°C) in dark	Minutes*
Fluoride	Polyethylene	Refrigerate (4°C) in dark	7 d‡
Sulfate	Polyethylene, glass	Refrigerate (4°C)	28 d†
Sulfide	Polyethylene, borosilicate glass	Add zinc acetate (4 drops, 2 *M*) and NaOH to adjust to pH > 9	7 d*

*APHA/AWWA/WEF, (1998). *Standard Methods for the Examination of Water and Wastewater.* American Public Health Association, Washington.

†Bartram, J., and Ballance, R., eds. (1996). *Water Quality Monitoring.* E. & F.N. Spon, London.

‡U.S. EPA (1983). Sample preservation. In *Methods for Chemical Analysis of Water and Wastes,* pp. xv–xx. U.S. EPA, EPA-600/4-79-020, Cincinnati, OH.

In other situations, the sample should be stabilized by adjusting the pH, e.g., to avoid volatility losses of CN^- as HCN by ensuring that the sample remains in fully ionized form by increasing pH to 9 to 12. Similarly, to avoid oxidation (e.g., for CN^-) by residual chlorine, ascorbic acid is added. Because of the widely differing water quality conditions that can apply, it is desirable to conduct sampling quality assurance to ensure that sampling and storage losses or contamination is not occurring.

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P • A • R • T • 2

SOILS AND SEDIMENTS

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CHAPTER 11
INTRODUCTION TO SOILS AND SEDIMENTS

Ulrich Förstner

INTRODUCTION

Soils and sediments are repositories for physical and biological debris and sinks for a wide variety of chemicals. The concern associated with the chemicals sorbed to sediments and soils is that many commercial species and food-chain organisms spend a major portion of their life cycle living in or on aquatic sediments or on contaminated soil. This provides a pathway for these chemicals to be consumed by higher aquatic or terrestrial life and wildlife, as well as humans. Direct transfer of chemicals from soils and sediments to organisms is now considered to be a major route of exposure for many species. These issues are focusing attention on soil and sediment contamination and highlight the fact that sediments are also an important resource (Adams et al., 1992).

Due to the capacity of soils and sediments to store and immobilize toxic chemicals in so-called chemical sinks, the effects of pollution may not be manifested directly. This positive function of soils and sediments does not guarantee, however, that the chemicals are stored safely forever. Factors influencing the storage capacity of soils and sediments or the bioavailablity of the stored chemical can change and indirectly cause sudden and often unexpected mobilization of chemicals in the environment (Stigliani, 1988). From the discussions on the "chemical time bomb" (CTB) concept in the beginning of the 1990s, it became apparent that at first it is imperative to know what soil or sediment properties will control the toxicity levels of a chemical and how sensitive the chemical toxicity is to changes in these properties; second, the relevance of a soil or sediment property to a CTB depends on how this property is affected by long-term environmental changes, e.g., socioeconomic or climatic changes (Hesterberg et al., 1992).

In this handbook, soils and sediments are treated together. This makes sense because they are composed of essentially the same matrices, they receive similar pollutant inputs, major interactive processes between dissolved and solid constituents may just differ in intensity, and—perhaps most important—quality criteria assessment for soils and sediments become closer when these protocols are increasingly based on biological information. Nonetheless, there are still some differences in the monitoring of soils and sediments, and a few special features will be mentioned in this overview.

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SOILS

First and foremost, soils are carriers and media of important growth factors necessary for their respective types of vegetation. Yet their physical and chemical properties also determine other functions in the ecosystem, namely, their ability to transform, filter, and buffer solid, soluble, and gaseous substances.

The problems caused by abandoned contamination sites in particular have made abundantly clear that a comprehensive concept of soil protection is necessary, where the most important problem areas are treated in an integrated manner, including

- Protection of food supplies from hazardous substances that accumulate in the soil and have harmful effects on plants or those substances which enter the food chain
- Protection of soil from further acidification from the continuous and large-scale release of sulfur dioxide and nitrogen oxides that overburden the buffering and converting capabilities of the soil
- Protection of groundwater supplies from further contaminant loads, especially from nitrogen compounds in fertilizers
- Ecologically safe use of pesticides
- Remediation of abandoned contamination sites and abandoned industrial sites

Contaminants have an impact on the sensitive balance of physical, chemical, and biological processes on which soil fertility is based. The contamination of soil by heavy metals and organochlorine compounds inhibits microbial enzyme activity and reduces the biodiversity of soil flora and fauna. The transfer of contaminants to humans occurs either from direct ingestion of vegetable matter or through consumption of milk or meat from animals that feed on contaminated plants or which have ingested contaminated soil. The accumulation of contaminants in soil is cause for considerable concern because of the loads of toxic organic compounds and heavy metals in surface and groundwater, the transfer of pathogens via crops grown on soil subject to sewage sludge application, and the unintentional removal of nutrients from the soil into other ecosystems.

Persistent substances (i.e., substances that are decomposed over very long time periods) constitute a growing hazard potential since these substances continue to accumulate. If certain load thresholds are exceeded, this accumulation can lead to latent adverse impacts on the soil flora and fauna up to the acute endangerment of humans from accumulations in the food chain and in groundwater. With respect to persistent substances, it is therefore advisable to prevent their release early on if there is cause to suspect that they will have adverse effects on the soil.

In order to be able to predict the acute and long-term effects of contaminants in soil, it is necessary to know (Farrington and Westall, 1986):

1. The way in which critical compounds enter the soil environment and their movement into ecosystems, especially back to humans
2. The reactions of these compounds in the environment
3. The rates of movement and of reaction
4. The short-term (days to months) and long-term (years to decades) accumulation of such material in soil

A special problem with agricultural soils originates from certain additives intended to improve soil quality that may contain potentially toxic elements or substances. In addition

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to the natural constituents, trace elements also enter the soil via beneficial agricultural additives, such as lime, fertilizer, manure, pesticides, and irrigation waters, as well as via potentially deleterious materials such as sewage sludge, municipal compost, mine wastes, dredged materials, fly ash, and atmospheric deposits.

The main focus, however, is on abandoned contamination sites, including old garbage dumps and industrial production residues, contaminants from industrial facilities, areas in the vicinity of smoke stacks and discharge pipes, the concomitant contaminations and consequences of two world wars, military installations of the past and present, leaking wastewater lines, and buildings that were constructed with materials that have adverse effects on human health. On industrial sites, production residues often were buried superficially, or production input, intermediate, and end products were stored without any protective measures (e.g., former gas utilities, insecticide plants). Other subsurface contamination was caused by leaking pipelines used for chemicals or petroleum products or leaking above-ground storage tanks (ASTs), e.g., abandoned refineries and airports. Oil and gasoline leakage from underground storage tanks (LUSTs) has caused considerable soil contamination (e.g., gas stations). Soil contamination also was caused (e.g., in the port of Hamburg, Germany) by the effects of war, where organic chemicals and petroleum products from destroyed above-ground tanks and/or operating facilities seeped into the subsurface.

In Chap. 12, soil problems will be described, and a standardized approach will be presented for evaluating abandoned landfills and industrial sites. Contaminated-land risk assessment is still underpinned largely by scientific research done for other purposes. Further development and integration of the building blocks needed for risk assessment are of the utmost importance if assessment is to be more than a mere sequencing of separate disciplines such as soil and water sampling, chemical analysis, exposure modeling, and toxicology (Ferguson et al., 2000).

Chapter 13 will cover some aspects of soil remediation. In dealing with heavily contaminated soils, it is possible to draw on the experiences that have been gained from industrial waste treatment. The rapid technological progress is documented, for example, in the publications of the TNO conventions, "Contaminated Soil", in Utrecht, Netherlands (1985), Hamburg (1988), Karlsruhe, Germany (1990), Berlin (1993), Maastricht (Netherlands), Edinburgh, U.K. (1998), and Leipzig, Germany (2000). For low to moderately contaminated soils, the focus of attention is on reducing the release of contaminants and on processes to minimize contaminant transfer to crop plants.

During recent years, a major shift can be observed from typical ex situ technologies such as soil washing/extraction, solidification/stabilization, and thermal treatments to more natural, mostly in situ concepts such as reactive walls or biological in situ remediation. Major advantages of these concepts are avoidance of secondary wastes and reduction of hazards for people who are exposed. Permeable reactive barriers are installed as a passive in situ treatment zone of reactive material that degrades or immobilizes contaminants as groundwater flows through it. These barriers may contain reactants for degrading volatile organics, chelators for immobilizing metals, nutrients and oxygen for microorganisms to enhance bioremediation, or other agents (Anonymous, 1997a).

Natural attenuation or *intrinsic remediation* grew from a laboratory research phenomenon to become a commonly used approach for the cleanup of contaminated groundwater (MacDonald, 2000). The concept relies on natural subsurface processes rather than traditional engineered procedures. Typical for applications of the natural attenuation concept is the integration of biological, chemical, and geotechnical approaches. Common objectives are the characterization of the site with regard to the efficiency of the expected retardation/degradation mechanisms, proof of applicability of the natural attenuation concept (i.e., time frame), and elucidation of questions relating to the persistence of pollution sources.

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SEDIMENTS

Sediments are an essential and integral part of water systems. They provide the substrate for organisms and through interaction with the overlying waters (e.g., nutrient cycling) play an essential role in the aquatic ecosystem. Furthermore, after naturally occurring flooding, sediments are left as a deposit of fertile silt on flood plains. On the other hand, human-made changes alter the hydrodynamic conditions of waterways, resulting in accumulation of sediments at unwanted places. The removal of sediments from harbors, navigation channels, locks, flood plains, and river stretches is a high capital cost for authorities and agencies responsible for their maintenance and water quality (Anonymous, 2001).

Geochemical investigations on stream sediment have long been standard practice in mineral exploration (Hawkes and Webb, 1962); by more extensive sampling and analysis of metal contents in water, soils, and plants, the presumable enrichment zones can be narrowed down and, in favorable cases, localized as exploitable deposits. Generally, the variation in trace metal content of stream sediments can be characterized as a function of potential controlling factors' influence of lithological units, hydrological effects, geological features, cultural (human-made) influences, type of vegetational cover, and effects of mineralized zones (Dahlberg, 1968). Similarly, lake sediment geochemistry has been used as a guide to mineralization. This approach attracted much attention when mineral exploration was followed by large-scale mining and processing activities: "Both the exploration and environmental geochemist can be looking for the same type of areas, those with high metal concentrations, but obviously from a different motivation" (Allan, 1974). On a qualitative basis, sediment analysis can be used favorably to estimate point sources of pollutants that on being discharged to surface waters do not remain in solution but are adsorbed rapidly by particulate matter, thereby escaping detection by water monitoring. In this sense, sediment data play an increasing role within the framework of environmental forensic investigations (Meiggs, 1980).

Sediments are recognized increasingly as both a carrier and a possible source of contaminants in aquatic systems, and these materials also may affect groundwater quality and agricultural products when disposed of on land. Contaminants are not necessarily fixed permanently by the sediment but may be recycled via biological and chemical agents within both the sedimentary compartment and the water column. Bioaccumulation and food-chain transfer may be strongly affected by sediment-associated proportions of pollutants. Benthic organisms in particular have direct contact with sediment, and the contaminant level in the sediment may have greater impact on their survival than do aqueous concentrations.

In devising sediment management strategies, decisions need to be made bearing in mind the relationship between contaminated sediment and renewal of environmental quality, which goes far beyond setting numerical chemical cleanup criteria, because these strategies are not based on the need to fully recover natural ecosystem processes (Krantzberg et al., 2000): "What is needed is a pragmatic means of interpreting comprehensive sediment bioassessment data that leads to the selection of ecosystem-based and cost-effective options for management of contaminated sediments."

In the present overview, four aspects will be covered, which in an overlapping succession also reflect the development of knowledge in particle-associated pollutants during the past 25 years:

- The identification, surveillance, monitoring, and control of sources and distribution of pollutants (see Chaps. 12 and 14)
- The evaluation of solid/solution relations of contaminants in surface waters (see Chap. 16)
- The study of processes and mechanisms in pollutant transfer in various compartments of the aquatic ecosystems (see Chap. 16)

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- The assessment of the environmental impact of particle-bound contaminants, i.e., the development of sediment quality criteria (see Chap. 17)

Two other chapters will deal with sediment remediation procedures (Chap. 13) and with physical parameters and techniques (see Chap. 15); the latter information will be combined with the chapters on particle-associated pollutants to present a modern approach to integrated process studies (see Chap. 16).

During the last few years, it became increasingly evident that biology-based knowledge is the key for sediment management decisions. This information includes (Krantzberg et al., 2000) (1) benthic community structure, (2) laboratory bioassays for evaluating the toxicity of in-place pollutants, and (3) bioaccumulation and biomagnification information, including estimates of tissue concentrations in both invertebrates and vertebrates in the food web. For hazard assessment, combinations of different biotests are applied in sampling surveys to cover different sensitivities of organisms and pathways of exposure. Strong emphasis herein is placed on chronic tests. Since these have the disadvantage of taking a rather long time, and since toxic effects are often covered by resistance and repair processes in the organisms, development and application of biomarkers have been favored lately (see Chap. 17).

The basically biological knowledge requires strong support from other disciplines, e.g., on-site stability, including fate and transport; on the potential for mobility with disturbance over long time periods; on the bioavailability over a range of sediments, sediment pore waters, organismal microenvironments, and overlying water chemistry (pH, redox, and hardness); and on physicochemical sediment properties. In Chap. 12, a special example demonstrating the dispersion of highly contaminated sediments in a large catchment area will be shown from the so-called chemistry triangle of the upper Elbe River system. Unlike problems relating to conventional polluted sites, here the risks primarily are connected with transporting and depositing of contaminated solids in a catchment area, especially in downstream regions. Handling of such problems is a complex task that should include further fields such as law, planning, controlling, and public relations.

Remediation techniques on contaminated sediments generally are much more limited than for most other solid waste materials, except for mine wastes. The widely diverse contamination sources in larger catchment areas usually produce a mixture of pollutants that is more difficult to treat than industrial waste. For most sediments from maintenance dredging, there are more arguments in favor of disposal rather than treatment. Mechanical separation of less strongly contaminated fractions, however, may be a useful step prior to final storage of the residues (see Chap. 13).

Methods for the assessment and treatment of contaminated sediments, among others, were compiled in the Assessment and Remediation of Contaminated Sediments (ARCS) program of the U.S. Environmental Protection Agency (Anonymous, 1994). Examinations relating to the use of sediments were carried out primarily in the Dutch POSW (Programma Outwikkeling Saneriug processen Waberbodems) program (Anonymous, 1997b). Most expertise has been gained for the treatment of dredged material, whereas for the management of contaminated flood sediments, experience is still widely lacking. Here in particular, results from integrated process studies (see Chap. 16) can be used, and major emphasis will be placed on mechanical effects such as compaction and loss of water as well as on hydrodynamic parameters such as erosion stability of sediments (see Chap. 15).

Recent proposals for in situ remediation include combined approaches for sediment stabilization such as physical ripening processes (dehydration and shrinkage, increase of permeability, change from soft consistency to friable or hard) (Vermeulen et al., 2000), biological mechanisms (phytostabilization, i.e., precipitation or adsorption near or at plant roots) (Joziasse and Gun, 2000), and a wide range of physicochemical aging processes. Subaqueous capping of both in situ sediments and subaqueous deposits of dredged materials has become an attractive concept for isolating contaminated sediments to prevent

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contaminant release into the surface water and, subsequently, into the food chain (Azcue et al., 1998). Similar to the permeable reactive barrier concept for groundwater treatment, these passive technologies first of all offer apparent economic advantages. Furthermore, they may be considered moderate with respect to interference with natural and ecological resources because they do not require any transporting of contaminated materials, treatment plants, or upland deposits.

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CHAPTER 12
SOIL AND SEDIMENT PROBLEMS

Ulrich Förstner

SOIL PROBLEMS

The enormous problems arising from the thoughtless dissipation of chemicals in the environment in the past has become obvious in all parts of the world. The detection of extremely toxic chemicals at Love Canal, Lekkerkerk, and Georgswerder points up only a few of the harsh lessons. During the last decade, our society has taken a new attitude toward soil and its functions (Thoenes, 2001): Attention is paid to soil and areas of land when reasonably priced sites are being sought for building projects and in particular when changes to soil involve a situation that is subjectively threatening to people, leading to the need for hazard control. In particular, residential areas on former landfills and sites with historical contamination arouse wide interest among the public and in the media. This situation promoted the regulatory framework for the protection of the soil medium 30 years after the installation of water and air legislation (Miehlich, 2001). For example, in the German Federal Soil Protection Act (BBodSchG) it is laid down that "the party who caused a harmful soil change or contaminated site shall be obliged to remediate the soil and contaminated sites [Sec. 4(3)]. Harmful soil changes within the meaning of this act are harmful impacts on soil functions that are able to bring about hazards, considerable disadvantages, or considerable nuisances for individuals or the general public [Sec. 2(3)]."

For the investigation and assessment of suspect sites, two types of values are defined in the BBodSchG [Sec. 8(1)]:

1. Values which, if exceeded, shall mean that investigation with respect to the individual case in question is required, taking the relevant soil use into account, to determine whether a harmful soil change or site contamination exists (trigger values).
2. Values for impacts or pollution which, if exceeded, shall normally signal the presence of a harmful change or site contamination, taking the relevant soil use into account, and mean that measures are required (action values).

Action and trigger values are given for three pathways: soil–human being (direct contact), soil–food plant, soil-groundwater. The soil or the contaminated site shall be remediated so that none of the problems occur in the long term; "as part of fulfilment of obligations relative to the soil and to contaminated sites…the permissible use of the piece of land under planning law, and the resulting protection requirements, shall be taken into account, as far as this is compatible with the protection of the soil functions." This means

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that remediation values vary with planned use of the site and the role of soil functions. Every decontamination method influences the natural soil functions and serves as an archive of natural and cultural history (Miehlich, 2001). With regard to the degree of disturbance of soil functions, there are considerable differences among the decontamination methods (see Chap. 13).

In the following sections, an overview will be presented of the type and extent of pollution of agricultural soil, groundwater contamination by abandoned waste disposal sites, and management of contaminated sites, including an evaluation scheme, a risk-assessment approach, and an overview on policy and practice in European countries.

Pollutants in Soil

Heavy Metals. Current notions of tolerable heavy metal concentrations in soils are merely crude benchmark limits and cannot serve as the sole criterion for evaluating actual examples because the mobility and availability of all heavy metals are strongly influenced by different soil characteristics such as pH, clay content, or humus content.

In an overall assessment of anthropogenic effects and the mobility of heavy metals, cadmium contamination should receive high priority. The mean cadmium level of the population of industrialized countries has reached about one-third the concentration considered critical by the World Health Organization, and the largest proportion of this cadmium comes from vegetable food. It should be noted that regionally lower pH values and clay and humus contents can effect a significantly higher cadmium transfer from the soil into plants.

The heavy metal impacts caused by agriculture itself are limited—aside from municipal waste and some herbicides and pesticides—to cadmium in phosphate fertilizers and locally to the copper content of liquid hog manure. At the earliest, a measurable accumulation of 0.1 parts per million (ppm) is theoretically expected after 100 years. Since phosphate fertilizers are a necessary means of maintaining soil fertility, the associated minimal cadmium load must be accepted for the time being, and the focus should be on reducing or eliminating the other cadmium sources.

Organic Contaminants. Some pesticides and their metabolites are so tightly bound in the soil that it puts into question their alleged limited persistence. On the other hand, there are active substances whose degradation in the soil is accelerated after multiple applications as a consequence of microbial adaptation. This illustrates that sweeping generalizations in this area are unsubstantiated. The history of chemical plant protection is simply too short and the number of persuasive long-term studies of all relevant active substances is far too low to permit a look toward the future with confidence.

Among the multitude of potentially harmful organic compounds, chlorinated hydrocarbons (CHCs), polychlorinated biphenyls (PCBs), and polycyclic aromatic hydrocarbons (PAHs) are especially pertinent for soil because of their high stability. Since their degradation in biological sewage sludge digestion is very limited or extremely slow, an impact is to be expected when these sludges are applied to agricultural lands. Therefore, it is necessary to closely monitor heavy metal and organic contaminant contents in sludges and municipal waste.

Combustion gases and industrial and municipal wastes have contributed to the accumulation of PAHs in soils. Their persistence in the soil is a function of the degree of condensation and the concentration of these substances. Due to their strong bonding to humic substances in the soil, the uptake of PAHs through plant roots is relatively low, and their marked lipophility minimizes their transfer not only to the root interiors but also even more to the parts of the plants above ground. However, at this point in time, no serious problems are associated with PAH contamination either in general or from soils treated with municipal waste (compost).

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The same applies to PCBs, and their average concentration in agricultural soils is very low. The transfer from soils into plants is also minimal and as such is largely limited to low level chlorinated biphenyls. However, higher concentrations of these substances have been found in the milk and fat of animals that were grazed on pastures where sludges containing PCBs were applied. For this reason, a limit of 10 ppm of PCBs for land-applied sludges has been considered for some time in the United States. In the future it should be emphasized that exotic substances that are difficult to degrade, such as highly concentrated and highly chlorinated and particularly aromatic hydrocarbons, should not be added to any soils.

Groundwater Contamination

Many particularly organic substances found in groundwater contaminated by waste sites are exclusively anthropogenic. So far about 1000 organic substances have been identified in contaminated groundwater downstream of waste deposits. However, experiences in the United States (Plumb, 1985) and Germany (Schleyer et al., 1988) show that only a few organic substances are found frequently and that most others are found rarely in groundwater downstream of waste sites. Based on 358 U.S. and 92 German objects, Schleyer et al. (1988) performed a statistical evaluation of organic "priority pollutants." The predominance of aliphatic halogenated hydrocarbons becomes evident from a comparison of both studies regarding the 15 contaminants detected most frequently in groundwater: There are 9 in Germany and 10 in the United States, of which 7 are identical. Another striking fact is that in both studies, although in a different sequence, tetrachloroethene and trichloroethene are the most predominant organic contaminants, with a detection frequency of more than 35 percent. Among the 15 most frequently occurring contaminants, the monoaromatic hydrocarbons constitute the second most frequent group of contaminants in groundwaters of Germany, with halogen-free ones (i.e., benzene, xylenes, toluene, and ethylbenzene) being more frequent than the halogenated ones (i.e., chlorobenzene, dichlorobenzene). In the United States, this group of substances is represented by toluene and benzene only. Instead, the spectrum of contaminants at U.S. sites is enlarged by phenol, acetone, and bis-(2-ethylhexyl)-phthalate. As a result, 9 organic contaminants are common to both lists.

The detection frequency of contaminants in groundwaters is closely related to their groundwater currency (i.e., mobility, accumulation, and persistence). The priority contaminants evaluated here are characterized by a high mobility potential (high solubility and high vapor pressure) and a low potential for bio- (low octanol-water partition coefficient) and geoaccumulation (Sabljic, 1987; Kerndorff et al., 1988).

The evaluation procedure for waste sites given here holds true in a limited way for contaminated industrial land only because investigations of the latter have to take into account substances that are expected due to specific production processes (Schleyer et al., 1988).

Management of Abandoned Contamination Sites

From a regulatory perspective, abandoned landfills are abandoned and inactive waste disposal sites (regardless of the point in time at which they were rendered inactive), illegal waste disposal sites that existed before the enactment of the respective waste laws (so-called illegal dumps), and other abandoned/inactive dumps or fills, whereas abandoned contamination sites are "sites of inactive installations that handled environmentally hazardous substances" (i.e., these are primarily old industrial and commercial facilities).

Since the mid-1980s, a standardized approach has been developed for evaluating abandoned landfills that begins with determining the hazard potential and developing a remediation concept. After the existence of the contamination has been confirmed, the next step

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is usually a combination of source control measures, which often consist of capping [in some cases, encapsulation with a retention wall has been used, but there is no example yet for a subsurface (below waste) liner] and hydraulic processes. The length of the first period is about 10 years. This is an indication that solving these kinds of contamination problems is a task that will take a century to complete. In the face of this complex situation and the expected high costs for some of the larger abandoned landfills, it is doubtful whether they will ever end up in the second phase of actual remediation.

Suspected contaminated sites have to be assessed as to their potential environmental hazard in order to identify which sites have a high priority for remediation. For economic reasons, it is necessary to use a systematic approach for assessing these sites. Prerequisites for public acceptance of the necessary administrative decisions and measures include the ability to follow through and the ability to provide straightforward responses (Anonymous, 1990). The respective hazard potential of a suspected site can be described as a function of the three independent criteria: substance characteristics, site characteristics, and use characteristics.

With regard to the substance characteristics, there are solid data available on which to base decisions—especially for aqueous components but also for contaminated solids. The substance approach therefore should have priority during the investigation of abandoned contamination sites.

Evaluation Scheme. As an example for the sequence of steps taken during the assessment of abandoned contamination sites, the following subsections describe an approach that has developed in Germany since 1985.

Phase 1: Data Collection. Sources for the collection of data on abandoned contamination sites used to be company files, maps, documents, and/or plans at building inspection offices (i.e., national, regional, county, and municipal archives); interviews with former employees; and monotemporal analyses of maps and aerial photographs. The weaknesses of these data-collection methods lie in the facts that this data gathering is random and incomplete and does not necessarily cover the entire area, that it does not follow a chronology, and that it provides inaccurate information of the areal extent of contamination. It is becoming increasingly clear that only multitemporal aerial photograph and map analyses provide objective, comprehensive, precisely identifiable, and largely corroborated data on abandoned contamination sites.

Phase 2: Comparative Assessment. Based on a formalized assessment and classification procedure, priorities for conducting investigations on known sites are determined. Assessment criteria that need to be known in order to classify abandoned contamination sites are

- Substance inventory of the suspected contaminated area
- Emissions from the suspected contamination site
- Migration potential of the substances into various environmental media
- Land use of the suspected site and use of the potentially affected environmental media

The comparative assessment usually is based on the information available in a listing of suspected contamination sites. In addition, some states have begun conducting preliminary studies of groundwater and soil in order to better support priority ranking and to improve the ability to recognize the need for immediate emergency action. In this process, a phased approach is used where preliminary chemical analyses of a few parameters are performed to find out whether there are any impacts to air, water, or soil and, after positive findings, proceeds to more detailed studies to determine more accurately the type of contamination. In the usual three-step analysis (screening, contaminant identification, and areal investigation), the third step involves a detailed areal investigation (phase 3) and includes gathering data to guide the process up to a site-specific evaluation (phase 4).

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An example of the three-step analysis conducted by scientists of the Institute for Water, Soil, and Air Hygiene of the German Environmental Office (Kerndorff et al., 1985) is provided in Fig. 12.1. It shows the preliminary results of groundwater quality downgradient of 33 abandoned contamination sites. A screening for boron, sulfate, and absorbable organic halides (on activated carbon) (AOX) and a gas chromatographic fingerprint comparison of typical organic substances identified, for most samples, positive evidence of groundwater contamination. The next phase (contaminant identification) included analyses for additional landfill-typical inorganic and organic trace compounds, which resulted in shortening of the suspected list to 24 sites. For the sites where highly impacted groundwater was identified, further detailed areal investigation (phase 3) was conducted.

Phases 3 and 4: Detailed Areal and Site-Specific Investigation. Aside from chemical analyses in the vicinity of the suspected contaminated sites and in the surrounding environmental media, it is necessary to conduct geophysical and geological investigations for an areal assessment of the site. The extend of the assessment depends on the local conditions and on the goals of the subsequent site-specific evaluation. The parameters of concern in groundwater, soil, and air emissions of abandoned contamination sites are similar to the characteristic quantities that are important for monitoring landfills.

Risk Assessment. Risk generally is considered as the result of a process where some potential hazard (a toxic substance or other agent) could lead to an adverse effect in the receptor (i.e., people, animals, and plants, ecosystem processes, water resources, and buildings). For this process to operate, there must be a connection (a pathway) between the potential hazard (the source) and target for protection (the receptor). Theoretically, therefore, risk reduction may be achieved by removing the source, by breaking the pathway, and/or by removing the receptors (Anonymous, 2000).

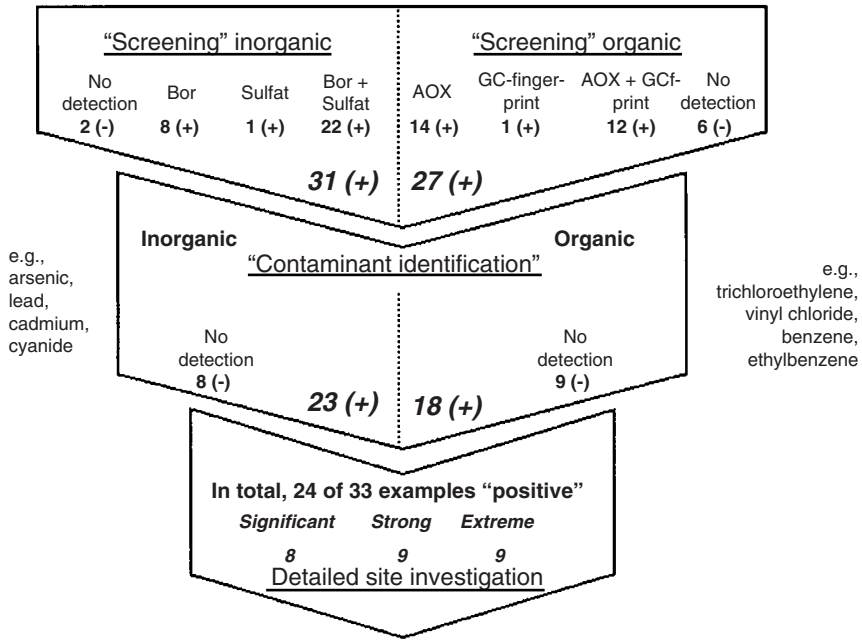

FIGURE 12.1 Example of the three-step analysis for groundwater sampling. *(After Kerndorff et al., 1985.)*

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Risk assessment of contaminated sites is somewhat different from risk assessment in other fields (Vegter, 1998). The evaluation of the risk of soil contamination is not a preventive approach. Unlike in the other fields, the source is already there. This makes the assessment easier in principle because claims about exposure and risks can be verified at the site. In practice, however, this advantage is rather limited due to the complexity of the soil environment and difficulties in performing experiments. If solutions to soil problems (i.e., cleanup goals) involve risk considerations, a predictive risk assessment must be performed, which has more in common with risk-assessment methods used in other fields.

Contaminated land risk assessment generally considers the following end points (Vegter, 1998):

- *Human health.* Acceptable daily intake (ADI), tolerable daily intake (TDI), and cancer risk levels are used to quantify this end point.
- *Ecological risk.* This is mostly quantified at present on the basis of laboratory toxicity experiments.
- *Groundwater risk.* This risk is related to the dispersion of pollution in groundwater.
- *Construction.* Effects of soil pollution on structures and construction work.

A general overview of risk assessment, from preliminary investigations to conclusions about risks and communication, is illustrated in Fig. 12.2. Although risk perception and communication are located at the end of the assessment process, it must be stressed that perception already may influence decision making as soon as preliminary investigations suggest that the site of concern is suspect. The strength of the risk-assessment methodology is to keep decision making as objective and transparent as possible in order to prevent politicization due to different perceptions and interests of the parties involved.

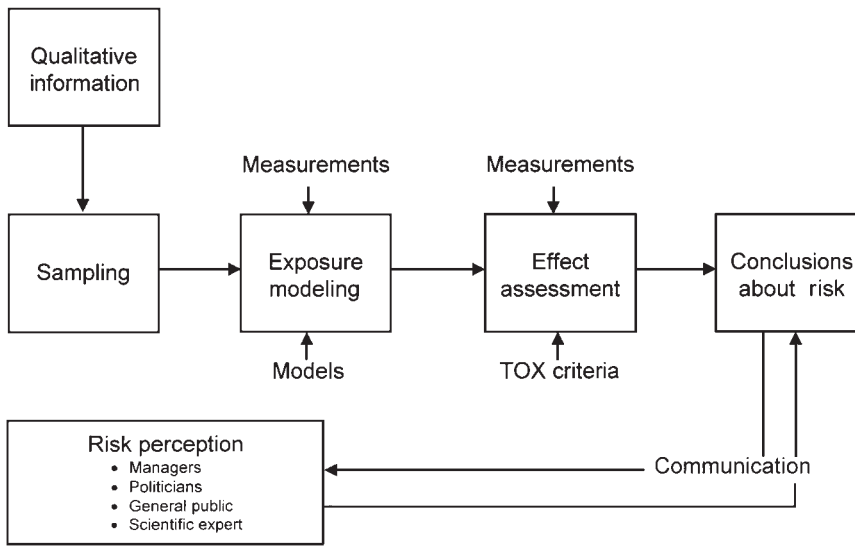

FIGURE 12.2 The different steps to be taken in risk assessment.
(After Vegter, 1998.)

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The risk-based land manager has to address the following requirements in order to ensure the sustainability of the solution for a contaminated land problem (Anonymous, 2000):

- Land-use-related requirements
- Spatial-planning requirements
- Management requirements

Land Use. Different land uses have divergent needs. For example, some land uses require direct access to the soil, preventing the use of containment measures such as capping with concrete or asphalt. Others may require preparation of the site for geotechnical purposes, e.g., to support foundations.

Spatial Planning. Whether land use will be allowed to change may be incorporated in spatial planning, which may then contain specific requirements for the number of potential uses for which the site should be treated. Spatial planning also should address the subsoil, especially in view of groundwater and surface water. If a land-use change is considered, the consequences for the hydrogeology and the behavior of contaminants that may be present must be assessed properly.

Management. Solutions for contaminated land problems have to be sustainable. Environmental side effects of remediations, available space and facilities, local perceptions, and socioeconomic issues such as funding mechanisms and communication with stakeholders and the general public may affect the choice of certain solutions over others. The manager also will have to deal with values that hardly can be expressed in terms of risk or utilitarian concepts such as land use or function. The conservation of pristine underground environment and geological and archeological values are examples of this. Moreover, legal constraints may prohibit some treatment options and risk-management solutions. There is also the question of how the decision-making process is organized. Will it be a dynamic and open decision-making process involving all interest groups, or can a standard flowchart protocol or mandatory decision-support system be applied by a single decision maker?

Contaminated land risk assessment is still underpinned largely by scientific research done for other purposes (Ferguson et al., 2000). The nature of the assessment is to a large extent determined by the availability of these more or less usable scientific building blocks. Whether current assessment procedures really address the question of risk in a rigorous, quantitative way may be questioned. Further development and integration of the building blocks needed for risk assessment are of the utmost importance if assessment is to be more than a mere sequencing of separate disciplines such as soil and water sampling, chemical analysis, exposure modeling, and toxicology. In a fully integrated approach, choices of toxicological end points must have consequences for the design of sampling schemes and exposure models, and vice versa. Uncertainties at each stage in the assessment should be recognized and may lead to the use of probalistic or other techniques for dealing with uncertainty. Decision-support systems may provide guidance for risk managers to help balance reduction of uncertainties against the costs of additional investigation. Integrated risk-assessment procedures have yet to be fully developed, and progress will depend on research in two main areas:

- The nature of contaminated land, which deals with the identification and analysis of pollution and its impact on human health, water resources, and other environmental receptors
- The relationship between soil and water contamination and fitness for use, which specifies the conditions for sustainable land use in urban and rural areas (Ferguson et al., 1998).

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Policy and Practice. Contaminated land approaches in various countries show differences in their legal basis and policy formulations. In practice, however, it seems that the outcomes of decisions about how to remedy a polluted site often are very similar for similar circumstances. There are a number of reasons for this in the European situation (Anonymous, 2000):

1. The repertoire of applicable remediation techniques is rather limited.
2. The emerging European consensus on risk-based decision making and risk management is based on controlling the source-pathway-receptor linkage.
3. Decisions have to take the very large uncertainties in risk assessment into account and often are precautionary, irrespective of some differences in remediation targets in various countries.
4. Practical constraints, costs, and other resource limitations affect remediation projects in all countries. For large sites, remediation can be very costly and therefore is related mostly to the intended use of the site, or the use of the site is made dependent on the results of a feasible remediation.

The idea that the results of contaminated land remediation would be more similar than the underlying national policies might imply was first discussed at a Water Environment Federation conference in Washington in 1993 and since then has been considered as an interesting statement to test in practice.

In October 1997, two concerted actions funded by the European Union (EU), Concerted Action on Risk Assessment for Contaminated Sites in the European Union (CARACAS) and Network for Industrially Contaminated Land in Europe (NICOLE), identified a number of research needs, such as behavior and biological availability of soil contamination, ecotoxicology, and human toxicology, as well as the development of integrated assessment approaches and their implementation. There are certain fundamental principles on which all 16 countries participating in the CARACAS project appear to agree (Ferguson et al., 2000):

- The need to prevent or limit future pollution
- The polluter pays principle, usually with a mechanism for helping innocent land owners
- The precautionary principle
- The use of risk-based philosophy for identifying, prioritizing, and assessing the need for remedial action

Nevertheless, despite a convergence of philosophy, there appear to be large differences in the practice of dealing with land contamination in the various countries. There is a distinct lack of research on these differences and their implications, but they appear to include the extent to which the designs of site investigations and risk assessments are integrated and the role of statistically based data quality objectives in those designs, the use of generic guideline values and other risk-assessment methodologies, decision-support procedures for identifying optimal remedial strategies, and procedures for communicating about risks and benefits to relevant stakeholders (Ferguson, 1999). These differences inevitably affect the cost of dealing with land contamination from one country to another. Such cost differentials, in turn, will affect company profits, business confidence, attractiveness to inward investors, and so on. Differences in risk-management outcome also may affect public health and levels of ecosystem protection and/or the perception of these.

A major issue for all industrialized countries is how to reduce the cost of dealing with land contamination without compromising public health and water quality or business confidence in the benefits of land regeneration and sustainable use of soil. These issues are

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being addressed in the concerted action project (by Contaminated Land Rehabilitation Network CLARINET; 1998–2001; information available at *http://www.clarinet.at.*)

Current contaminated land approaches as developed by CLARINET focus on sustainable solutions, which will restore the usability and economic value of the land. These solutions can be characterized by four elements (Anonymous, 2000):

1. *Fitness for use.* This is achieved by reducing human health risks and ecological risks as necessary to permit the safe (re)use of the land. It is focused on quality requirements of the land for its uses and functions.

2. *Protection of the environment.* For example, one approach involves preventing further spread of pollution by surface water and groundwater. Environmental protection of soils as a resource also may lead to policies favoring land recycling by redevelopment of brownfields instead of greenfields.

3. *Reduction of aftercare.* Sustainable solutions minimize the burden of aftercare. Endless pump and treat solutions or containment walls that require monitoring and maintenance forever may be less desirable in view of the amount of aftercare required.

4. *The design of the solution.* This involves the best strategy to meet all requirements in a sustainable way, including environmental side effects, available space and facilities, local perceptions, and other issues. Concerning the technical aspects, optimal solutions are likely to involve a mixture of approaches. An interesting possibility is to combine a fast-acting temporary measure with a longer-term extensive treatment to provide an optimal balance of risk management, maximizing wider environmental merits and limiting costs. Moreover, the soil environment itself has some interesting characteristics that may help in reducing the risk. Soil has a natural capacity to act as a barrier, which can be used in containment approaches, and it has a natural capacity to biodegrade substances. If these natural capacities can be used, the costs of solutions will decrease. The use of the natural capacities of the soil environment in remediation or contaminated land management solutions needs to be further explored from both a scientific and a regulatory point of view in order to meet the general sustainability requirements of soil protection.

SEDIMENT PROBLEMS

Even until late in the twentieth century, sediment was regarded as a very valuable source for humans (agriculture) and nature. This perception rapidly and drastically changed when it became clear that sediments not only were enriched with nutrients but also were, as a legacy of industrialization and related mass consumption, a perfect sink for natural and human-made hazardous pollutants. From this moment on it took only a few decennia to no longer praise sediment as a source but to disqualify it as a hazardous waste, thus leaving an immense problem for water quality managers and other stakeholders to deal with (Anonymous, 2001).

Historical Review

Modern research on particle-bound contaminants probably originated with the idea that sediments reflect the biological, chemical, and physical conditions in a water body (Züllig, 1956). Based on this concept, the historical evolution of limnological parameters could be traced back from the study of vertical sediment profiles. In fact, early in the 20th century, Nipkow (1920) suggested that the alternative sequence of layers in a sediment core from

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Lake Zürich might be related to variations in the trophic status of the lake system. During the following decades of limnological research on eutrophication problems, sediment aspects played only a marginal role until it was recognized that recycling from bottom deposits can be a significant factor in the nutrient budget of an aquatic system. Similarly, in the next global environmental issue, the acidification of inland waters, sediment-related research only gradually became involved. Here too it is now accepted that particle interactions can affect aquatic ecosystems, e.g., by enhancing the mobility of toxic metals.

In contrast to the eutrophication and acidification problems, research on toxic chemicals has included sediments aspects from its beginning: artificial radionuclides in the Columbia and Clinch rivers in the early sixties (Sayre et al., 1963); heavy metals in the Rhine River system in the late sixties (De Groot, 1966); and methyl mercury (Jensen and Jernelöv, 1967) at Minamata Bay in Japan, in Swedish lakes, in alpine lakes, in the Laurentian Great Lakes, and in the Wabigoon River system in Canada; organochlorine insecticides and PCBs in St. Clair Lake and Lake Erie during the seventies (Frank et al., 1977); and chlorobenzenes and dioxins/furanes in the Niagara River system and Lake Ontario in the early eighties (Oliver and Nicol, 1982; Smith et al., 1983).

The study of dated sediment cores has proven particularly useful because it provides a historical record of the various influences on the aquatic system by indicating both the natural background levels and the human-induced accumulation of elements over an extended period of time. Marine and, in particular, lacustrine environments have the ideal conditions necessary for the incorporation and permanent fixing of metals and organic pollutants in sediments: reducing (anoxic) and nonturbulent environments, steady deposition, and the presence of suitable fine-grained mineral particles for pollutant fixation. Various approaches to the dating of sedimentary profiles have been used, but the isotopic techniques, using ^{210}Pb, ^{137}Cs, and $^{239+240}$Pu, have produced the most unambiguous results and therefore have been the most successful (see review by Alderton, 1985).

On the basis of data from a sediment core from Lake Constance, Fig. 12.3 demonstrates the development and the present situation of environmental pollution with specific contaminants:

- During the last decades of the twentieth century, environmental pollution history began with an increase in heavy metals, reaching a maximum between about 1960–1970.
- A series of artificial radionuclides (e.g., ^{137}Cs, ^{239,240}Pu, ^{55}Fe) was introduced into the environment as a result of atmospheric weapons testing during 1952 and 1962. The sedimentary record reflects the intensity of the radionuclide emissions in the high atmo-sphere with a delay of only 1 year. Concentrations begin to rise from 1953 to 1963; from then on, a steady decrease is observed. Emissions of radionuclides from the Chernobyl catastrophe in May 1986 provided a pulse that now presents an opportunity to study transport processes in atmospheric, terrestrial, and aquatic reservoirs and specifically mechanisms involved in sedimentary processes (Santschi et al., 1988).
- Worldwide studies (Müller, 1981) revealed that individual heavy metals and polycyclic aromatic hydrocarbons (PAHs) show parallel evolution patterns, and it is concluded that both groups of pollutants could stem from a common source: combustion of coal and lignite as a consequence of increasing industrialization, chiefly in the northern hemisphere.

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- There is a certain similarity between the heavy-metal/PAH profiles and the temporal development of dioxins and furans in Lake Constance sediments, indicating that part of these compounds could originate from combustion of coal and lignite as well.
- Since World War II, halogenated hydrocarbons have become significant toxic compounds in marine and other ecosystems.

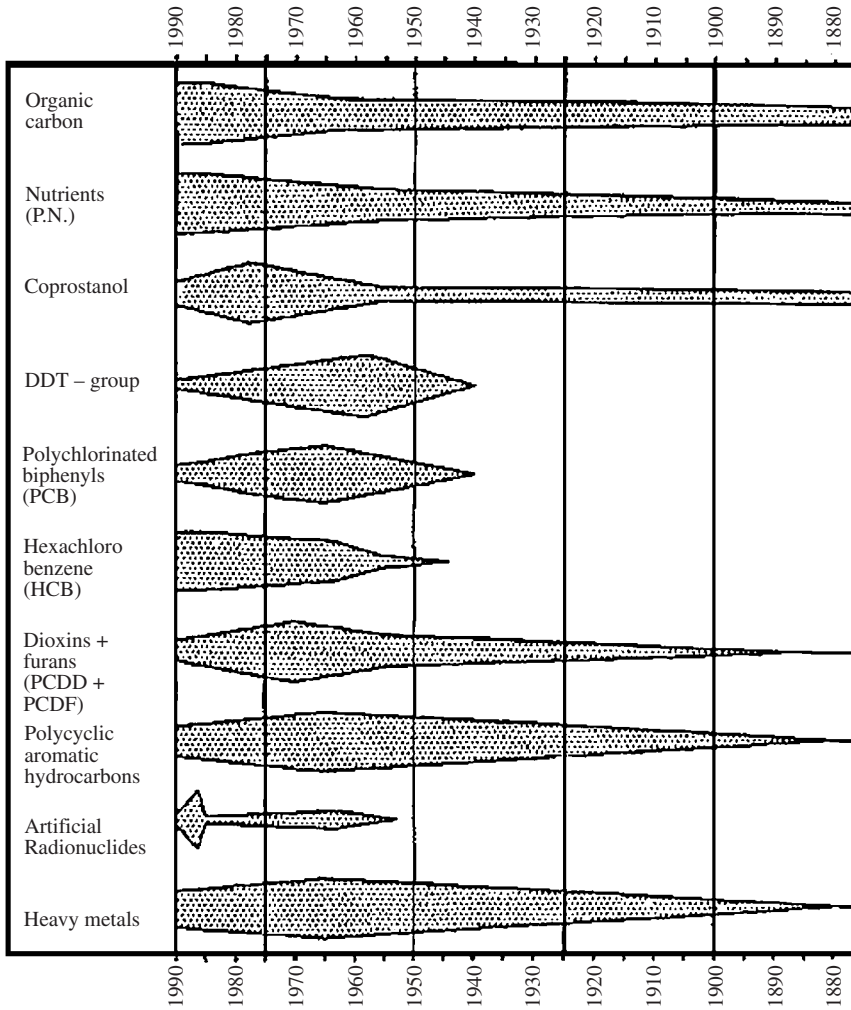

FIGURE 12.3 Lake Constance sediment geochronology for contamination and eutrophication. *(From Müller, 1991.)*

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- Polychlorinated biphenyls (PCBs), which have been used as plasticizers in paints, plastics, resins, inks, copy paper, and adhesives (open use), first occur in sediments around 1935–1940, and although their application had been legally restricted to closed systems—dielectric fluids in transformators and capacitors and as components of hydraulic fluids—a decrease in concentration in the most recent sediment layers has not yet been observed.
- The same holds true for DDT (totally banned in most Western countries between 1970 and 1975) and its metabolites. Concentrations begin to rise around 1945 and reached their maximum between 1960 and 1970. The sharp increase of the lindane concentrations is a result of the application of this chemical after the ban of technical γ-benzene hexachloride and other chlorinated insecticides.
- The history of fecal pollution can be traced back in sediments even into preindustrial times. Coprostanol, one of the principal sterols of excreta of higher animals and humans, is an indicator of this type of pollution.

These substances as well as the nutrients phosphorous and nitrogen and organic matter reflect the trophic status of the lake. Recent studies demonstrate that the concentrations of these indicator substances are leveling off or are even declining as a consequence of intensive efforts on water purification around the whole of Lake Constance (Müller, 2000).

Problems with Dredged Material

Many sources contribute to sediment contamination in a river catchment area (Fig. 12.4). These include wet and dry fallout from air emissions; agricultural runoff from farms; solid and dissolved inputs from mines; discharges from landfills, industrial plants, and sewage treatment plants; and direct dumps into rivers, lakes, and coastal seas. At several areas of a river basin the water current is low enough to allow the polluted suspended solids to settle down. The biggest sediment trap can be found, of course, at the end of the river, where, for instance, yearly dazzling amounts of freshwater sediment are trapped in large ports (e.g., annually 10 million m^3 at Rotterdam). However, substantial amounts of polluted sediments are also trapped upstream at flood plains, locks, dams, and smaller ports, as well as at channels connected to the river.

To keep the ports and channels open to ships, to allow a proper functioning of locks and dams, or even now and then to improve the quality of the aquatic ecosystem, the sediment needs to be dredged regularly. Fortunately, the water quality in many large rivers has improved significantly due to the success of transboundary source-reduction measures. Nevertheless, a great deal of the dredged material still remains contaminated to such an extent that free disposal (in water or on land) is not allowed and the (re)use of this material is restricted. Most of this polluted dredged material is therefore disposed of in depots at high cost. Only a small amount of the material is cleaned up because there is still a lack of large-scale, cost-effective treatment techniques. Furthermore, present tools and approaches are insufficient for the sustainable management of sediment and dredged material on a river basin scale (Anonymous, 2001).

Size of the Problem. Dredging is a human activity that can compete with highly dynamic natural sedimentary processes such as landslides. In the 1980s, the International Association of Ports and Harbors estimated that about 350 million tons of maintenance dredging and 230 million tons of average annual new construction dredging occurred. For example, in the harbors around the North Sea, approximately 100 million m^3 of sediment has to be dredged annually—about 10 times the average annual sediment discharge of the Rhine River. Typical problems with these sediments are

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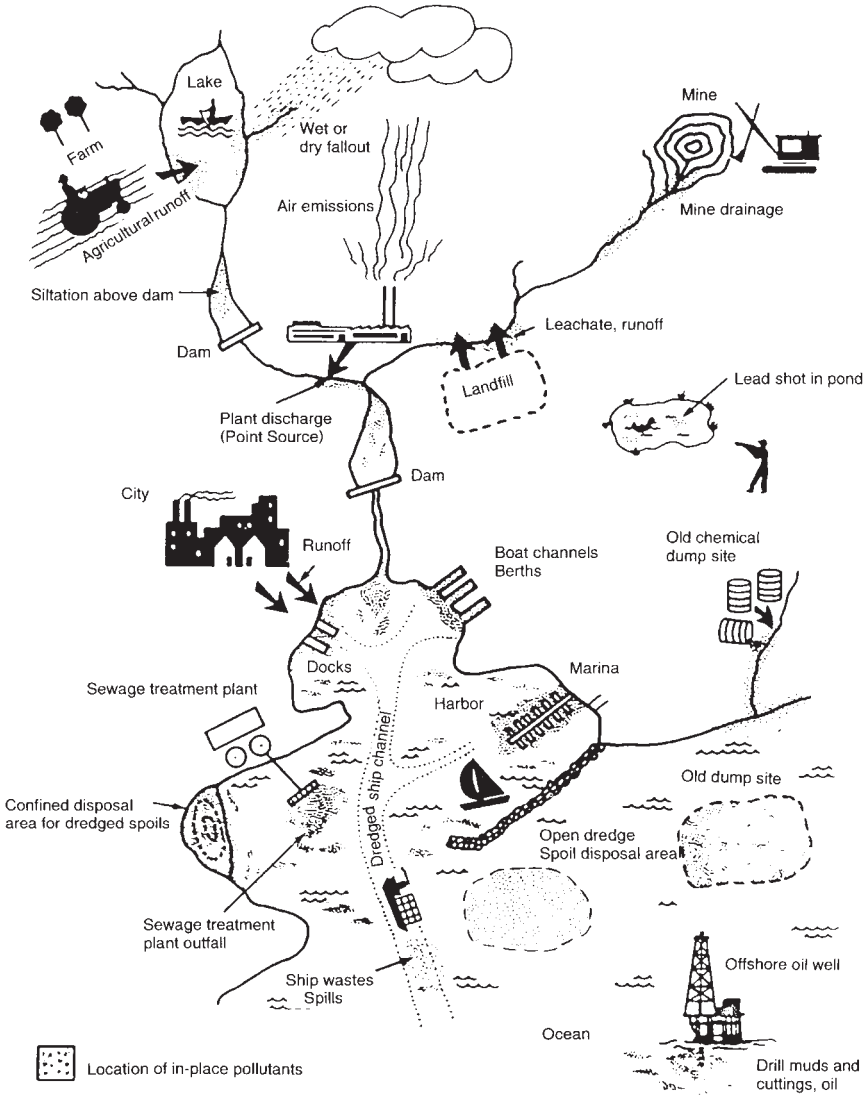

FIGURE 12.4 Location of in-place pollutants.
(From Shea, 1988, after A. D. Little, Inc.)

- Increasing volumes of dredged materials
- High concentrations of toxic substances

And these problems have been concentrated mainly at the mouths of large rivers and in coastal areas.

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Problem Solutions. Given the economic implications, there is increasing worldwide interest in the development of dredging and disposal technologies. Among the authorities dealing with the subject of contaminants in dredged materials, the U.S. Army Corps of Engineer Waterways Experiment Station at Vicksburg, Mississippi, has played a leading role. In the early eighties, the environmental laboratory of this institution, together with U.S. Environmental Protection Agency (EPA), initiated a decision-making framework for management of dredged material disposal that includes test procedures on physicochemical conditions, aquatic bioaccumulation, and water-column effects both at the site of dredging operations and at disposal sites of dredged materials. Further coordinated research was performed by the Assessment and Remediation of Contaminated Sediments (ARCS) group of U.S. EPA, which has been focusing on the Great Lakes areas of concern (1990–1993); an integrated contaminated sediments assessment approach (Anonymous, 1994) includes six topics: sampling design and quality control, sample collection, chemical analysis, toxicity testing, benthic community structure and survey, and tumors and abnormalities. In addition, the ARCS program was charged with assessing and demonstrating remedial options for contaminated sediment problems in the Great Lakes; laboratory tests were conducted using 13 processes, and pilot-scale (field-based) demonstrations of bioremediation, particles size separation, solvent extraction, and low-temperature thermal desorption were conducted (see Chap. 13).

Management of In Situ Sediment Contamination

While remediation and storage of contaminated dredged materials constitute a key issue at harbor sites, there is another type of sediment pollution problem that mainly originates from large-scale dispersion of contaminants in flood plains, dike foreshores, and polder areas. In recent years, catastrophic cases of sediment contaminations have occurred in connection with the failure of tailing dams from mines (Table 12.1).

A special example demonstrating the dispersion of highly contaminated sediments in a large catchment area will be shown from the so-called chemistry triangle of the upper Elbe River system. Unlike problems relating to conventional polluted sites, here the risks are connected primarily with transporting and depositing contaminated solids in a catchment area, especially in downstream regions. Handling of such problems is a complex task that will go beyond the coordinated project described in Chap. 16; it should include other fields such as law, planning, controlling, and public relations. The Spittelwasser area was chosen by the organizers of the international conference ConSoil 2000 for a case comparison, and four expert teams from Denmark, Germany, the Netherlands, and the United Kingdom were invited to participate in this case study; evaluation of the plan was done by members of the Network for Industrially Contaminated Land (NICOLE) and the Contaminated Land Rehabilitation Network (CLARINET). The following information stems from the official report of the German group (Förstner et al., 2000).

Spittelwasser Case. In the course of production of chemical base materials and products for more than 100 years, the production plant areas of the former chemical enterprises as well as the groundwater in the region Bitterfeld-Wolfen were polluted by harmful substances. (e.g., HCH isomers, hexachloroethane, DDT, and other chloroorganic sludges, benzyl chloride residues, distillation residues, lyes, and salts). Chemical analysis and multivariate statistical methods gave significant indication that inorganic processes such as magnesium production could be the main sources for the dioxin pollution (Götz et al., 1996).

Parts of the land surrounding Bitterfeld-Wolfen such as the approximately 60-km^2 large lowland area known as Spittelwasser are affected by pollutants. As a result of floods, the lowland area has been transformed into a large lake landscape of approximately 10 to 30 km^2. With the flowing water, the sediments are deposited and rearranged along the river's

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TABLE 12.1 Examples of Problems with Contaminated In Situ Sediments and Usual Measures Applied for Such Situations

	Problem (example)	Usual measures
Flood sediments	Rhine flood, 1992; Odra flood, 1997*	Analysis of pollution load
Mining accidents	Guadiamar, 1998†; Vasar/Theiss, 2000	Analysis of pollution load
Flood sediments in dike foreshores and polder areas	Alluvial meadows and marshy lands as depressions for polluted sediments of the Elbe River‡	Monitoring measures, restrictions of use

*The flood in the Odra River 1997, *Acta Hydrochim. Hydrobiol.* **27** (1999).

†The environmental impact of the mine tailing accident in Aznalcollar, *Sci. Total Environ.* **242** (1999).

‡Friese, K., Witter, B., Miehlich, G., and Rode, M., eds., *Stoffhaushalt von Auenökosystemen* (Springer, Berlin, 2000).

Additional references:

Friese K., Witter, B., Miehlich, G., and Rode, M. eds. (2000). *Stoffhaushalt von Auenökosystemen: Böden und Hydrologie, Schadstoffe, Bewertungen.* Springer-Verlag, Berlin

Miehlich, G. (1987). Substratgenese und Systematik von Böden der Hamburger Fluβmarsch. *Mitt. Dtsch. Bodenkdl. Ges.* **55**(II): 801–803.

Müller, A., and Wessels, M. (1999). The flood in the Odra River 1997: Impact of suspended solids on water quality. *Acta Hydrochim. Hydrobiol.* **27:**316–320.

Schuster, J., and Miehlich, G. (1989). Tideabhängige Konzentrationsveränderungen in Prielwässern als Ausdruck von Austauschvorgängen zwischen Vordeichsland und Elbeästuar, *Mitt. Dtsch. Bodenkdl. Ges.* **59**(I): 483–488.

Wolska, L., Wardencki, W., Wiergowski, M., Zygmunt, B., Zabiegala, B., Konieczka, P., Poprawski, L., Biernat, J. F., and Namiesnik, J. (1999). Evaluation of pollution degree of the Odra Basin with organic compounds after the 1997 summer flood: General comments. *Acta hydrochim. hydrobiol.* **27:**343–349.

course. Notably in the case of a higher rate of flow the pollutants bound to suspended particles are flushed out of the Spittelwasser. Thus the polluted sediments of the Spittelwasser represent a risk for the areas downstream—for flood sediments of Mulde and Elbe rivers and in particular for the Port of Hamburg an economic risk due to the increased treatment costs; for the North Sea rather an ecological risk.

The problem of the Spittelwasser floodplain area is remarkable in two ways:

1. Soils, sediments, and biological stock of the concerned nature reserve and flood basin are partly strongly contaminated by various inorganic and organic harmful substances due to former industrial activities upstream of the area.
2. Unlike problems relating to conventional polluted sites, here the risks are connected primarily with transporting and depositing contaminated solids in a catchment area, especially in downstream regions.

In Situ Alternatives. To reduce durably the transfer of polluted sediments from the Spittelwasser area, on principle the technical measures listed in Table 12.2 come into consideration. However, all technical measures indicated to prevent hazards in the sense of Sec. 2 of the Federal Soil Protection Act show a number of considerable disadvantages and risks. There should be mentioned in particular

- The use of the dredged material obtained shall be secured as regards waste and soil protection law. The contaminated mass shall be removed as waste requiring special monitoring (comp. Annex 4). The volume and the detailed location of the contaminated sediment portions are not known. There is an essential cost risk.

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- The feasible dewatering and excavation measures represent massive interventions into the nature and landscape protection area the consequences of which may not be assessed at present. The functionality of the floodplain area is, altogether, doubted.

As a result of these considerations, variants connected with massive interventions in the natural household will not be further considered here.

Interdisciplinary Approach. In the study by the German team, a stepwise approach combining different monitoring techniques and remediation measures was proposed (Table 12.3). These include point excavations of critical material, promotion of plant growth as an element for stabilizing the soil and flood sediments, as well as the installation of sediment traps. The design mainly depends on the flow patterns of the water course during flood events and the potential to install some diversions or dams against the inflowing water from the Mulde River.

In the first step, the development of the ecotoxicological effect potential of sediments and soils in terms of time, with special regard to the potential threat to the groundwater, may be investigated and interpreted with the aid of a biological test battery. Appropriate biomarkers should be determined equally. The test battery should be used in a quarterly rhythm, in particular after flood events, to judge the course of the natural processes in terms of time and the measures undertaken.

TABLE 12.2 Potential Technical Measures and Estimated Costs to Reduce Pollutant Transfer from In Situ Sediment Contamination.

Techique	Method	Estimated Costs
I. Poldering	The lowland area shall be dewatered by means of pump and treat methods and be covered with noncontaminated material.	40 million Euros; 15 Euros/m^3 operating costs
II. Sediment excavation	The river bed will be completely desludged (~20,000 m^3 of sludge to be removed). Sediment obtained shall be secured as waste.	14 million Euros including equipment
III. Sediment covering	*IIIa:* Mineral cover (e.g., concrete); *IIIb:* Artificial cover (geotextiles) *Advantage:* Waste requiring special monitoring will not be obtained. *Disadvantage:* River seeks its way. Nature reserve will be damaged.	*IIIa:* 5 million Euros (100 Euros/m^2) *IIIb.* 3 million Euros (60 Euros/m^2)
IV. Shift of river bed	The Spittelwasser River will get a new river bed. The unpolluted material will be used for covering contaminated sediments.	12 million Euros including equipment
V. Course correction	Following correction of the Spittelwasser course, the highly polluted bank sediment will be covered with unpolluted, dug-out material	6 million Euros; ~400 Euros/m^2

Source: Förstner et al. (2000).

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TABLE 12.3 Stepwise Implementation of a Combination of Monitoring Systems, Technical Measures, Testing Devices, Operation, and Aftercare

I. Monitoring system	Detection of the flood-dependent pollutant transport behavior shall be monitored by hydromechanical methods and air-based systems.	400,000 Euros, 1 to 48 months
II. Regulation project	(1) Implementation of models for sediment and pollutant transport, (2) installation and use of sediment traps (point excavation of soil), (3) utilization of "natural attenuation" (incl. promotion of plant growth).	Projects (1) and (3): 530,000 Euros, 12 to 30 months
III. Testing	This refers notably to the functionality and effects of sediment traps. The results shall be used for predicting the pollutant output.	250,000 Euros, 30 to 40 months
IV. Permanent operation	(a) Efficiency control of the complete implementation, e.g., by GIS. (b) Establishment of citizens' advice bureau (children, hunters, etc.).	770,000 Euros, 24 to 48 months
V. Efficiency control	The aftercare shall be carried out continuously and long term according to the example of other permanently observed areas.	225,000 Euros (15,000 Euros/yr ~15 years)

Source: Förstner at al. (2000).

In the second step, measures such as the installation of efficient sediment traps, a point withdrawal of sediments rich in pollutants, yet also the use of the processes of natural attenuation in the floodplain area and promotion of plant growth may be investigated. Methods of efficiency control shall be detected. A conclusive concept for the discharge and treatment of sediments according to the legal targets of soil protection and waste law shall be prepared.

The third step in the proposed project involves testing of the different systems. This refers notably to the function and effect of the traps if these are applied in the one or other form. In the fourth step, the data obtained shall be recorded for the efficiency control of the complete implementation of the concept. Recording is planned in a geographic information system (GIS). It shall be checked if the GIS existing in the administrative district will be suited to meet the requirements. The efficiency control and aftercare, the fifth step, should be carried out continuously and in the long term.

Notably, the following advantages have to be mentioned:

- The contamination in the floodplain area is dealt with in conformity with other regional remediation measures. Their effects can be considered, and synergetic effects can be used. This refers, for example, to dealing with the dredged material obtained, groundwater modeling and groundwater management, and the interdisciplinary cooperation of experts.

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- The transfer of sediments from the floodplain is reduced with an increasing tendency in a way that in the long run no further transport via the Mulde and Elbe rivers into the North Sea is to be expected. The nature reserve will be scarcely disturbed. The growth of plants on top of dry-lying sediments will be supported, and thus susceptibility to erosion will be reduced. The effects of the natural pollutant retention and degradation will be used.

By implementing the proposed measures that also meet the requirements resulting from the EU Water Framework Directive (WFD), a major contribution may be made to developing appropriate strategies for other catchment areas of rivers.

Evaluation by CLARINET and NICOLE. The first impression after reading the plans is that national policies seem to converge and that the plans prepared by the different teams for solving the Spittelwasser problem all point in the same direction. All remediation strategies proposed are risk-based and take land use into consideration; they are trying to find solutions that are to a large extent in line with CLARINET's sustainable contaminated land management concept.

To reduce human health risks and risks for the environment, all plans favor the use of natural processes with various degrees of enhancement. The reasons for this are the expectation of lower costs and minimized damage to the Spittelwasser floodplain nature reserve. The approach to the problem and the development of the plans are different, however, and there are also differences in emphasis on certain aspects of the Spittelwasser problem (Table 2.4).

The Danish plan illustrates the basic approach to the problem by focusing on dioxins. This simplifies the discussion, but other pollutants need to be addressed as well. However, the proposed management schemes and remedial measures also may be effective for other pollutants. The German plan puts much emphasis on management and organization. The necessity for a management organization is also mentioned explicitly in the Danish plan and to a lesser extent in the Dutch plan. The U.K. plan seems to imply that all management issues will be dealt with by the so-called local authority.

The Dutch plan puts the design of integrated system-oriented solutions up front. Groundwater is addressed as a source of contamination, which implies that inputs of pollution to the Spittelwasser system are addressed together with the output of the system to downstream areas and the behavior of the polluted sediment-water system itself. The Dutch plan shares the large concern for destruction of the nature reserve with the German plan, which considers various excavation and capping scenarios too destructive for the nature reserve. Some of these remedial options also were mentioned in the Danish plan but were then considered acceptable.

The U.K. proposal is centered around risk assessment, which is transparently explained for human health risks. The necessity to assess ecological risks is just mentioned but not worked through. By putting risk assessment and local risk reduction up front, the plan leaves the dynamic aspects of the flood plain unapprised. In the U.K. approach, the transport of pollution to the Mulde/Elbe basin and in the end to the North Sea may continue until the source (the Spittelwasser area) is sufficiently cleaned by natural processes. The Danish, German, and Dutch plans give more priority to the pollution-spreading mechanism; they want to control the hydrological system first and aim for risk reduction in the controlled system. The United Kingdom may have had the opposite in mind; if risks can be reduced sufficiently in the first place, then there may be less need to control the dynamic behavior of the system.

Considerable differences are observed in the costs of the remediation as described in the four plans. They depend on the costs of specific control measures and decontamination technologies but also to a large extent on the scope of the problem addressed in the plans.

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TABLE 12.4 Comparison and Evaluation of Country Remediation Plans for Bitterfeld

	Denmark	Germany	Netherlands	United Kingdom
Future land-use restrictions	No use of concern in the Danish approach No restriction of uses	Prohibit groundwater use Restrict growth of edible crops and rearing of animals in residential gardens Undefined restrictions on agricultural areas, nature reserve, and forest	Nature reserve: No picking of fruits, no consumption of fish, no consumption of wild animals Agricultural land: No accumulating crop species, no root crops, grazing of cattle not recommended	Restrict access of humans and other sensitive species where bioremediation is being applied to superficial contamination (e.g., riverbank, woodland) Remove and incinerate vegetation from contaminated areas Monitor agricultural produce; destroy if necessary
Information/ communication	Yes	Extensive, especially in redemption/management strategy	Yes	Yes
Time frame				
Project	3–4 years	4 years	5 years	Many years
Monitoring	—	15 years	30 years	20 years
Costs (Euros)	4 million	2.2 million	61–237 million	188—472 million

Source: Anonymous (2000).

The German and Danish plans mention much lower costs than the Dutch and U.K. plans. On the other hand, the Danish plan only addresses PCDD/F and does not deal with residential areas and groundwater. The German plan consists of low-cost land-use restrictions, and natural attenuation and retention may improve the situation gradually. The Dutch approach leads to higher costs because it addresses more substances, considers the remediation of groundwater as a source of pollution for the Spittelwasser area, and involves management and enhancement of natural capping and biodegradation processes. The high costs mentioned in the U.K. plan are due to the larger number of land uses in the area around the Spittelwasser floodplain (also residential areas) that are considered for remediation with more intensive biological and ex situ treatment.

European Sediment Network (SedNet). At numerous well-respected research institutes around the world, a lot of effort is put in research aimed at providing stakeholders with the knowledge, tools, and approaches needed to be able to assess and manage polluted sediments and dredged material. The complexity of the subject and the general awareness that an international overview of ongoing research activities and thus transfer of knowledge is missing urge the need to set up an international sediment research network (SedNet). Supporting parties are competent authorities, researchers, consultants, dredgers, and stakeholders such as port authorities, water quality managers, and water users. Also, already existing EU networks, such as CLARINET, expressed that they would welcome SedNet because it would be complementary to their networks.

The objective of SedNet is to support the EU Water Framework Directive through helping to provide the tools, knowledge, and integrative approaches needed for the sustainable management of sediments and dredged materials at river basin scale. In general, this objective will be achieved through providing a platform where parties can meet who are interested in issues related to the management of sediments and dredged materials. This is all done in order to catalyze, optimize, or facilitate

- Research activities, which are driven by stakeholder demands
- The coordination of these research activities
- The cooperation between researchers and users
- The dissemination and exploitation of knowledge

SedNet will provide a platform to facilitate information and knowledge exchange via (1) annual conferences, open to all organizations interested in sediment issues, (2) freely accessible proceedings of these conferences, (3) participation of SedNet in working group (WG) meetings, (4) dissemination of state-of-the-art sediment documents via the Web site, (5) an electronic billboard where organizations can find each other and leave their sediment announcements and related questions, (6) a newsletter to the SedNet participants, and (7) reports on SedNet activities in a column in the *Journal of Soils and Sediments.*

In order to ensure manageability, transparency, flexibility, and decisiveness, specific sediment issues will be handled in specific working groups (WGs), three that are technical oriented (WGs 1 to 3) and three that are socioeconomic oriented (WGs 4 to 6):

WG1: Site Investigation and Characterization: Focus on technical issues regarding the physical, chemical, and biological investigation and characterization of contaminated sediment at specific sites and its dredged material. Specific issues dealt with are, for example, development and implementation of monitoring techniques and strategies, data collection and handling (e.g., mapping), sampling and strategies, harmonization of protocols, toxicity identification evaluation (TIE), bioassays, biomarkers, bioaccumulation, and sediment quality assessment, e.g., by using the triad approach.

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WG2: Contaminant Behavior and Fate. Focus on technical issues regarding understanding of the behavior and fate of contaminants in sediment and dredged materials. This WG also will focus on the possibilities to manipulate the behavior and fate and on understanding of the availability of contaminants to aquatic organisms (bioavailability).

WG3: Sediment Treatment. Focus on technical issues regarding the development and implementation of techniques and strategies aimed to treat contaminated sediment and dredged materials. This WG will deal with in situ as well as ex situ treatment techniques: biological (bioremediation) as well as physical and chemical. Disposal of sediment in depots or pits in open water is also part of the scope of this WG.

WG4: Planning and Decision Making. Focus on issues regarding planning and decision making with respect to contaminated sediments and dredged materials. Specific issues dealt with are, for example, the development of decision-support/management tools and systems, sustainable solutions (e.g., reuse), integrative approaches, modeling, prelegislative research, implementation of risk-based criteria, catchment planning and source reduction, and coordination of activities and strategies.

WG5: Risk Management and Communication. Focus on how to deal with the risks of contaminated sediments and dredged materials and how to communicate about these risks. Specific issues dealt with are, for example, the development of sediment quality criteria (chemical, ecological, and bioassays) including the developments of a yardstick for results effect assessment, how to derive from hazard (the potential of a pollutant to cause harm) to risk (the actual adverse effect of the pollutant), communication with citizens (transparency), education and dissemination of knowledge, and risk-assessment strategies.

WG6: Financial and Economic Aspects. This WG will help WGs 4 and 5 to optimize management strategies and construction integrative approaches, among others, by performing benefit-cost analysis.

SedNet is Eu-funded since January 2002 and actually comprises 325 participants from 250 institutions and 25 countries. Contact with and participation of sediment specialists outside Europe will be stimulated. (**http:www.SedNet.org**)

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CHAPTER 13
SOIL AND SEDIMENT REMEDIATION

Ulrich Förstner, Eberhard Beitinger, Frank Tarnowski, Manuel Gehrke, Harald Burmeier, and Patrick Jacobs

INTRODUCTION

Remediation of soils and sediments initially was based on similar processes and technologies, but during the last decade, focus has changed both within and in particular between the two areas. In both fields, the traditional techniques involving mechanical, biological, and—to a minor extent for sediments—thermal processes are still practiced. However, in both areas, a tendency toward so-called geochemical engineering approaches can be seen. *Intrinsic remediation,* using natural attenuation processes to minimize the adverse effects of contamination, is discussed in the scientific world but still has to be implemented in practice. At the same time, however, it becomes clear that technical soil protection has been developed into an acknowledged scientific discipline, where an integrated cooperation among scientists from the disciplines of engineering, chemistry, microbiology, soils, geology, and environmental planning is essential (Research Center "Treatment of Contaminated Soil" of the German Research Foundation, 1988–2000; Stegmann et al., 2001).

At this stage, on the basis of characteristic findings in various research disciplines, a series of example investigations can be listed, which, along with other investigations, can bridge the gap between theoretical process studies and the practical needs for field applications. For soil remediation, this is primarily a characterization of organic matrices, sorption/desorption behavior of hydrophobic organic compounds, and their availability for biological degradation. In the field of contaminated sediments, combined approaches for stabilization include physical ripening processes such as dehydration and shrinkage, increase in permeability, and change from soft consistency to friable or hard; biological mechanisms such as phytostabilization, i.e., precipitation or adsorption near or at plant roots (Joziasse and Gun, 2000); and a wide spectrum of physiochemical aging effects. These techniques could be used for the types of sediment pollution problems that mainly originate from large-scale dispersion of contaminants in flood plains, dike foreshores, and polder areas (see Chap. 12).

In this Chap. 13, both for soil and sediment remediation, innovative securing techniques of the type "*in situ* barriers" are described in two original contributions: (1) In the field of soil management, *in situ* barriers using reactive media to degrade the contaminants present in the groundwater are a promising alternative to the pump and treat technology (O'Hannesin and Gillham, 1992). The design of permeable reactive barriers is discussed with reference to preventing negative effects such as inflow of fine soil particles; precipitation of carbonates, iron,

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and manganese; and loss of effectiveness by uncontrolled growth of biomass (E. Beitinger, F. Tarnowski, M. Gehrke, and H. Burmeier; pp. 13.11 to 13.18).

(2) With respect to the management of dredged sediments, alternative disposal techniques such as underground storage in a salt cavern and subaqueous disposal/capping are presently being evaluated. In particular, subaqueous capping, a relatively new method, has become an attractive concept for isolating contaminated sediments in order to prevent contaminants from being released into the surface water and subsequently into the food chain (Zeman, 1994). As a typical passive in-situ technique, there are no operation costs following installation of the barrier. Ongoing research work focuses particularly on the selection of materials for active barrier systems (P. H. Jacobs; pp. 13.37 to 13.44).

SOIL REMEDIATION

What should be done once soil contamination has been discovered? Here are some of the alternatives available (Thomé-Kozmiensky, 1989; Stegmann, 2001):

- Leaving the contaminated soil in place and limiting use of the site
- Capping or encapsulating the soil in place with impermeable material and applying a layer of clean topsoil
- Excavating the contaminated soil and disposing of it at a hazardous waste landfill
- Treating the contaminated soil in situ (e.g., without excavation), on-site (i.e., at the site), or off-site (e.g., at a facility located elsewhere).

The choice of the remediation method is also of importance for the later use of the site or of the soil. The intensity of handling, i.e., changing the soil, increases from biological treatment to soil flushing to thermal soil treatment. It is possible for some biological and flushing methods to change the original chemical soil properties drastically by adding chemicals and nutrients and by enhancing the growth of microorganisms; the physical soil properties, however, remain the same, and the disturbed soil biology can regenerate within a few years and will again adapt to site conditions. Subsequent land-use restrictions can be the consequence of possible groundwater contamination from applying nitrates and from the release of nitrogen from the endogenous decomposition of microorganism (Slenders et al., 1997).

With in situ soil flushing methods, the residues of cleaners and solvents can contaminate local groundwater temporarily. With on-site (ex situ) soil washing methods, the cleaned coarser material is freed of clay and organic substances; these sand mixtures are suitable primarily as construction material for backfill or subgrade fill. The most extensive change of the soil material occurs during thermal treatment. High-temperature methods largely destroy the organic components and clay minerals, hydroxides are converted into oxides, and primary minerals are reduced to fines. The pH values of thermally treated soils reduced to slurry are very high (pH 11); the products therefore are problematic with respect to any future use. Sandy and rocky soils possibly can be used as backfill; the clayey substrates with a high share of pelletized material are not appropriate for many types of construction stresses. Therefore, it does not seem beneficial to strive for reusing remediated subsoils. The covering of areas intended for horticultural and agricultural use with low- or uncontaminated topsoil is usually a simpler and more economical solution (Leitzinger et al., 1995).

Securing Abandoned Contamination Sites

Remediation methods at abandoned landfills and contamination sites include the excavation, disposal, and/or intermediate storage; the construction of a barrier system with

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SOIL AND SEDIMENT REMEDIATION

surface, vertical, and subsurface liners; and the solidification and/or chemical immobilization of contaminated materials. These safety measures actually do not destroy the contaminants but rather prevent the formation of hazardous conditions caused by the site by reducing the spread of contaminants into the environment. Safety measures, especially excavation and the use of barriers, are justified by the fact that they can be put into place rapidly in the case of acute hazards, with the understanding, of course, that complete remediation will occur at a later point in time (Weber, 1993). Safety measures that disrupt migration pathways are in principle equivalent to decontamination if by their use the protection of human health and the environment can be guaranteed. However, with respect to long-term protection of the environment, decontamination should have a higher value if environmentally compatible methods are employed (Anonymous, 1990).

Excavation and Removal. Although excavating a contaminated area appears to be the most radical and seemingly optimal solution for the site, increasingly this measure is seen in a more critical light. Excavating the soil means in most cases disposal into specially lined and monitored hazardous waste landfills. The required landfill space is simply no longer available today, and "it is an illusion to believe that hazardous waste landfills with sufficient space will ever be available to make excavation a generally desirable remediation method" (Barkowski et al., 1993). The individual steps for excavating are (1) loosening, excavating, and loading, (2) hauling, and (3) unloading and disposing.

One central problem during excavating is the—sometimes unexpected—release of harmful gases. This includes volatile substances that formed anaerobically in the landfill body [e.g., gaseous arsine (AsH_3) from arsenic-contaminated waste]. On the other hand, the possibility should not be overlooked that the oxygen in the previously aerobic landfill body initiated chemical processes that are difficult to predict in risk assessments (Barkowski et al., 1993). Under certain conditions, e.g., when highly volatile chlorinated hydrocarbons are present, it may be possible to withdraw soil vapors (preferably with activated carbon filters). Materials containing a complex mixture of contaminants should—if at all—be removed only after a very careful risk assessment is completed.

Barrier Systems

Hydraulic Measures. Technically speaking, groundwater extraction is one of the simplest ways to control existing contamination and to avoid large-scale contaminant migration. Hydraulic measures not only are used in conjunction with initial remedial measures but also can be used as the primary remediation technology itself by reducing or eliminating contaminants in a treated system. A distinction is made between passive and active hydraulic measures (Thomé-Kozmiensky, 1989):

- Passive measures include the use of interceptor, injection, infiltration, and extraction wells to create a change in the hydromechanical conditions of groundwater. Extraction wells usually are constructed in the immediate vicinity of the contamination, and the groundwater is withdrawn, thus reducing the groundwater level around the well in a cone of depression.
- Active measures are used to collect and treat contaminated groundwater. Collection techniques include the use of extraction wells and shafts, drainage trenches, and open ditches.

Capping. The capping of an abandoned contamination site serves primarily to prevent the infiltration of precipitation into the contaminated area, e.g., the landfill body. It is composed of topsoil, surface water diversion, and water and gas drainage layers as needed.

Cutoff Walls. Vertical containment of waste in abandoned landfills is accomplished by using sheet piling, narrow piling, and slurry curtains. For the construction of *narrow piling,* individual boards, usually between 6 and 8 cm thick, are pile-driven into the ground.

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Slurry curtains offer several advantages (Meseck, 1989): (1) the thickness, depth, and direction of the wall can be specifically adapted to local conditions, (2) the process can be used with specialized equipment even under low ceilings, (3) the native soil is excavated so that the slurry curtain is keyed into an impermeable layer present at the site, (4) practically all types of soil can be incorporated into slurry curtains, (5) the necessary width of the wall can be determined precisely, and (6) it is possible to install prefabricated inserts, plastic liners, or other attachments in the curtain.

Solidification, Stabilization, and Inertization. In its *Handbook of Stabilization/Solidification of Hazardous Waste* (Anonymous 1986), the U.S. Environmental Protection Agency (EPA) defines stabilization and solidification as waste treatment methods that have the following objectives: (1) to improve manageability and physical properties, e.g., by the sorption of free liquids, (2) to reduce the surface area of waste that can be caused by contaminant migration and/or loss, and (3) to limit the solubility of hazardous waste components, e.g., by pH adjustment or by sorption processes.

- *Solidification* describes a process where a bonding agent is mixed with the waste material to create a mechanically solid product (Wiles, 1987). The associated testing methods usually originate in soil mechanics and soils testing (strength, permeability, temperature and moisture resistance, etc.). Together with its technical implementation, this term describes primarily a method of waste treatment.
- *Stabilization* describes the goal of solidification as it relates to harmful components, which is to convert the waste material into a chemically more stable form and to limit solubility of its hazardous constituents. The degree of stabilization is determined by leach tests and studies of sorption, diffusion, and volatilization. At best, stabilization results in immobilization through solidification; the migration of contaminants from the wastes' surface area is prevented or at least minimized.
- *Inertization* describes the mechanisms that cause stabilization or immobilization. The type of inertization is determined by special physical (e.g., electron-optical or x-ray) or chemical methods (e.g., for heavy metals with valence-specific sequential extractions).

Some solidification methods serve only to improve transportability and storability. To do this, liquid and pasty wastes are converted so that any seepage of liquids is prevented and above-ground storage is allowed. In other cases, the goal is material recovery (recycling), especially for large-volume waste materials such as dredge spoils and power plant fly ash.

The processes and techniques of stabilization/solidification (S/S) have matured into an accepted part of environmental technology (Means et al., 1995; Conner and Hoeffner, 1998a). There are different generic and proprietary S/S processes that can be conveniently categorized as follows:

- *Chemical processes.* Cement-based, pozzolan-based, lime-based, phosphate-based, additive-intensive.
- *Physical processes.* Macroencapsulation/containerization, nonchemical microencapsulation.
- *Thermal processes.* Thermoplastic polymer encapsulation, vitrification.

For metals, the primary factors affecting immobilization are pH control, chemical speciation, and redox potential control. For organics, immobilization of constituents can be broken down into two primary classifications: reactions that destroy or alter organic compounds and physical processes such as adsorption and encapsulation (Conner and Hoeffner, 1998b).

S/S processes develop a wide variety of strength and durability values, depending on many factors: waste type, water content, reagent type, reagent addition ratio (mix ratio), curing time, and temperature. Contrary to the opinion held by many, rock-hard solids are

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not always desirable. In landfill operations, a friable, compactable material usually is preferable, and low permeability, while desirable from a leaching point of view, may make operation of a landfill difficult in wet weather (Conner and Hoeffner, 1998b).

Remediation of Abandoned Contamination Sites

The methodological approaches introduced in this section are primarily destructive or decontaminating methods, where the contaminants are eliminated or destroyed in the contaminated soil. The efficacy of individual remediation methods depends on their level of sophistication and the type of contamination.

Chemical-Physical Methods. All remediation methods that remove, convert, or destroy contaminants in a matrix, i.e., soil or groundwater, except thermal and biological methods, are defined as chemical-physical methods. It is possible to pursue a variety of strategies with chemical-physical methods (Offutt et al., 1988):

- Generation of small quantities of concentrated contaminants through conversion and separation
- Generation of relatively large quantities of diluted contaminant streams from which concentrated contaminants have to be separated before disposal

Typical examples of separation methods include washing and extraction processes used for relatively highly concentrated liquids and sludges requiring disposal. The end products of the washing process generally are sludges, saturated absorbents, or distillation residues from the regeneration of extracting agents. Typical examples of division methods include leaching of contaminants from native soil (in situ) with the generation of relatively low contaminated, treatable wastewater or air stripping (extracting soil vapor) with subsequent adsorptive scrubbing. The end products of this scrubbing process are similar to those produced in the concentration process.

Soil Vapor Extraction. For the removal of highly volatile substances with high vapor pressures from the unsaturated zone, suitable extraction techniques are employed. Soil vapor technologies generally are considered relatively trouble-free and low maintenance. The legally required control of exhaust air can be achieved with adsorption, scrubbing, and condensation processes or through incineration. As a rule, adsorption with activated carbon is used (Otten et al., 1995).

Soil Washing Methods. In extractive soil washing, the contaminated materials are cleaned with detergents. The advantage of this process is essentially that no biologically dead soil is generated, and when the extraction is done correctly, inorganic contaminants also can be removed efficiently. In cases where the desired degree of remediation is insufficient, it is possible to add a microbiological treatment step (Hinsenveld, 1993).

The application of on-site chemical washing and flushing methods, which is practiced almost exclusively, requires several process stages. First, the material is homogenized, reduced in size, or divided into fractions through screening. The actual leaching process takes place in a mixer; particularly favorable is contact between the solids and the solution in a fluidized bed reactor. In the next stage, the solution and the decontaminated solids must be separated, e.g., in settling ponds, with filter presses, in hydrocyclones, or in centrifuges. Posttreatment generally consists of a washing process, where the generated solution is processed, e.g., precipitation of inorganic components, volatilization and adsorption, incineration, chemical or microbiological treatment of organic components, and possibly recovery of the extraction agent (Rulkens and Bruning, 1995).

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The properties of water as a washing agent and a solvent can be enhanced with additives. Several types of additives include (1) surfactants that improve the wettability of the soil components and improve the solubility of lipophilic impurities, (2) complexing agents that convert heavy metals and their insoluble compounds into water soluble compounds, (3) flotation agents (collectors and foamers) that convert certain insoluble substances into a separable phase, and (4) acids or bases for pH control, which is necessary for the stability of compounds and for the selectivity of the flotation processes (Venghaus and Werther, 1998; Wilichowski, 2001).

The sufficiently long treatment of each part of the soil particle can be achieved by feeding the soil-water mixture through a screw conveyor that transmits additional axial movement to the particles. In other processes, the soil is thoroughly mixed and homogenized with air and water in a high-pressure jet pipe. Most of the processes have achieved large-scale operational status for cleaning oily organic contamination with throughputs of between 3 and 40 tons of input material per hour. They differ primarily in the details of the individual technological components (Neeβe and Grohs, 1991; Neeβe, 2001; Werther et al., 2001).

Contrary to solvent extraction, in soil washing processes the pollutants are not attacked directly. Therefore, soil washing processes are suitable for the treatment of soils contaminated with both organic pollutants and heavy metals. However, a fairly high proportion of the soil remains as a highly contaminated fine fraction and has to be disposed of.

Although soil washing has proved to be a successful technique for soil remediation for the last 15 years, the initial hope that soil washing would find a considerable market has not been realized. After a fairly strong boom in the beginning of the 1990s, both the state of the market and the technological development have now stagnated. The main reasons are the costs of soil remediation and the possibilities of alternative utilization of contaminated soils (Wilichowski, 2001).

Electrochemical Remediation. Heavy metals and other contaminants can be removed from soil and groundwater with the help of electrokinetic phenomena (e.g., electroosmosis, electrophoresis, and electrolysis). In electrochemical remediation processes, a continuous electrical field is generated with electrodes that are inserted into the contaminated soil (Shapiro et al., 1989; Ottosen et al., 1995; Hansen et al., 1997). Laboratory and pilot tests have been conducted, for example, with acetic acid and phenol as cleaning solutions (Renaud, 1990). With electrochemical treatment, toxic hexavalent chromium has been reduced to a stable nontoxic trivalent species (Haus and Czurda, 2000).

Biological Treatment. Microbiological processes (bioremediation) can be applied in a variety of ways for soil remediation. The abundant soil microflora in the subsurface provide a high decomposition potential for certain organic contaminants such as aromatic and aliphatic hydrocarbons, benzene, toluene, xylene, phenol, or naphthalene. More difficult to break down are chlorinated solvents, chlorophenol, chlorinated pesticides, polycyclic aromatics, and iron cyanides. There are only a few synthetic low- and high-molecular-weight compounds that have proven resistant to microbial decomposition.

Microorganisms. The naturally existing microorganisms at most remediation sites, even under optimal conditions, are insufficient in quantity and ability to break down and effect biological decomposition within reasonable time periods. By selective and specialized growth of microorganisms in laboratory settings, it is possible to develop adapted bacterial strains with particular zest for consuming contaminants. These bacteria are then marketed in dried form for contaminant-specific site remediation (Anonymous, 1990).

The majority of experts in the field consider it more reasonable and cost-effective to use naturally occurring microorganisms in the soil or groundwater to break down the contaminants than to select and/or develop petri-dish microorganisms (Rissing, 1989). For example, a survey of indigenous bacterial flora yielded a heterogeneous spectrum of species, identifying representatives of the genera *Acinetobacters, Alcaligenes, Bacillus, Flavobacterium,*

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and *Pseudomonas.* The diversity of bacteria in such a system is evidence for a high degree of process stability during the decomposition of hydrocarbons.

Despite the general preference for indigenous microorganism populations, the development of contaminant-specific microorganisms (bioaugmentation) has been promoted during the last 15 years (Müller and Mahro, 2001). The use of "specialists" in bioremediation is still a matter of debate. Some people suggest using these specialists only in special cases such as fresh oil spills, where adaptation of the autothonous flora has not yet occurred. In contrast, Portier et al. (1988) stress the importance of specialists in the treatment of old contaminated soils. They suggest that the degradative potential of a site could be enhanced by the exchange of genetic information between the specialists and the autochthonous flora. Schwefer (1988) doubts the usefulness of specialists when the autochthonous microflora are stimulated sufficiently; he claims that exogenously added microorganisms cannot survive in a given environment. From their own studies in the Research Center "Treatment of Contaminated Soil" of the German Research Foundation, Müller and Mahro (2001) conclude that bioaugmentation is only successful when the pollutants are "available" but the autochthonous microflora did not have time to adapt to the pollutant. This is the case in fresh contaminations, e.g., after accidents. In cases where the physiological conditions have not been suitable for biodegradation after the change in conditions, bioaugmentation certainly helps to stimulate the degradation in the initial stages of remediation. In cases where despite the bioavailability of pollutants and of the correct physiological conditions no degradation occurs, antagonistic effects of mixtures of contaminants have to be considered. However, intensive research is still needed in this area to understand the underlying mechanisms and to solve the problems.

Environmental Conditions. In all biological aerobic processes, an optimal environment must be provided for the microorganisms that decompose the contaminants by adding nutrients such as nitrogen and phosphorus compounds, trace elements, and a sufficient oxygen supply. The application spectrum for adding oxygen ranges from aeration with pure oxygen or air to oxygen donors, such as hydrogen peroxide or ozone (Behrendt and Wiesmann, 1989), to indirect oxygen donors such as nitrate. The majority of applications are based on the use of hydrogen peroxide, which breaks down into the environmentally friendly products of water and oxygen. Surfactants may enhance bioavailability of contaminants (Volkering et al., 1992; Breure et al., 1995).

In Situ Applications. Aside from the avoidance of additional environmental hazards, an important cost advantage of in situ processes with microbial methods is the opportunity to collectively remediate soil and groundwater (Alphenaar et al., 1995; Vermeulen, 1995). In order to effect the flushing of the contaminants, clean water is added to wells upgradient of the remediation area (from a deeper aquifer) to raise the water table; this also creates "interceptor wells" that prevent upgradient groundwater from flowing through the contaminated area. In a study where nitrate was used as an oxygen carrier, a mass balance calculated at the end of the study showed that during the 2 years of remediation, about 90 tons of nitrate were denitrified, resulting in the breakdown of about 30 tons of hydrocarbons (Battermann and Werner, 1984).

On-Site (Ex Situ) Methods. These methods require the excavation of contaminated soil. The advantage of these methods is the opportunity to homogenize and loosen the soil. Sometimes materials such as fine gravel, chopped straw, or tree bark are added to serve as carrier materials for microorganisms (Rissing, 1989).

In *landfarming,* agricultural implements are used to thinly spread the contaminated soil over a wide area (Soczo and Staps, 1988; Dubourguier et al., 1995). Any water seeping through is collected in the drainage system and either diverted or recirculated. Depending on the composition of the soil, nitrogen and phosphate fertilizers, lime, and/or soil conditioners (e.g., compost) are added. Conditioning of the soil in landfarming also includes the

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control of temperature and of oxygen and water content; the temperature can be raised by injecting warm air or by creating a greenhouse effect.

Based on the extensive research in the Research Center "Treatment of Contaminated Soil" of the German Research Foundation (1988–2000; Stegmann et al., 2001), mainly at laboratory scale, a full scale process has been developed using high windrows (3–5 m height) with forced aeration (Hupe et al., 2001). It is regulated on the basis of the actual oxygen consumption of the bacteria. The windrows are prepared at optimal water content, which is also monitored and regulated by the addition of adequate additives that ensure sufficient nutrients, organisms, and structure. Due to a self-heating process as a result of biological degradation, the temperature rises and enhances the process. The windrows should be operated under a roof in order to avoid the production of polluted water (Koning et al., 2001).

Thermal Treatment of Contaminated Soils. In general, thermal processes are used where soils are contaminated with volatile or combustible substances. High-temperature treatment is only appropriate for soils contaminated with especially problematic organic compounds (in high concentrations). Thermal treatment processes have the highest efficiency—at least for nonhalogenated organic contaminations—but they are also the most expensive because the subsequent treatment steps for the gases require significant expenditures to destroy or concentrate the contaminants (afterburning and multistage gas scrubbing). All thermal treatment processes are characterized by the need for additional fuel, e.g., heating oil, natural gas, or electricity.

Thermal remediation must take into consideration the properties of the matrix (e.g., the soil type), but the bonding characteristics of the contaminants are also important. The necessary combustible material in the soil, except for humus or wood chips, is usually provided by the contaminants themselves. This share is rarely higher than 20 percent; indeed, usually it is 1 to 2 percent or less. Contaminated soil does not provide enough energy to sustain the heating process and the destruction of contaminants.

With respect to their suitability for thermal remediation, it is useful to divide the soil contaminants into two groups:

Group 1. Volatile, nonhalogenated organic compounds, e.g., solvents, petroleum, and coal-derived hydrocarbons such as heating oil, BTEX, aromatics, and PAHs.

Group 2. Halogenated organic compounds such as highly volatile CFC s (chloro-fluorocarbons), chlorinated herbicides and pesticides (HCH isomers, 2,4,5-T), and natural PVC, PCB, PCDD, and PCDF (as impurities contained in many products and waste products).

Substances in group 1 vaporize at temperatures around 550°C and are partially broken down. This also applies to volatile organometallic compounds and to cyano complexes. PAHs with higher boiling points are borderline compounds in which adsorption to soil particles also plays a role. The complete destruction of organic and cyano compounds takes place in an afterburner at temperatures between 800 and 1400°C with residence times between 0.3 and 0.5 second.

Substances in group 2, which are halogenated compounds, require particular attention because they are the precursor substances for the formation of PCDD and PCDF. For the low-volatility substances, a release from the matrix occurs only at temperatures higher than those for substances in group 1. The residence times for the input substances in the furnace are between 15 and 180 minutes at the required temperature depending on the compound and the process employed. For the afterburning of waste gas, there are relatively large fluctuations in temperatures and residence times: temperatures of between 1100 and 1300°C and residence times between 1.5 and 3.0 seconds are considered to be necessary (De Leer, 1986).

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A classic example of the thermal treatment of contaminated soil is the Ecotechniek-System, which treated more than 800,000 tons of soil in The Netherlands between 1982 and 1990 (Koopmans and Reintjes, 1988; Noorman and Vis, 1995). It has a capacity of 50 tons/h and consists of a rotary kiln, a thermal afterburner, and an exhaust-gas scrubber. The soil enters in precisely metered quantities at the cold end of the 15-m rotary kiln, proceeds through the kiln while constantly being turning, and is heated initially by indirect heat exchange and later directly by hot gas in countercurrent flow. After multistage waste heat recovery, the waste gas is dedusted and then scrubbed. The use of a spray dryer for the scrubbing residues permits the system to operate wastewater-free (Fortmann, 1990).

Two further techniques of thermal treatment have been studied in the German Research Foundation (1988–2000; Stegmann et al., 2001).

- Residues from soil washing, for example, can be further treated by means of extraction with "critical water" at temperature of 374°C and a pressure of 22.1 MPa (Brunner et al., 2001). This system has been developed on a laboratory scale and has proven to be of general applicability.
- Organic residues in the fine soil particles as a result of soil washing have been treated in the so-called steam stripping process, which consists mainly of a pipe reactor in which the polluted fine particles are fed as a suspension (Niemeyer, 2001). Due to the energy input, the water is evaporated spontaneously, and the organic pollutants are transferred into the steam phase.

Good experience so far has been gained with soils polluted with mineral oil and low condensed PAHs. The advantages of this process are the relatively low operation temperatures of around 300°C and low off-gas volumes. In addition, the fine fraction from soil washing can be reused without the need for a further dewatering step (Höhne and Niemeyer, 2001).

Innovative Treatment Technologies

Innovative treatment technologies—according to the definition of U.S. EPA—are alternative treatment technologies for which routine use at superfund and similar sites is inhibited by lack of data on performance and cost (Anonymous, 1996).[1] In general, a treatment technology is considered innovative if it has had limited full-scale application. Often, it is the application of a technology or process to soils, sediments, sludge, and solid-matrix waste (such as slag) or groundwater that is innovative. Examples include the following:

Soil Technologies

- Contained recovery of oily wastes (CROW)
- Cyanide oxidation
- Dechlorination

[1]An overview on various aspects of innovative site remediation technology has been published by WASTECH, a multiorganization cooperative project managed by the American Academy of Environmental Engineers with grant assistance from the U.S. Environmental Protection Agency, the U.S. Department of Defense, and the U.S. Department of Energy in an eight-volume series edited by William C. Anderson (1995). The U.S. EPA has a vast source of information on remediation technologies that is accessible via the World Wide Web. The Clu-In Bulletin Board System (BBS) has a Web page at *http://www.clu-in.com/.* Some publications are listed on the Web as document numbers only. These can be ordered from the U.S. EPA's National Center for Environmental Publications and Information via FAX at (513)489-8695.

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- Hot air injection
- In situ flushing
- Plasma high-temperature metals recovery
- Solvent extraction
- Thermal desorption
- Vitrification

Groundwater Technologies:

- Air sparging
- Dual-phase extraction
- In situ oxidation
- In situ well aeration
- Passive treatment walls

The latter method (i.e., in situ barriers using reactive media to degrade the contaminants present in the groundwater) is a promising alternative to the pump and treat technology (O'Hannesin and Gillham, 1992). Zero-valent iron has been shown to rapidly dechlorinate a wide range of chlorinated hydrocarbons in laboratory batch and column experiments and has been used successfully to dechlorinate trichloroethylene and perchloroethylene in a field demonstration of a reactive barrier system (funnel and gate technique) (Gillham, 1996). In the following subsections, the design of permeable barriers according to a patented treatment wall construction of WCI Umwelttechnik GmbH is presented.

In Situ Groundwater Remediation with Permeable Reactive Barriers. According to the U.S. EPA (Anonymous, 1997), "a permeable reactive barrier (PRB) is a passive in situ treatment zone of reactive material that degrades or immobilizes contaminants as groundwater flows through it. Natural gradients transport contaminants through strategically placed treatment media. The media degrade, sorb, precipitate, or remove dissolved organics, metals, radionuclides, and other pollutants. These barriers may contain reactants for degrading volatile organics, chelators for immobilizing metals, nutrients and oxygen for microorganisms to enhance bioremediation, or other agents."

Permeable reactive barriers commonly have been or are designed to be installed through excavation and replacement. This method is limited to approximately 8 m in depth, and the costs becomes prohibitive at greater depths. Alternative installation methods for greater depths include slurry wall construction, high-pressure jetting, deep soil mixing, and hydrofracturing in the United States. In Germany, large-diameter vertical borings, slurry methods, and a modified deep wall construction are under evaluation or investigation but have not yet been tested in the field.

The hydraulic behaviors of the two major permeable treatment wall design types—funnel and gate systems or continuous reactive walls—are based on the hydraulic permeability of the whole construction system, including permeability of filter layers, screens, and the treatment medium itself. The system permeability of the wall construction should be at least 2 times higher than the permeability of the aquifer. It might be better to choose a factor of 10 times higher permeability for the wall system with respect to all limitating parameters that will reduce permeability with time. The major limitating factors are expected to be as follows (Beitinger et al., 1998):

- Inflow and settling of fine-grained soil particles, which will block the pore spaces and reduce the permeability

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- Precipitation of carbonates such as calcium or magnesium carbonates, iron oxides/hydroxides, and ferrous carbonate or other metal precipitants in the filter layer or the treatment medium
- Uncontrolled growth of microorganism, such as bioclogging
- Other, mainly long-term and unknown effects, which may reduce the permeability

Major design objectives are:

- Prevent the inflow of fine-grained soil particles by installing a filter layer between the adjacent soil and the treatment medium according to the well-known filter criteria
- Prevent changes to the physical and chemical properties of the groundwater such as temperature, pressure, pH value, oxygen content (redox potential), and nutrients or be aware that those changes will result in precipitation or microorganism activity that might be of advantage in a specific case
- Design a wall system that allows removal and replacement of the treatment medium after a period of several years or decades
- Design a pipe system in the wall to allow the injection of water and/or air for flushing to eliminate precipitants or sludges or to remix the medium by turbulence
- Design openings for inspection, removal, or sampling of the treatment medium

Design of the Permeable Treatment Walls (E. Beitinger, F. Tarnowski, M. Gehrke, and H. Burmeier). WCI Umwelttechnik GmbH has developed a special method of wall construction that allows the adsorbing or other reactive medium to be recovered without the need to demolish and rebuild the wall structure. The patented system includes filtration layers to prevent inflow of fine soil particles and measures to avoid precipitation by oxidation of iron and manganese.

As shown in Fig. 13.1, the main design components are

- A filter layer consisting of gravel or sand pack located between the trenched aquifer and the interior wall elements
- Interior wall elements made of specially designed brick elements or precast concrete shells to define an interior filling space for the treatment medium including openings for the groundwater through flow and horizontal elements to stabilize the earth pressure
- A clay seal to prevent inflow of storm water and contact with the atmosphere
- A cover plate as an opening device for recovery and replacement of the treatment medium (additionally, these covers can be made waterproof and airtight)

Typical dimensions are shown for a cross section of the wall construction in Fig. 13.2.

The installation consists of the following steps (see Figs. 13.3 through 13.6):

1. In phase 1, sheet-pile walls will be driven into the earth. The distance between the piles will be 1 m or more, according to the chosen system width. The sheet piles will be installed to 2 m into the bottom layer of the aquifer.
2. In phase 2, excavation will commence within the two sheet-pile walls. An open ditch will be used to lower the groundwater table below the excavation level (Fig. 13.3).
3. After completion of the excavation, a concrete base layer will be cast in situ, and dewatering will be continued. The horizontal earth pressure will be supported with beams.

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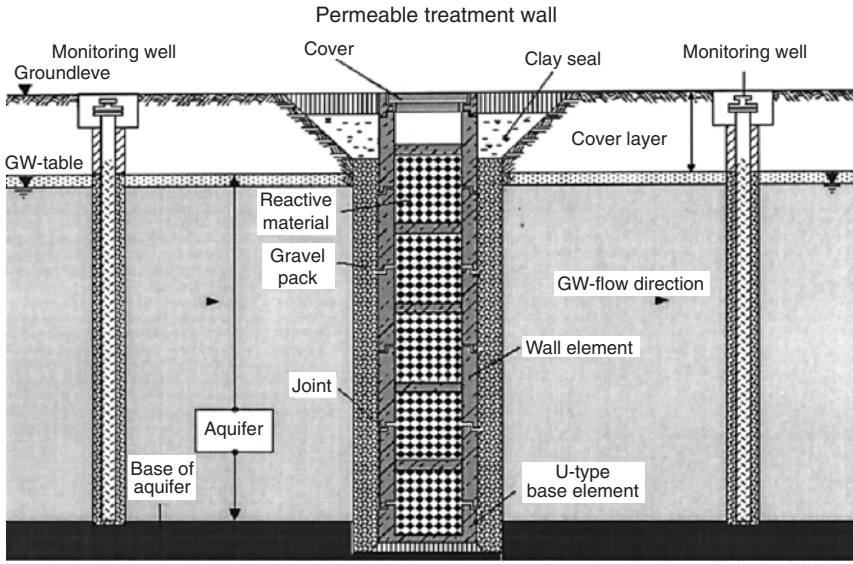

FIGURE 13.1 Permeable treatment wall construction.

4. Then the installation of the form-work elements and placement of the filter gravel can begin on the concrete layer. When the construction grows, the groundwater level can be allowed to rise again (Fig. 13.4).
5. As the wall construction continues, sheet piles can be raised accordingly, and the treatment medium will be filled into the interior space of the form-work elements (Fig. 13.5).
6. Finally, the wall cover, the clay seal, and some other measures can be installed to complete the construction. Additionally, bank protection [if located near a shore, as in the example given in Beitinger et al. (1998)], monitoring wells, and a roadway for the tank trucks (to remove and replace the treatment medium) may be installed (Fig. 13.6).

The construction costs for permeable treatment walls with a depth of 8 m are calculated to range from US$500 to US$900 without the treatment medium (additional US$180/m^2 for an activated carbon layer of 0.3 m thickness).

Precipitation, Bioclogging, and Field Test Results

Precipitation. The potential for precipitation of calcium and magnesium carbonate mainly depends on the hardness of the groundwater, temperature, pressure, and carbon dioxide concentration. Usually the equilibrium of calcium and carbon dioxide within a given range of temperature and pressure will be heavily influenced by pumping the groundwater to an above-ground treatment system. The resulting effect is the precipitation of calcium carbonate on filters or inside stripping columns in the groundwater treatment plant.

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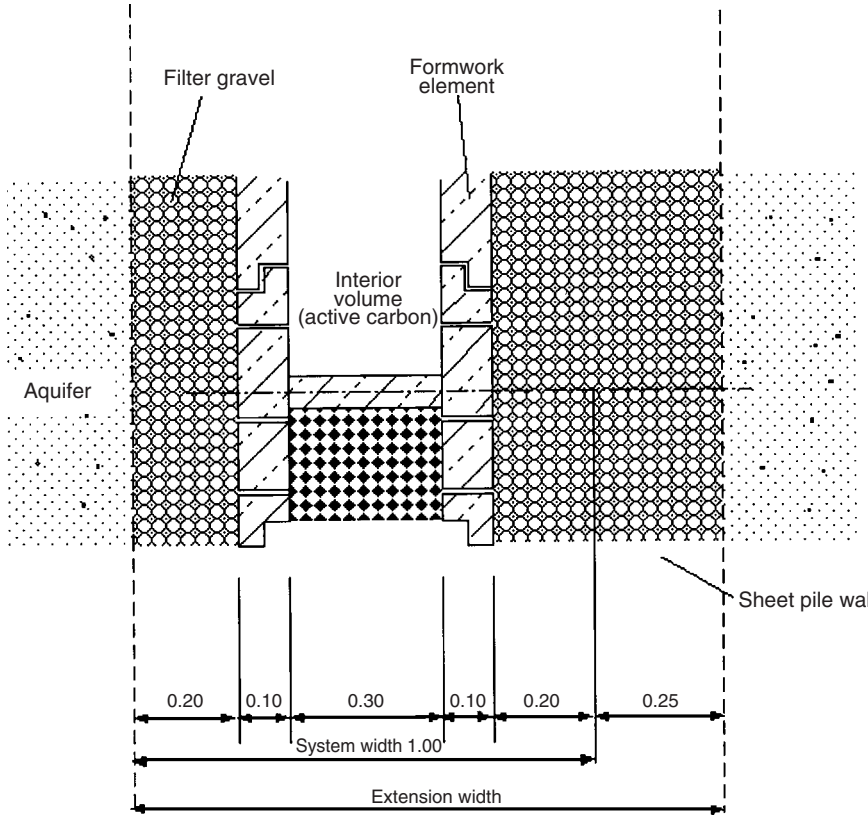

FIGURE 13.2 Dimensions wall construction (cross section) details.

One of the advantages of using permeable reactive barriers with a fill of activated carbon is that neither temperature, pressure, nor carbon dioxide concentrations will be changed in the groundwater as it flows through the wall structure. Negative effects that cause precipitation of calcium carbonate may be avoided in this way. Covering the filter layers and the treatment medium to match with the thickness and qualities of the existing unsaturated zone will help to keep temperature, carbon dioxide concentration, and pressure in the given range.

In general, all changes to groundwater chemistry and physical conditions may result in negative effects. Intensive investigations and analyses of groundwater will help to evaluate the potential for precipitation or other limitating factors.

Precipitation of iron or manganese is also a well-known effect for the design of pumping systems, wells, and treatment plants. Often precipitation of iron or iron oxides is related to the increase of oxygen in groundwater. Well screens and stripping columns are blocked by iron precipitates due to the increased availability of oxygen.

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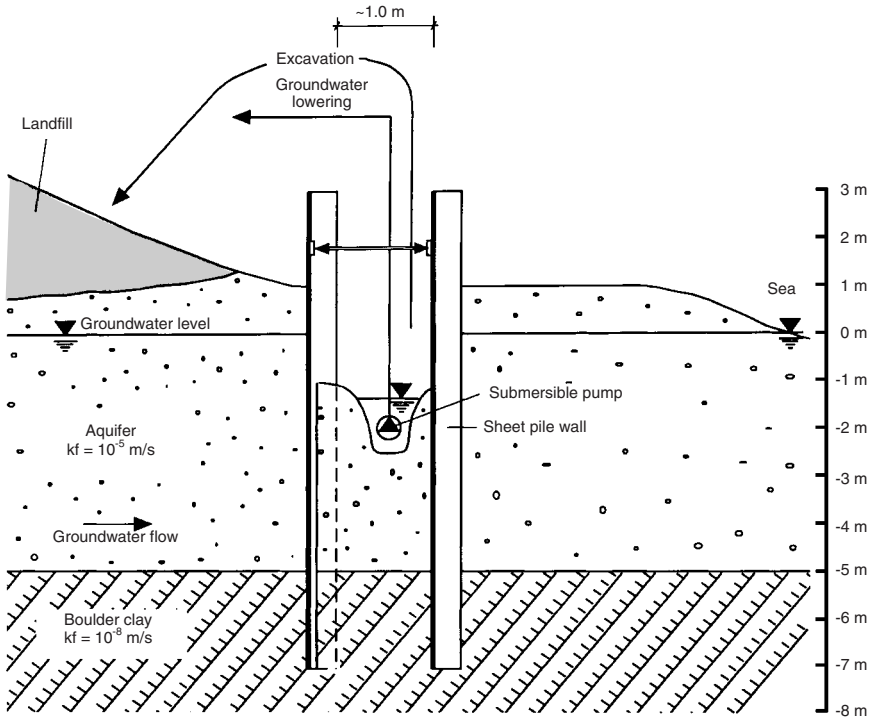

Phase 2: Excavation and dewatering of the sheet wall construction

FIGURE 13.3 Construction phase 2.

Bioclogging. Activated carbon is an ideal settling medium for microorganisms. The adsorbed organics may be used as nutrients if desorbing effects can reactivate the concentrated contaminants. One of the major concerns related to microorganims is that their biomass may block the reactive zones of adsorbing or other reactive media. Theoretically, the aerobic bioactivity can be controlled by reducing the delivery of oxygen and other nutrients.

As a result of the above-mentioned effects, an uncontrolled growth of biomass can be limited by keeping the wall construction water- and airtight. On the other hand, a controlled biomass may help to degrade contaminants directly on the carbon and help to prolong the long-term performance of the adsorbant capacity.

Long-term field studies should be performed to evaluate the control of biomass on permeable reactive barriers. At the present time, we do not have enough experience to precisely calculate the influence of biomass activity on the effectiveness of the treatment medium.

Field Test Results. A field test was conducted by WCI for a period of 5 months in 1997 at a site contaminated with many different chlorinated and nonchlorinated solvents. Benzene, ethylbenzene, toluene, xylene, and trichloroethene were detected in groundwater at high concentrations. Soil permeability and groundwater flow velocity were low. The aquifer itself was several meters thick.

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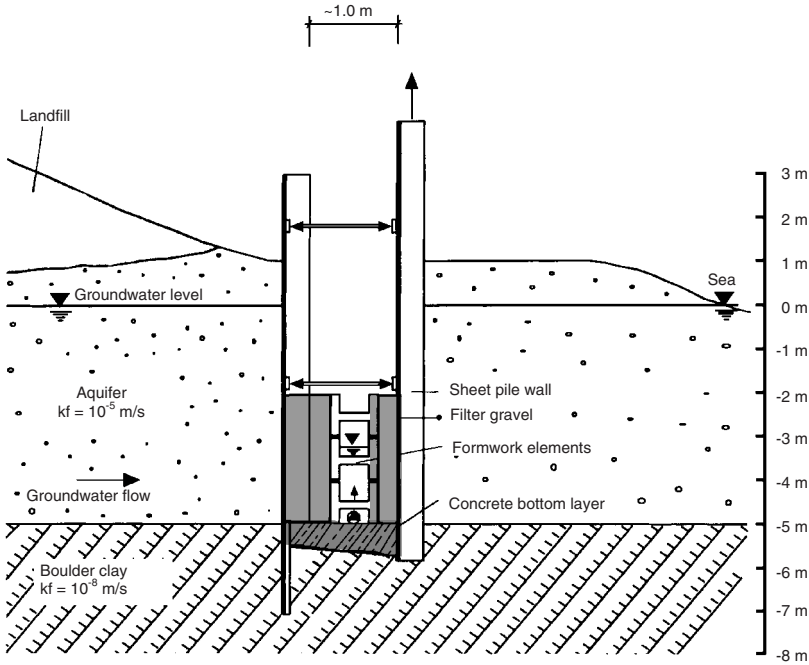

FIGURE 13.4 Construction phase 4.

The field test objectives were (1) to evaluate the choice of the best available activated carbon material within given economic limits, (2) to test the period of performance until the first contaminant breakthrough, (3) to test treatment efficiency by analyzing water quality and the inflow and outflow of the test equipment, (4) to evaluate the effectiveness of the gravel filter, (5) to evaluate precipitation of iron and manganese, and (6) to evaluate biological activity.

The test results are as follows:

- Activated carbon commonly used in drinking water treatment was found to be the most suitable and was chosen for field testing.
- The period for breakthrough was approximately five times higher than calculated. A much thinner layer of reactive medium is sufficient.
- No pressure losses through operation were detected.
- Treatment efficiency was as expected. All major organic contaminants were below the detection level.
- No precipitation was detected.
- Biomass grew specifically in those areas of the carbon with high adsorbed organic mass; no visual biomass and no loss in hydraulic performance could be detected.
- The balance of inflow, accumulation, and outflow concentrations was identified correctly in the analyses.

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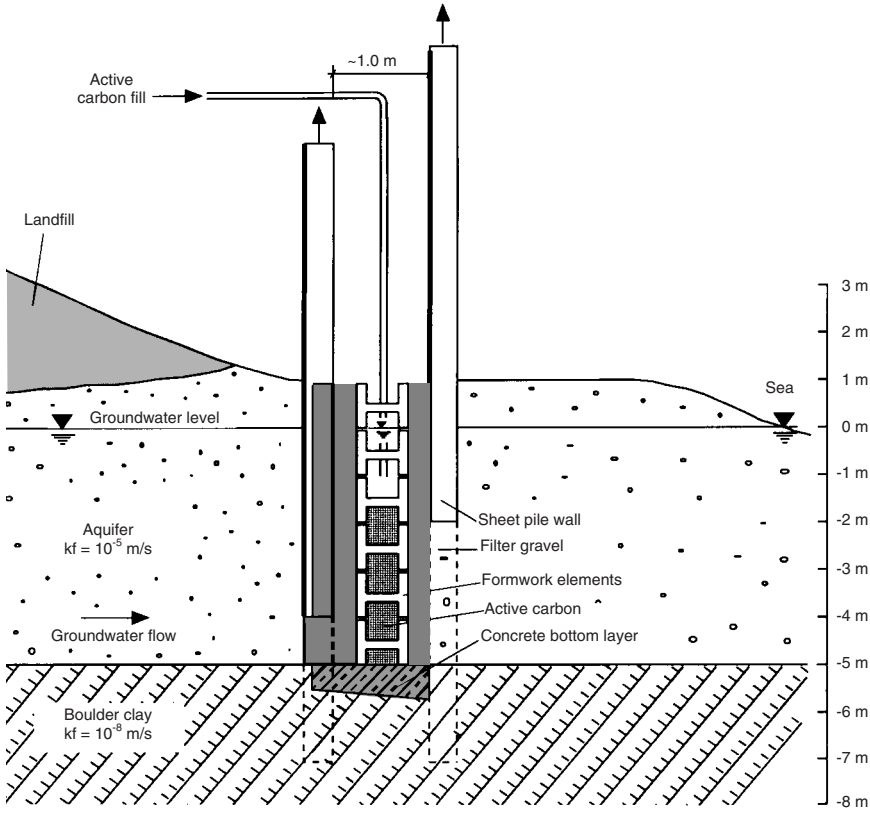

Phase 5: Placement of bulk material in formwork elements, complete removal of sheet pile wall

Top view:

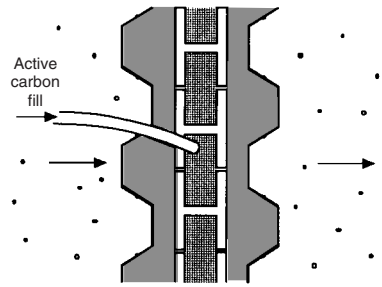

FIGURE 13.5 Construction phase 5.

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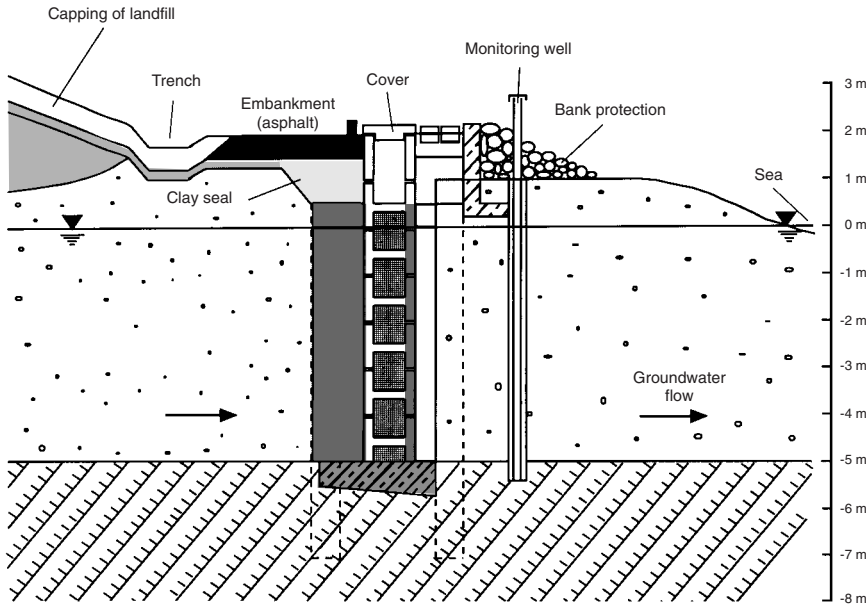

FIGURE 13.6 Construction phase 6.

The field test equipment, including two columns of activated carbon to be operated under parallel conditions, was proved to be usable for such tests. One column was tested under real-time conditions; the other with a factor of 333 times faster.

Regarding the faster column to differ from site conditions because residence time in the reactive zone in the second column is short due to the high-volume flow, the comparison of both columns gives good-quality information for choosing design criteria for the full-scale implementation.

Natural Attenuation

After solving a few spectacular cases with intensive efforts, it now seems that financial restrictions may inhibit the use of many newly developed remediation techniques (e.g., chemical extraction, high-temperature incineration, and some biological procedures) to sanitize contaminated land on a large scale (i.e., for areas of hundreds of square kilometers). Although this relates primarily to parts of eastern Europe, the tens of thousands of old landfill sites that must be excavated, treated, and recultivated soon will strain even more prosperous economies. It may well be that economic considerations will strengthen the popularity of geochemically engineered solutions in these situations, as well as for large waste masses such as mine residues, dredged materials, and filter ashes. However, even if traditional engineering continues to dominate practical solutions, the specific potential of geochemistry to provide instruments for long-term assessment of processes should be used and expanded.

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During the 1990s, natural attenuation grew from a laboratory research phenomenon to a commonly used approach for the cleanup of contaminated groundwater (MacDonald, 2000). The concept of natural attenuation/intrinsic remediation relies on natural subsurface processes rather than traditional engineered procedures. Typically, applications of natural attenuation concepts involve the indentation of biological, chemical, and geotechnical approaches. Common objectives are characterization of the site with regard to the efficiency of the expected retardation/degradation mechanisms, proof of applicability of the natural attenuation concept (i.e., time frame), and elucidation of questions relating to the persistence of pollution sources.

Major advantages of the concept are—as for most in situ procedures—avoidance of secondary wastes and reduction of hazards for exposed people compared with ex situ treatments. Problems may arise from the long time periods to reach the remediation goals inclusive of subsequent surveillance. In the opinion of U.S. EPA, intensive instruction will be needed to gain public acceptance of this concept (Anonymous, 1999).

Regarding the effects on pollutant reduction in the subsurface environment, *destructive processes* such as biological and abiotic degradation, humification, and biological-chemical transformation can be distinguished from *nondestructive processes,* such as sorption, immobilization, dilution, and volatilization (Track and Michels, 2000). When relying on natural attentuation processes for site remediation, the U.S. EPA prefers processes that degrade or destroy contaminants; also, the EPA generally expects that natural attenuation will be appropriate only for sites that have a low potential for contaminant migration (Anonymous, 1999). The destructive processes mainly will induce a reduction of contaminant mass and discharge; the nondestructive processes—by physical-chemical mechanisms—may lead primarily to a decrease of concentration and mobility of pollutants. Sorption either can be reversible, or, in connection with diffusion in micropores, may effect a long-term retardation of pollutants. Due to sorption processes, a decrease in bioavailability can be reached.

With increased practical experience and with scientific understanding of the processes involved in the so-called monitored natural attenuation (MNA), the EPA (Anonymous, 1999) provided some general rules regarding the areas of application that are summarized in Table 13.1.

Likelihood of Success. In late 1997, the U.S. National Research Council (NRC) appointed a natural attenuation committee because of concerns expressed by some members of the National Academy of Engineers about the controversies surrounding natural attenuation; a central part of the committee's task was to assess current scientific understanding of the fate of different contaminant classes in the subsurface absent human intervention (Anonymous, 2000). On the basis of a review of scientific and technical literature, field reports, and protocols, the committee rated the likelihood that natural attenuation will succeed as a remediation strategy as being high, moderate, or low for different types of contaminants.

TABLE 13.1 Areas of Application for Monitored Natural Attenuation

Soil/groundwater	Applicable for both media
Monitoring	Prerequisite; unsuitable sites are eliminated
Cross-medium transfer	Not permitted
Time frame	Reasonable in the range of other methods
Source control measures	MNA mostly in combination with other methods

Source: Anonymous (1999).

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The committee developed a three-part recommended process for evaluating the occurrence of natural attenuation at contaminated sites: (1) providing a conceptual model of the site, (2) looking for "footprints" (i.e., changes in water chemistry left by the attenuation reactions), and (3) monitoring the site. Due to variations in the types of contaminants, the chemistry of the groundwater, and the geological characteristics of the site, the search for footprints of natural attenuation must consider the unique conditions of site (the NRC study gives such footprints of natural attenuation reactions at a dozen field sites that the committee reviewed as case studies) (Anonymous, 2000).

The NRC report made recommendations on future guidelines for protocols on natural attenuation. A significant weakness of some protocols is the use of scoring systems that rate the likelihood that natural attenuation will occur based on-site data. "Scoring systems are generally too simple to represent the complex processes involved and often are used erroneously in judging the suitability of a site for natural attenuation." Instead, the national consensus guidelines should apply a type of three-part evaluation process.

Destructive Processes. Biological degradation of contaminants is the dominant destructive process in soil and groundwater. Several factors in soil and groundwater influence the velocity of pollutant transformations (Table 13.2). In the first place, the role of redox processes should be emphasized, which directly or indirectly influences other factors such as pH value, sorption processes, and biocoenosis of soils and groundwater.

Important milieu parameters for estimating natural attenuation are the concentration of oxygen, nitrate, iron(II), sulfate, methane, and—less significant—manganese, calcium, bicarbonate, and pH. Interpretation of such data can rely on combinations of in situ microcosms, laboratory batch studies, and field observations (Christensen et al., 1994). More advanced methodological concepts include geochemical speciation models, mainly for iron (oxide, sulfide, and carbonate Fe complexes). Aquifer sediment has a far larger redox buffer capacity than the groundwater, and any evaluation of capacities must include sediment analysis; the strength of sediment redox characterization is that only the sediment accumulates information about past processes and provides a basis for evaluating future capacities. However, in pollution plumes, redox changes over depth may be very dramatic. Changes may occur within a few centimeters, suggesting that mixing of samples over depth may be detrimental to accurate assessing of redox conditions. In addition, local, small-scale, low-permeable hydrogeological heterogeneities may have natural redox conditions not associated with the plume and should not to be mistaken as representing redox conditions in the plume (Christensen et al., 2000a).

Control of the Groundwater Plume. Most experts agree that cleanup contaminant source zones for industrial sites where non-aqueous-phase liquids (NAPL) such as petroleum hydrocarbons, chlorinated solvents, or tar oils have penetrated into the ground are hardly achievable at reasonable costs (Teutsch and Rügner, 2000a). As a consequence, concepts that focus on the control of groundwater plume rather than elimination of the source have received increasing attention during recent years. For compounds that are sufficiently biodegradable, natural attenuation (NA) can be a valid concept (Wiedemeier et al., 1999).

Tracking a groundwater plume is hard to achieve in practice due to the complexity of the contaminant distribution and the hydraulic properties, which can be extremely heterogeneous within an industrial area (Whittaker et al., 1998). In order to overcome these limitations, a new site-evaluation approach has been developed by Teutsch et al. (2000b) that aims at quantifying the entire contaminant mass flux across given control planes. The technique can be coupled conveniently with measurements of redox-sensitive parameters and degradation products from the organic chemicals. Recently, contaminant-specific stable carbon isotope ratios have been used for the quantification of degradation processes of chlorinated solvents (Sherwood-Lollar, 1999). Similarly, this technique can be used for BTEX compounds (Meckenstock, 1999).

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TABLE 13.2 Factors Influencing Biological Transformation of Contaminants

Factors	Type of effects
Redox potential	Concentration and ratios of electron donators/acceptors determine both pathways and efficiency of degradation.
pH value	Organisms and enzymes exhibit pH-dependent activity optima.
Temperature	Influences composition of biocoenosis/velocity of degradation.
Solubility, volatility, particle surface, sorption, occlusion	Limit bioavailability of a contaminant; limitation may negatively influence velocity of degradation; for toxic substances, limitation of bioavailability even could be useful.
Water content	Sufficient water content is essential for degradation of contaminants as well as for the transport of educts and products.
Auxiliary (co)substrates	Enable cometabolic transformation of contaminants that cannot be degraded productively or do not induce biological decay.
Nutrients	Essential for growth and reproduction of microorganisms.
Biocoenosis	Pollutant-tolerant and degradation-active organisms and consorties determine the rate of material turnover; development will be driven decisively by potential selection advantage from degradation processes (e.g., energy surplus).
Cocontaminants	Accompanying contaminants can be degraded preferentially but may influence bioavailability and may inhibit biodegradation.
Age	Age of a soil contamination influences bioavailabilty of pollutants by the time suitable biocoenoses can develop.

Source: Track and Michels (2000).

Whether NA can be used as a remedy option at a contaminated site will depend on the actual NA activity as well as on the ability to quantify and monitor the relevant NA processes with a satisfactory level of certainty. In every case, the decision should be based on site-specific investigation. Similarly, after NA is selected as a remedy option, an adequate site-specific monitoring concept needs to be developed (Teutsch and Rügner, 2000b).

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SEDIMENT REMEDIATION

Sediment remediation methods can be subdivided according to the mode of handling (e.g., in-place or excavation) or to the technologies used (containment or treatment). Important containment techniques include capping in situ and confined disposal. Biological processes may be applied with in-place treatment. Excavated sediments—apart from physical separation—can be treated to immobilize pollutants, mainly metals (Table 13.3).

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TABLE 13.3 Technology Types for Sediment Remediation

	In place	Excavated
Containment	In situ capping Contain/fill	Confined aquatic disposal/capping Land disposal Beneficial use
Treatment	Bioremediation Imobilization Chemical treatment	Physical separation Chemical extraction Biological treatment Immobilization Thermal treatment

Source: Anonymous (1994).

Remediation techniques on contaminated sediments generally are much more limited than for most other solid waste materials, except for mine wastes. The widely diverse contamination sources in larger catchment areas usually produce a mixture of pollutants that is more difficult to treat than an industrial waste. For most sediments from maintenance dredging, there are more arguments in favor of disposal than treatment. Mechanical separation of less strongly contaminated fractions, however, may be a useful step prior to final storage of the residues.

Treatment of Strongly Contaminated Sludges

This section reviews the traditional techniques for treating strongly contaminated dredged materials —solidification/stabilization, solvent extraction, and bioremediation. A general conceptual scheme related to excavated sediment material was first proposed by the TNO, the Netherlands scientific technological organization (Van Gemert et al., 1988). A and B techniques are distinguished: A is for large-scale concentration techniques such as mechanical separation; these techniques are characterized by low costs per unit of residue and low sensitivity to variations, and they may be applied in mobile plants. B techniques are decontamination procedures, which are especially designed for relatively small-scale operations. They involve higher operating costs per unit of residue, are more complicated, need specific experience of the operators, and usually are constructed as stationary plants. B techniques include biological treatment, acid leaching, solvent extraction, and so on.

Classification of Dredged Sludge. As an example of A techniques, the classification of harbor sludge from Hamburg is described (Detzner et al., 1993). In March of 1993, the first large-scale plant for treatment of sediments, known as METHA (mechanical separation of harbor sediments), commenced operation in the Port of Hamburg. This plant processes dredgings amounting to an annual quantity of approximately 2 million cubic meters for accommodation as filling material, thus making an important contribution to traffic safety for harbor operations. The process for separation and dewatering of harbor sediments was developed systematically from initial laboratory tests followed by a pilote phase and then on an industrial scale. Contaminants such as heavy metals and organic contaminants contained in the sediments are separated as fine fractions and dewatered to such an extent that they can be stored on a sealed land disposal site.

Figure 13.7 shows the combination of hydrocyclonage and elutriator as designed by Werther (1988). In the hydrocyclone, the separation of the coarse fraction (relatively

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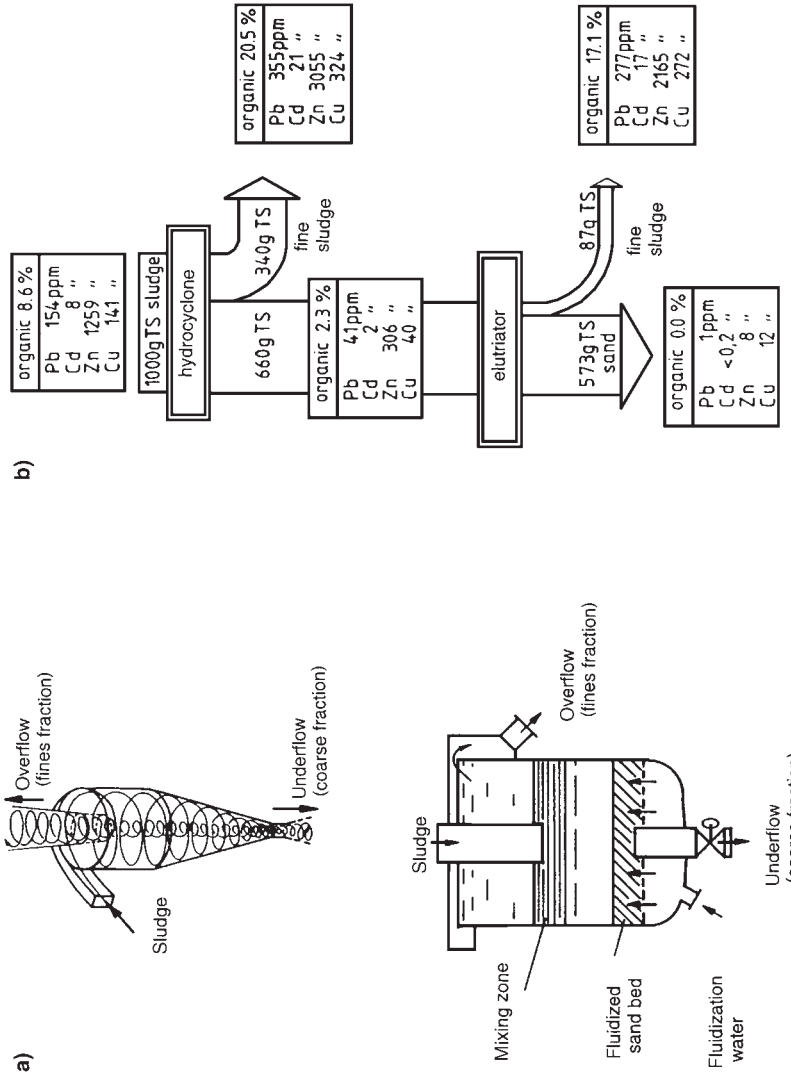

FIGURE 13.7 Classification of harbor sludge: (*a*) schematic view of a hydrocyclone (*above*) and an elutriator (*below*); (*b* mass balance and distribution of heavy metals. (*From Werther, 1988*)

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clean sand) from the highly polluted fines is effected by the action of centrifugal force. The coarse fraction leaves the cyclone in the underflow, whereas the fines are contained in the overflow. The advantage of the hydrocyclone is its simplicity and its ability to handle large throughputs; a disadvantage is that the sharpness of the separation is fairly low. The elutriator, which follows in the classification scheme, effects a much better sharpness of separation. The basic principle here is separation according to the settling velocity of the particles in an up-flowing water stream. There are virtually no fines found in the underflow of the elutriator. The efficiency of the separation procedure is illustrated in Fig. 13.7*b,* which demonstrates that the sand thus separated from the sludge has a heavy metal content that is on the same order of magnitude found in naturally occurring sandstone.

Solidification/Stabilization. In general, solidification/stabilization technology (see the section on soil remediation) is considered a last approach to the management of hazardous wastes. The aim of these techniques is a stronger fixation of contaminants to reduce the emission rate to the biosphere and to retard exchange processes. Most of the stabilization techniques aimed for the immobilization of metal-containing wastes are based on additions of cement, water glass (alkali silicate), coal fly ash, lime, or gypsum (Goumans et al., 1991).

Laboratory studies on the evaluation and efficiency of stabilization processes on harbor sludge from Hamburg were performed by Calmano et al. (1986). Best results are attained with calcium carbonate, since the pH conditions are not changed significantly on addition of $CaCO_3$. Generally, maintenance of a pH of neutrality or slightly beyond favors adsorption or precipitation of soluble metals (Gambrell et al., 1983). On the other hand, it can be expected that both low and high pH values will have unfavorable effects on the mobility of heavy metals.

Several factors interfere negatively with the objective to solidify or stabilize (Table 13.4): organic compounds; oil and grease; inorganic salts such as nitrates, sulfates, and chlorides; small particles sizes; volatile organic compounds; and low solids content.

TABLE 13.4 Factors Affecting Immobilization Processes

Factor	Effect
Organic compounds	Interfere with bonding of waste materials
Oil and grease	Interfere with the hydration of cement, reduce product strength, and weaken bonds between waste particles
Inorganic salts (e.g., nitrates, sulfates, chlorides)	Reduce product strength and affect curing rates
Halides (e.g., chlorides)	Retard setting and leach easily
Particle size	Small particles coat larger articles and weaken bonds
Volatile organic compounds	May produce air emission due to heat generation
Solids content	Low solids content (high water content) requires large amounts of reagent

Source: Anonymous (1988).

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Solvent Extraction. The primary application of solvent extraction is to remove organic contaminants such as halogenated compounds and petroleum hydrocarbons (Anonymous, 1988). Extraction processes also may be used to extract metals, but these applications, which usually involve acid extraction, have not proven to be cost-effective for contaminated sediments. Fine-grained materials are more difficult to extract, and the presence of detergents has an adverse impact on oil-water separation. The procedure is less effective for high-molecular-weight compounds and very hydrophobic substances (Table 13.5). In any case, careful selection of reagents and laboratory testing are required.

Biodegradation and Biorestoration. Biological treatment has been used for decades to treat domestic and industrial wastewater and in recent years has been demonstrated as a technology for destroying some organic compounds in contaminated soils (see the section on biological treatment). Bioremediation or biorestoration may be applied in certain cases to organically contaminated sediments. However, since in large catchment areas contamination with only organic compounds is rare, the expectations in this technique of remediation seem to be overestimated. Often the request for such procedures is a simple indication of ignorance about sediment pollution problems. Even in optimal cases, there are many limitations to biodegration processes; temperature, nutrients, and oxygen are the most important ones (Table 13.6).

Bioremediation and other advanced techniques have been studied in the Dutch POSW program, which is reviewed in more detail in the following subsection.

Dutch POSW Program. The Dutch Development Program for Treatment Processes for Contaminated Sediments (POSW), starting in 1989 and running until 1996, was aimed at the development of ecologically sound dredging and processing techniques to be used in

TABLE 13.5 Factors Affecting Extraction Processes

Factor	Effect
Particle size	Fine-grained materials more difficult to extract; larger particles may not pass close clearances in process equipment.
Water content	Most processes require slurry of 40 to 80 percent water.
pH	pH adjustment depends on the process selected.
Presence of detergents and/or emulsifiers	Adversely impacts oil-water separation; retains contaminants in competition with solvents; foaming hinders separation and settling.
Metals	Metals in fine-grained sediments are not easily removed.
Types of organic compounds	Less effective for high-molecular-weight organic compounds and very hydrophobic substances.
Reactivity	Certain contaminants are incompatible with some solvents; requires careful selection of contaminants and laboratory testing.

Source: Anonymous (1988).

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TABLE 13.6 Characteristics That Limit Biodegradation Processes

Characteristic	Reason for potential effects	Action to minimize effects
Nonuniform size	Minimizes microorganism contact	Remove coarse-grained material
Water solubility	Low solubility, so harder to degrade	Addition of surfactants/emulsifier
Temperature	Less activity outside 15–30°C range	Monitor/adjust temperature
Nutrients	Lack of adequate nutrients for biology	Adjust carbon:N/P ratio
Oxygen	Lack of oxygen is rate-limiting	Monitor/adjust oxygen
pH	Less activity outside 4.5–8.8 range	Add acidic/alkaline compounds
Heavy metals, high HOCs (halogenated or ganic carbons), some pesticides, inorganic salts	Can be highly toxic to microorganisms	Reduce concentration of toxic compound to the nontoxic range by pretreatment processes or dilution with amendments

Source: Anonymous (1988).

the remediation and reuse of polluted sediments (Anonymous, 1997a; Rulkens, 2001). Technical applicability had to be demonstrated in practice as part of an integrated remediation chain. Attention also was paid to the economic and environmental consequences of the several types of techniques as part of entire cleanup chains.

Typical research issues of the POSW stage II (1990–1996) program were (Anonymous, 1997a; Rulkens, 2001)

- Separation of sludge into subflows (e.g., hydrocyclone separation, upstream separation, settling, flotation, dewatering of fine fractions, practical experience in pilot remediation)
- Thermal and chemical treatment methods (e.g., thermal desorption, incineration, wet oxidation, solvent extraction)
- Biological treatment (e.g., landfarming, greenhouse farming, slurry treatment in bioreactors)
- Immobilization of pollutants in products (e.g., melting, sintering, practical experience in pilot remediation)
- Assessment of the environmental effects of processing chains (based on life-cycle analysis, LCA)
- Scenarios for large-scale processing, varying from natural processes in treatment plants (e.g., sedimentation, dewatering, landfarming and ripening) to maximum deployment of classifying and polishing methods

An example for biological treatment of sludge is given from the Amsterdam Petroleum Harbor (Rulkens, 2001). To treat this sediment, contaminated by mineral oil (to 20,000 mg/kg) and PAHs (to 1000 mg/kg), a continuous type of bioreactor was used. Preconditions were quality requirements for the final product and a decontamination period of 100 days. A total of 5000 m^3 of sludge was dredged and processed. Pretreatment with a hydrocyclone produced a coarse and a fine fraction. The former was subjected to flotation, whereas the fine fraction was dewatered to the desired density. It was next treated biologically in a continuous process in a series of bioreactors and finally dewatered. Tests with a few cubic

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meters of material showed that PAHs and oil could be removed from the sludge by 92 and 76 percent, respectively.

Likelihood of Success, Costs. Similar to the experience in soil remediation, the initial hope that physical-chemical treatment would find a considerable market has not been realized for these materials. The only widespread application is the method of separation according to grain size, but even with the positive effects of processing—less dumping space needed and savings on the extraction of primary materials—the processing itself has negative side effects (Rulkens, 2001). The separation of sand is energy-consuming and requires water to dilute the input. The water is recycled during the process, but any surplus will have to be treated, either locally or in a purification plant elsewhere.

Cost estimations for decontamination techniques cover a wide range for individual examples from the fields of bioremediation, chemical dechlorination, soil washing, solvent extraction, thermal desorption, and vitrification (Anonymous, 1994). These are mostly well-known examples from industrial waste technology. Typical cost factors for sediments include water quantity, moisture contents, and physical and chemical characteristics (e.g., grain size and organic material content).

In Situ Remediation

Remediation techniques often are unacceptable economically because of the large volume of contaminated materials to be treated. In such cases, the concept of *geochemical engineering* (Salomons and Förstner, 1988) can provide both cost-effective and durable solutions. Geochemical engineering applies geochemical principles (such as concentration, stabilization, solidification, and other forms of long-term self-containing barriers) to determine the mobilization and biological availability of critical pollutants. In modern waste management, the fields of geochemically oriented technology include

- The optimization of elemental distribution in high-temperature processes
- The selection of favorable milieu conditions for the deposition of large-volume wastes
- The selection of additives for the solidification and stabilization of waste materials
- The development of test procedures for long-term prognoses of pollutant behavior

As shown from the examples of large-mass wastes, dredged materials, mining residues, and municipal solid waste, long-term immobilization of critical pollutants can be achieved by promoting less soluble chemical phases, i.e., by thermal and chemical treatment, or by providing respective milieu conditions. Selection of appropriate environmental conditions predominantly influences the geochemical gradients, whereas chemical additives are aimed toward enhancing capacity-controlling properties in order to bind (or degrade) micropollutants. In general, microscale methods (e.g., formation of mineral precipitates in the pore space of a sediment waste body) will be employed rather than using large-scale enclosure systems such as clay covers or wall constructions. A common feature of geochemically designed deposits, therefore, is their tendency to increase overall stability over time due to the formation of more stable minerals and closure of pores, thereby reducing water permeation.

Fields of Application. Joziasse and van der Gun (2000) reviewed a number of potentially relevant options for in situ remediation of contaminated sediment in order "to increase the decision maker's awareness that these options may be worth considering, if a number of

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boundary conditions are fulfilled; these refer to the risk reduction necessary, the time available, local conditions, etc."

In the past, the possibilities of in situ remediation by the addition of mixtures of various substances have been investigated for two purposes: (1) to stimulate the biodegradation of organic contaminants and (2) to stimulate the degradation of organic matter (humic and fulvic acids, humins) for reducing the volume of the sediment. The results obtained with the addition of these mixtures were disappointing mainly because of an oxygen deficit (Joziasse and van der Gun, 2000).

However, recently, a number of developments in remediation of terrestrial soil pollution with respect to both policy aspects and technical developments have led to a stimulation of in situ remediation options: (1) No longer do remediation actions have to be executed within a very short period of time, (2) the result is not necessarily a multifunctional soil, and (3) advantage is taken of natural processes (the self-cleaning capacity of the soil). Table 13.7 summarizes a number of potentially relevant options. It may be conceivable that the conditions for reductive dechlorination of chlorinated hydrocarbons are optimized. In addition, phytoremediation (e.g., degradation of contaminants near plant roots) may be beneficial in certain cases (Ferro and Kennedy, 1999). As to the immobilization of contaminants by adsorption, one can think of applying clay screens or clay layers (with or without additives). The advective dispersion of contaminants toward groundwater or surface water can be reduced by capping the polluted sediment with a clay layer, with organic matter (humus), or with other materials as possible additives.

It is stressed by Joziasse and van der Gun (2000) that for every single case, the effects of the actions (either dredging or in situ) on the aquatic ecosystem will have to be accounted for. In concrete cases, where a conventional approach encounters serious difficulties, an investigation dedicated to the prevailing conditions will have to give a decisive judgment on the feasibility of an alternative (in situ) approach.

Natural Attenuation (Aging) Processes. In the more science-based regulations, such as the U.S. EPA's sediment quality criteria (SQCs), sediment quality advisory levels (SQALs) and chemical specific fate scores are derived directly or indirectly on the basis of the linear equilibrium model (Anonymous, 1997b). The purpose of SQCs is to ensure that the pore water concentration of a certain compound does not exceed the final chronic water quality criteria (FCVs). Equilibrium partitioning models were applied mainly for the distribution of functionally diverse hydrophobic organic compounds, such as PCBs, PAHs, DDT, chlorobenzenes, etc. However, these models, derived from laboratory sorption studies and based mainly on partitioning with bulk organic carbon, may lead to a significant overestimation of risks, which is due to a wide spectrum of aging processes. It has been shown by Chen et al. (2000) in their study on five chlorinate benzenes and four natural sediments that, for example, the SQC of 1,4-dichlorobenzene would be nearly 2 orders of magnitude less strict when the process of irreversible adsorption on the resistant fraction in sediment is taken into account (Fig. 13.8).

Initial findings from soil studies were that as the residence time of compounds such as phenanthrene and 4-nitrophenol in soil increases, they become increasingly unavailable to microorganisms and resistant to mild extraction (Hatzinger and Alexander, 1995). Subsequently, chemical extraction procedures were developed to predict bioavailability of soil-aged organic chemicals (Kelsey et al., 1997; Tang et al., 1999), and the role of nanoporosity and hydrophobicity in sequestration and bioavailability of typical organic contaminants has been studied with model solids (Nam and Alexander, 1998). The conclusions are that "correlations are needed to assess the role and contribution of organic matter, clay content, nanoporosity, surface area, or other soil properties in governing the rate and extent of decline in bioavailability so that predictions of diminished exposure will be possible" (Chung and Alexander, 1998).

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TABLE 13.7 Options for in Situ Sediment Remediation

Remediation type	Scope (type of contaminants)	Technological concept	Technological implementation	Feasibility 1	Feasibility 2
Stimulation of aerobic microbiologic degradation	Organics (PAH, mineral oil, etc.)	Increase degradation rates by addition of electron acceptors	Oxygen injection	−	−
			Rooting up of sediments (e.g., with turbine jets)	±	−
			Addition of nitrate as electron acceptor	−	±
			Addition of humic substances as electron acceptors	±	+
			Application of biologic screens or alternative reactive zones, if necessary, combined with electrokinetic transport	±	+
		Increase degradation rates by addition of microorganisms	Addition of especially grown organisms	−	+
			Inoculation with adapted organisms	±	±
			Addition of nutrients	−	−
		Increase degradation rates by addition of nutrients	Use enhanced degradation of contaminants in soil near plant	+	+
Stimulation of microbiologic reductive dechlorination	Chlorinated organics	Increase degradation rates by changing the environmental conditions	Application of microbial mats	±	+
		Increase degradation rates by addition of electron donors	Addition of electron donors to capping layers, c lay screens, etc.	±	+
Stimulation of biologic concentration and removal of contaminants	Metals (Ni, Zn, Cu, Cd)	Uptake of metals by plants	Introduction of plants (e.g., willow herb or sedge), harvest, and incinerate	±	+
	Phosphates	Uptake of phosphates by plants (phytoextraction)	Introduction of plants, harvest and incinerate	±	+
Using chemical transformations	All (if they can be oxidized or reduced)	Chemical oxidation or reduction of contaminants	Addition of oxidants (e.g., H_2O_2)	−	−
			Electrokinetic remediation	−	−
	Metals	Precipitation of metals as sulphides	Admission of salt seepage (sulphate containing water)	±	±
			Construction of wetlands (marshy zones)	±	+
Fixation of contaminants (sorption or immobilization)	Metals	Precipitation of metals as hydroxides or insoluble complexes	Increased pH by addition of lime or alternative hydroxides	±	±
			Precipitation or adsorption near or at plant roots phytostabilization)	+	+

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		Binding of metals in inorganic matrix	Addition of cement (and additives, if necessary)	±	+
			Vitrification using electrical current	−	−
		Adsorption of metals at clay or aluminum silicate surfaces	Application of a clay screen (with, for instance, zeolite or beringite, if necessary)	±	+
			Application of a capping layer	±	0
			Addition of adsorption marbles	±	+
		Adsorption at plant roots	Introduction of plants	±	+
	Organics	Adsorption of organic contaminants at clay surfaces and/or absorption in organic matter	Application of a clay screen, with addition of organic matter (humics) and/or oxygen release compounds, if necessary	±	+
		Adsorption at plant roots	Application of a capping layer with clay, or compost	±	0
			(and oxygen release compounds, if necessary)	±	+
			Addition of adsorption marbles		
			Introduction of plants	±	+
	Phosphates	Precipitation of phosphate as iron phosphate	Injection of iron chloride, or iron sulphate	−	−
Reduction of advective dispersion toward surface waters	All contaminants	Increased hydrological resistance	Application of a capping layer	+	0
			Densification of the sediment	±	+
		Reduction of bank erosion and washout	Introduction of plants	+	+
		Hydrologic insulation	Deflection of brooks	+	0
Reduction of advective dispersion toward groundwater	All contaminants	Increased hydrologic resistance	Application of a clay screen	+	+
		Hydrologic insulation	Watermark control measures	+	0
Refraining from action	All contaminants	Risk reduction	Change function of waterway, or surroundings	+	0

Source: Joziasse and van der Gun (2000).

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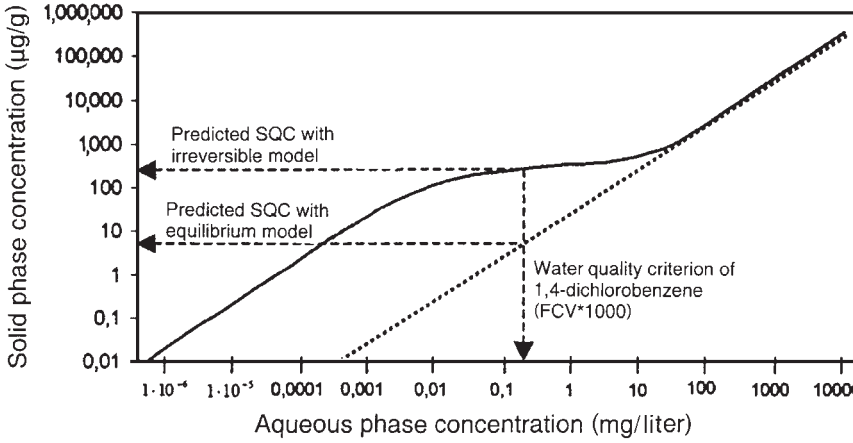

FIGURE 13.8 Implications of irreversible adsorption on sediment quality criteria. *(After Chen et al., 2000).*

Hydrophobic Organic Substances

Aging phenomena. Since the middle of the 1990s there has been increasing evidence that the constituents of the sediment matrix vary in a very wide range with respect to their sorption kinetics and intensity, competition of binding sites, and extractability of sorbed pollutants. In the first instance, such mixed sorption phenomena on geosorbents (Luthy et al., 1997) with their hysteresis and aging effects complicate the interpretation of macroscopic data on the diffusion of hydrophobic organic substances in and from different sediment matrices (Huang and Weber, 1997), as well as the quantification of biological availability and transformation of pollutants (Bosma et al., 1997). On the other hand, however, such effects, which are attributed mainly to a steric inhibition of diffusion processes in the fine pores of variably sized organic substances, can be considered as an important attenuation mechanism in addition to abiotic and biotic pollutant degradation (Pignatello and Xing, 1996).

Sediments are heterogeneous at various sample, aggregate, and particle scales. Adherent or entrapped non-aqueous-phase liquids (NAPLs; e.g., solvents, oils, and tars) and combustion residue particulate carbon (e.g., chars, soot, and ashes) also can function as sorbents. Complex assemblages of these constituents can cause complex mass-transfer phenomena, and the term *sequestration* refers to some combination of diffusion limitation, adsorption, and partitioning (Luthy et al., 1997). Some geosorbents exhibit typical nonlinear sorption behavior (Farrell and Reinhard, 1994; Huang and Weber, 1998). The observed trends of increasing apparent hysteresis and decreasing desorption rates and extractabilities of hydrophobic organic contaminants (HOCs) as a function of the sorbate residence time on geosorbents are incompatible with a simple-phase partitioning process.

Hysteretic sorption/desorption. Geosorbents have been characterized as comprising several domains or components that exhibit distinctly different sorption reactivities (Grathwohl, 1990; Weber et al., 1992). A qualitative comparison of hypothesized mechanisms and macroscopic observations that may be useful to assess sorption mechanisms of nonpolar organic compounds with geosorbents is given in Table 13.8. From these findings it has been suggested that the organic matrices of soils and sediments can be divided into two primary categories manifesting mechanistically different sorption behavior, i.e., an amorphous, gellike soft-carbon matrix or domain and a condensed, glasslike hard-carbon

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TABLE 13.8 Comparison of Mechanisms and Macroscopic Observations to Assess Sorption of Nonpolar Organic Compounds with Geosorbents

Mechanism	Absorption into amorphous or soft natural organic matter[a]	Absorption into condensed or hard organic matter or combustion R	Adsorption onto water–wet organic surfaces (e.g., soot)	Adsorption to exposed water–wet mineral surfaces	Adsorption into microvoids or microporous minerals[b]
Kinetics	Fast (<min) if disaggregated	Slow (>days) s/d hysteresis	Fast (<minutes)	Fast (<minutes)	Slow (>days) s/d hysteresis
Isotherm	Linear	Nonlinear if variable pore size	Nonlinear	Linear because competion H_2O	Nonlinear if variable pore size
Activation energy	Low	High	Low	Low	High
Heat of sorption	Low	Moderate to high[c]	Low to high[d]	Low	Moderate to high[e]
Competition	No	Yes	Yes	No	Yes
Sorbate	Steric effects not important	Steric effects important[f]	Steric effects important[g]	Steric effects important[g]	Steric effects important[h]
Solvent extraction	High	Low	High	High	Low

[a]Or NAPL.
[b]For example, zeolites, with porous surfaces at water saturation < 100 percent.
[c]Increasing with density of organic matter.
[d]Depending on hydrophobicity.
[e]Increasing with decreasing micropore size.
[f]For diffusion through matrix.
[g]Insofar as they allow planar interaction region between sorbate and sorbent.
[h]Insofar as they influence sorbate ability to diffuse through constricted pores in the sorbent.
Source: Luthy et al (1997).

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matrix or domain. Because the relaxation speeds of the glassy (by analogy to the glassy state of a polymer) structures are both slow and dependent on solute concentration, diffusion of solute molecules into and out of condensed organic matter can be extremely slow, and the associated sorption process likely would be nonlinear, hysteretic, and subject to solute-solute competition. Therefore, absorption into condensed organic matter (second column in Table 13.8) or diffusion into hydrophobic microporous regions of minerals (fifth column) may require protracted times (Luthy et al., 1997). In contrast, and by analogy with a rubbery polymer, the soft-carbon or amorphous organic matter domain may exhibit partitioning behavior associated with linear local isotherms, rapid diffusion, no competition for sorption, and sorption reversibility (first, third, and fourth columns in Table 13.8). Other workers (e.g., Xing and Pignatello, 1997) have hypothesized that the presence of microvoids of nanometer or smaller scale within natural organic matter (NOM), primarily associated with the more condensed fraction, also may play a significant role in the hysteretic desorption behavior [see review by LeBoeuf and Weber, (2000)].

In addition to irreversible adsorption, several other mechanisms have been proposed to explain the observed resistant desorption. Comparisons with model sorbents indicate that diffusion through pores in the organic matter or pores coated with organic material plays a role in slow desorption of PCBs and chlorobenzene from sediments (Cornelissen et al., 1998). Heterogeneous adsorption with varied adsorption sites is one of the preferred explanations; here, a fraction of the chemical is assumed to adsorb to sites with high adsorption energy or specificity, e.g., soot, a condensed organic phase (Gustafsson et al., 1997), or specific adsorption sites on an organic polymer (Weber and Huang, 1996). Preferential sorption of planar contaminants, such as chlorobenzenes and PAH, on sootlike material has been found in sediments from Lake Ketelmeer, The Netherlands (Jonker and Smedes, 2000). In fact, differentiation with regard to the type of organic matter could be a key issue for the interpretation of slow sorption processes. Complementary mass spectrometric and spectroscopic techniques on sediment samples from Milwaukee Harbor indicated that PAH concentrations on coal- and wood-derived particles were several orders of magnitude higher than on silica particles (Ghosh et al., 2000); the authors suggested that these particles may be removed by density separation from heavier clay, silt, and sand.

Methods. Several chemical and physical methods have been considered as ways to measure the bioavailability of organic compounds in soil, and results of analyses by such procedures have been correlated with bioavailability to earthworms, springtails, nematodes, and microorganisms [see review by Alexander (2000)]. Solid-phase microextraction (SPME) presents a very promising technique to determine bioavailable concentrations of hydrophobic chemicals in aquatic environments (Urrestarazu Ramos et al., 1998). Experimental SPME–water-partition coefficients correlate well with octanol-water and membrane–water-partition coefficients, indicating that these passive sampling devices provide a good surrogate for lipid partitioning (Verbruggen et al., 2000). Measurements of dissolved concentrations of persistent and bioaccumulative pollutants (PBPs) in sediment porewater were undertaken by so-called matrix solid-phase microextraction (matrix SPME), which uses the entire sediment matrix as a reservoir for an equilibrium extraction (Mayer et al., 2000). The determination of dissolved porewater concentrations is crucial for the understanding and correct modeling of the distribution, the transport, the toxicity, and the biodegradation of PBPs in sediment.

Heavy Metals

Aging processes. For inorganic pollutants, mainly heavy metals and arsenic, the effect of aging predominantly consists of an enhanced retention via processes such as sorption, precipitation, coprecipitation, occlusion, and incorporation in reservoir minerals. During his investigations on the early diagenetic stages of sediments from the Rhine River, Salomons (1980) found that the proportion of cadmium, which was not desorbed with

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sodium chloride solution (in seawater concentration), increased from 24 percent after 1 day to 40 percent after 60 days of contact time between sediment and metal solution. Sediment samples from the river barrage of the Vallabreques/Rhône, which had been contaminated by artificial radionuclides from the nearby reprocessing plant, exhibit characteristic differences with respect to the extractability of geogenic and anthropogenic manganese isotopes in the reductive elution step (Förstner and Schoer, 1984).

Experiments with lead and cadmium on sediment samples from the oxidized surface layer of mudflats in the south San Francisco Bay estuary, where the reaction systems were equilibrated for 24 hours at the appropriate pH for approximately 90 percent metal adsorption as determined by prior experiments, indicate slow release of adsorbed cadmium within a time frame of 96 hours, whereas lead was substantially nonlabile over the 264-hour duration of the experiment (Lion et al., 1982). It was suggested that the proportion of solid organic matter constitutes the main cause for the observed irreversibility of metal sorption; this was confirmed experimentally on selected materials for copper and, less distinctly, for nickel and cadmium (Förstner, 1987). With regard to the increased fixation of zinc, nickel, cadmium, and arsenic in contact with various soil constituents, among other processes, long-term diffusion into the crystal lattice of goethite has been suggested by Gerth et al. (1993).

Effects on bioavailiability. Geochemical influences on assimilation of sediment-bound metals recently have been evaluated by Griscom et al. (2000) in a series of experiments using suspension-feeding mussel *Mytilus edulis* and facultative deposit feeder *Macoma balthica.* Oxidized and reduced radiolabeled sediments were fed to the animals, and the assimilation efficiencies (AEs) of ingested metals were determined. For oxic sediment, Cd and Co AEs in *M. edulis* decreased three- to fourfold with increased sediment exposure time to the metals, with a smaller but significant effect also noted for Zn and Se but not for Ag. Sequential extractions of the oxidized sediments showed a transfer of metals into more resistant sediment components over time, but the rate did not correlate with a decrease in metal AEs. The results imply that metals associated with sulfides and anoxic sediments are bioavailable, that the bioavailability of metals from sediments decreases over exposure time, that organic carbon content generally has a small effect on AEs, and that AEs of sediment-bound metals differ among species (Griscom et al., 2000).

Methods. Characterization of long-term reactivity and bioavailability of heavy metals in sediments can be performed by (1) acid producing potential (APP) (Kersten and Förstner, 1992); (2) relationship of acid volatile sulfide (AVS) and simultaneously extractable metals (SEMs) (DiToro et al., 1992); (3) redox buffer capacities (Heron and Christensen, 1995); (4) formation of metal hydroxide surface precipitates using molecular-scale techniques (Roberts et al., 1999; Thompson et al., 1999); and (5) microbial biosensors (Corbisier et al., 1999; Vangronsveld et al., 2000; Reid et al., 2000) combined with the extraction procedure. Particularly promising in predicting the kinetically labile solid phase of metals is the technique of diffuse gradients in thin films (DGT) (Zhang et al., 1998); with its robust plastic assembly and capability for determining up to 12 metals simultaneously, DGT offers the possibility of a simple test procedure for soils and sediments (Zhang et al., 2001).

Subaqueous Storage and Capping (P. H. Jacobs)

Regarding the various containment strategies, it has been argued that upland containment (e.g., on heaplike deposits) could provide a more controlled management than containment in the marine environment. However, contaminants released either gradually from an imperfectly impermeable barrier (also to groundwater) or catastrophically from failure of the barrier could produce substantial damage (Kester et al., 1983). On the other hand, near-shore marine containment (e.g., in capped-mound deposits) offers several advantages,

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particularly regarding the protection of groundwater resources, because the underlying water is saline and inherent chemical processes are favorable for the immobilization or degradation of priority pollutants.

In a review of various marine disposal options, Kester et al. (1983) suggested that the best strategy for disposing of contaminated sediments is to isolate them in a permanently reducing environment. Disposal in capped-mound deposits above the prevailing sea floor, disposal in subaqueous depressions, and capping deposits in depressions provide procedures for contaminated sediment (Bokuniewicz, 1983). In some instances, it may be worthwhile to excavate a depression for the disposal site of contaminated sediment that can be capped with clean sediment. This type of waste deposition under stable anoxic conditions, where large masses of polluted materials are covered with inert sediment, became known as *subsediment deposit.*

Under subsediment conditions, there is a particularly low solubility of metal sulfides compared with the respective carbonate, phosphate, and oxide compounds. One major prerequisite is the microbial reduction of sulfate. Thus this process is particularly important in the marine environment, whereas in an anoxic freshwater milieu there is a tendency for enhancing metal mobility due to the formation of stable complexes with ligands from decomposing organic matter. Marine sulfidic conditions, in addition, seem to repress the formation of monomethylmercury, one of the most toxic substances in the aquatic environment, by a process of disproportionation into volatile dimethylmercury and insoluble mercury sulfide (Craig and Moreton, 1984). There are indications that degradation of highly toxic chlorinated hydrocarbons is enhanced in the sulfidic environment relative to oxic conditions (Kersten, 1988).

Types of Subaqueous Dredged Material Disposals. International guidelines for managing dredged materials have been worked out during the last few decades to control and limit the contaminant input into the marine ecosystem. The London Convention (LC), the Oslo-Paris Convention (OSPAR), and the Helsinki Convention date back from the 1970s but are under permanent revision and development to account for the most recent state of knowledge. Two basic principles can be considered the heart of the LC and many regional conventions (Burt et al., 2000): the precautionary principle and the polluter-pays principle. This means that wherever a potential interference with the aquatic environment is apprehended (1) precautionary safety measures are to be taken, and (2) the costs for these measures are borne by the polluter. The annexes of the LC, furthermore, provide detailed information for the disposal of dredged materials comprising (1) a black list with materials prohibited from open-water disposal, (2) a gray list with materials that require safety measures when disposed of at sea, and (3) detailed suggestions about how to apply the convention in the countries having signed the convention.

According to national and regional stipulations, as well as the above-mentioned international conventions, generally only uncontaminated sediments are suited for unrestricted open-water disposal, i. e., sediments that do not exceed the relevant threshold values (Fig. 13.9*a*). Unrestricted disposal means that the dredged material is disposed of without any previous treatment or following technical protective measures. However, increasing efforts are made to prefer beneficial use of these materials over disposal, but not at unreasonable costs. Beneficial uses may be coastal defense and beach nourishment or habitat creation or production of construction materials.

Sediments that exceed relevant threshold values, consequently, may not be disposed of without any further protective measures. In this case, there may be distinguished three main options:

1. Treatment steps are applied to the sediment prior to disposal to meet the threshold values.
2. The material is disposed of on land.

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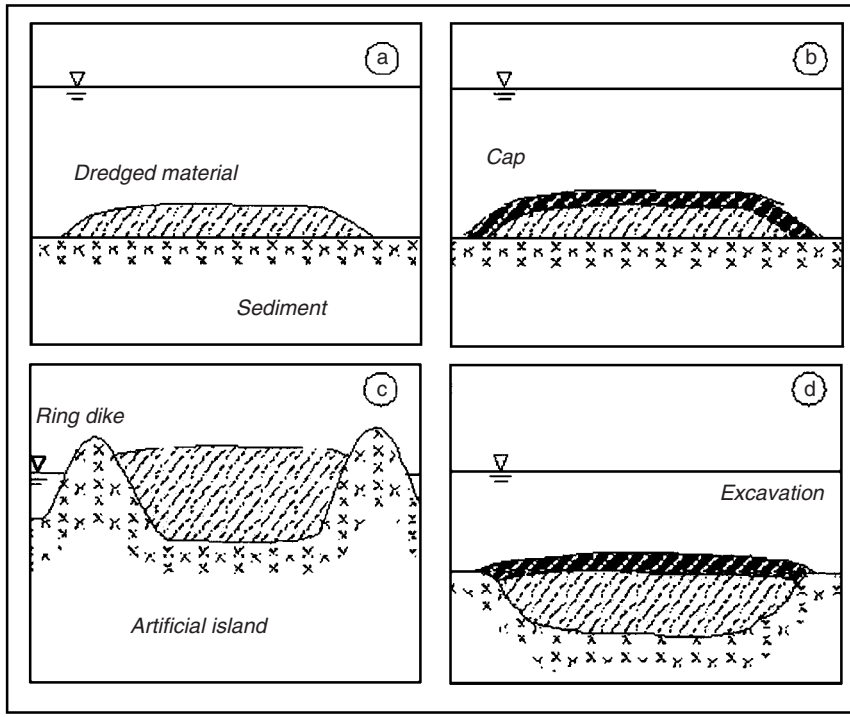

FIGURE 13.9 Options for subaqueous storage of dredged material: (*a*) unrestricted disposal; (*b*) capped mound; (*c*) artificial island; (*d*) subsediment deposit.

3. The disposal site is safeguarded by means of technical measures.

Pretreatment options are discussed in this chapter (see "Treatment of Strongly Contaminated Sludges"), and land disposal (upland containment) is beyond the scope of this chapter. The focus is thus on the third issue, the option of safeguarded subaqueous deposits. Figure 13.9*b–d* differentiates three main disposal types.

The first type, the subaqueous capping of the disposal site (see Fig. 13.9*b*), represents a straightforward and economic measure to isolate the contaminated material from the environment (see the section "Sediment Capping"). Due to its important role as an effective and economic passive technology, the capping concept is documented in the *Dredged Material Assessment Framework* (DMAF), the implementation guidelines of the LC, as well as in the guidelines of the U.S. EPA. The second type is the artificial island type, where the designated disposal area is excavated to a certain depth, and the sediment material obtained is used to pile up a ring dike that encircles the disposal site (example of Slufter for Rotterdam Harbor sludge). Within the ring dike, the dredged material is disposed of and may be finally covered with an additional cap. The third option is to excavate an area of uncontaminated sediment, to dispose of the contaminated dredged material into the excavation, and to cover the deposit with the clean excavated material (see Fig. 13.9*d*). This option is of particular economic interest because no capping material has to be transported to the disposal site.

In accordance with the precautionary principle, the choice of the appropriate disposal option has to be made by means of an effects-based assessment. This means that any poten-

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tial long-term impact of the planned disposal on the aquatic environment has to be evaluated. Therefore, a chemical and biological characterization of the dredged material in concert with an exact characterization of the disposal method and the disposal site is crucial. During the disposal process, any short-term risk may be due to suspension of contaminant-bearing sediment particles and desorption or dissolution of contaminants when passing through the water column. Another, possibly more serious threat is posed to the ecosphere by the potential continuous long-term release of contaminants. An underwater dredged material deposit without any further safeguards may be subject to (1) erosive forces resuspending contaminated sediment particles, (2) submarine groundwater discharge transporting dissolved contaminants into the water column or seawater intrusions into coastal groundwater, and (3) benthic organism resuspending and feeding on the contaminated sediment (Fig. 13.10*a*). Figure 13.10*b* shows the three main processes in a capping layer that counteract the release mechanism that will be discussed in detail in the next section.

Sediment Capping: Active Barrier Systems. Subaqueous capping, as mentioned earlier, has become an attractive concept for isolating contaminated sediments both in situ and following dredging/subaqueous storage. As discussed earlier, subaqueous capping is simply the placement of a layer of clean material (i.e., material that is suitable for unrestricted open-water disposal) over contaminated sediments. A clear distinction should be made, however, between in situ capping of contaminated autochthonous sediments, on the one hand, and dredged material capping that involves sediment removal by dredging, relocation, and subsequent capping of the disposal area by a cap on the other hand (Zeman, 1994).

As depicted in Fig. 13.10, three main mechanisms inhibit the release of contaminants from the sediment through a cap into the water column (Palermo et al., 1998). First, a stabilization of the sediments prevents sediment particles that may transport solid-phase-bound contaminants from being resuspended. Resuspension is considered a major path of release in waterways where strong bottom currents or ship traffic (anchoring, propeller wash) prevails. Second, a physical isolation of the sediment is achieved by transferring the zone of active bioturbation from the contaminated sediment into the clean cap. This prevents the benthos from getting into contact with the contaminants. Consequently, a direct uptake into the food chain and possible bioaccumulation can be ruled out. For an effective isolation, it is thus crucial to investigate the benthic community at the particular disposal site and, on that basis, determine the required minimum cap thickness. Third, a chemical isolation prevents contaminants from being transferred from the sediment to the overlying water by dissolution, desorption, or ion exchange at the sediment-to-water interface by sheltering the interface with a diffusion barrier.

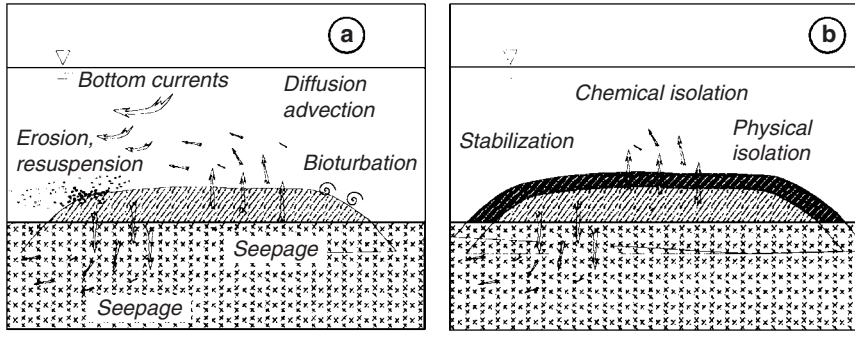

FIGURE 13.10 Potential long-term mechanisms in contaminant release from unrestricted dredged material disposals. (*b*) Mechanisms in capped disposals counteracting the contaminant release.

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The interaction of these three mechanisms can result in an effective prevention of contaminant release into the surface water if the cap design is adapted to the conditions at the capping site. The design of a cap requires the proper application of (1) hydraulic principles (i.e., armor and filter equations), (2) chemical principles (i.e., advection-diffusion-retention equations), and (3) geoengineering principles (i.e., settlement and stability equations) (Mohan et al., 2000). Implementation of in situ sediment capping thus is a typical example for collaborative projects involving strategic research, applied research and development, and technology sharing (Azcue et al., 1998). Major steps are (1) characterization of sediment materials (e.g., reactivity, mobility of pollutants), (2) suitability of capping techniques (e.g., currents, steep gradients, groundwater seepage), (3) provision of capping material (e.g., sand, granular materials, geotextiles, additives, logistics, soft sediment/coarse, dense cover, impermeable materials, water flow), (4) thickness of capping material, (5) reactive additives, and (6) monitoring of the sediment/cap system early warning systems.

Capping materials in projects completed to date usually have been either sand, gravel, or clean sediments. An overview over a selection of full-scale capping projects is given in Table 13.9. The cap can consist either of a basic single-layer design (e.g., a layer of sand) or a more complex multilayer design. After Mohan et al. (2000), such a multilayer design can consist of the following components:

1. A base stabilizing layer that provides local stability to the capped sediment to support the added weight of the cap
2. A base isolation layer that provides the primary isolation of the contaminants from the environment
3. A filter layer that provides hydraulic protection to the base isolation layer
4. An armor layer that provides erosion protection the cap

TABLE 13.9 Overview of Selected Capping Projects

Capping site	Contamination	Capped area	Cap design	Reference
Kihama Lake, Japan	Nutrients	3700 m^2	Fine sand, 0.05 and 0.2 m	
Akanoi Bay, Japan	Nutrients	20,000 m^2	Fine sand, 0.2 m	
Denny Way, USA	PAH, PCB	12,000 m^2	Sediment, 0.79 m	Sumeri (1995)
Simpson-Tacoma, USA	Creosote, PAK, dioxine	69,000 m^2	Sediment, 1.2–6.1 m	Sumeri (1995)
Eagle Harbor, USA	Creosote	220,000 m^2	Sediment, 0.9 m	Sumeri (1995)
Sheboygan River, USA	PCB		Sand	Eleder (1992)
Manistique River, USA	PCB	1858 m^2	Geomembrane	
Hamilton Harbor, Canada	Nutrients	10,000 m^2	Sand, 0.5 m	
Eitrheim Bucht, Norway	PAH, metals, nutrients	100,000 m^2	Geotextile, armoring	Instanes (1994)
St. Lawrence River, USA	PCB	6989 m^2	Sand, gravel, boulders	

Source: Modified from Palmero et al. (1998).

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The capping concept has been extended recently by the concept of active barrier systems (ABS) (Jacobs and Förstner, 1999). To enhance the chemical isolation component, the ABS concept employs capping layers that consist at least partly of one or more reactive components. The addition of reactive matrix components aims to actively demobilize the contaminants that are transported with percolating porewater. This a long-term retention of dissolved contaminants may be achieved even under unfavorable conditions such as a notable advective transport through the barrier. Advective transport can result, for example, from marine groundwater discharge or squeezing of porewater from compression of the sediment due to the additional load of the cap. Under these conditions, the chemical isolation potential of chiefly inert sand or gravel barriers may be exceeded. Actually, ongoing research work focuses particularly on the selection and characterization of reactive materials for active barrier systems. Potential materials have to meet a number of prerequisite properties: (1) they must have a good retention potential, (2) their chemical and physical properties (e.g., specific density, grain size distribution, and chemical stability) must be suited for an underwater application, (3) they must be suited for unrestricted open-water disposal (i.e., uncontaminated), and (4) they must be available at relatively low cost. Generally, industrial mineral by-products and natural (rock-forming) minerals are the most promising materials, but often they do not meet all requirements just listed (Table 13.10). Some of the listed properties may be altered by appropriate treatment of the material. For example, surfaces of clays and zeolites can be modified for an enhanced sorption of organics and anionic contaminants. Fine-grained materials that would rather form a hydraulic than a reactive permeable barrier may be granulated. However, this pretreatment apparently may raise the capital costs. Fortunately, natural microporous materials, and in particular natural zeolites, show highly favorable chemical-physical properties with respect to their application in subaqueous capping projects along with a worldwide availability at relatively low cost (Jacobs, 2000). Consequently, the actual research work focuses on these materials.

For the technical implementation of a cap, the same conventional dredging and construction equipment can be used that is used for relocation of the dredged material. This is of particular advantage from an economic point of view, but these practices must be controlled precisely. In general, the cap material must be placed so that it accumulates as an even and homogeneous layer covering the contaminated material. It must be prevented from displacing or mixing with the material due to the use of inappropriate placement methods or equipment (Anonymous, 1994). Several methods of cap placement using land- and sea-based equipment are discussed by Palermo et al. (1998).

As pointed out earlier, subaqueous capping is considered an economic management option. The capital costs of a capping project will be determined mainly by the cap materials, the equipment used for the placement, labor costs, and subsequently, by the monitoring program. However, most of the equipment is easily available because it is used for sediment dredging and relocation prior to cap placement. However, not all costs are covered by the dredging and transportation components when specialized equipment such as submerged diffusers is needed for cap placement. Generally, cap positioning requires a greater level of precision and control than disposal of the dredged material. The cap materials used are favorably low-cost materials, e.g., fresh sediment, sand, or natural mineral additives such as zeolites.

Perspectives of in Situ Methods. It was pointed out in the beginning of this chapter that soil and sediment remediation concepts and technologies traditionally were developed hand in hand, although a stronger distinction between these two fields has been made during the past decade. However, as a conclusion of the remediation aspects discussed in this chapter, it can be stated that the concept of permeable reactive barriers as a general approach applies as well for soil-groundwater systems as for sediment-porewater systems. This results, first of all, from the apparent economic advantages of the respective passive

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TABLE 13.10 Examples of Potential Reactive Materials for Active Barrier Systems

	Material	Contaminant retention	Physical-chemical suitability	Environmental acceptability	Availability/ costs
Industrial by-products	Fly ash	Metals	± (very fine grained)	− (high equilibrium pH, potential toxicity)	+
	Red mud	Metals	± (very fine grained, not stable under reducing conditions)	− (heavy metals)	+
Natural minerals and rocks	Calcite	metals, nutrients		+	+
	Apatite	Metals	+	+	±
	Clays (e.g., bentonite)	Metals	± (very fine grained)	+	+
	Zeolites (e.g., clinoptilolite)	Metals	+	+	+

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technologies: reactive walls and sediment capping. Due to their efficiency in isolating contaminants from the environment along with the greatly reduced capital costs and close-to-zero process costs, both technologies always represent attractive remediation alternatives, provided that they are technically feasible and do not interfere with national or regional legislation. Furthermore, these technologies may be considered moderate with respect to interference with natural and ecological resources because they do not require any transporting of contaminated materials, treatment plants, or upland deposits.

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CHAPTER 14

SEDIMENT SAMPLING, SAMPLE PREPARATION, GRAIN SIZE CORRECTIONS, AND CHEMICAL CRITERIA

Ulrich Förstner

INTRODUCTION

For water studies, standard analytical techniques are available to meet most sampling and analytical requirements, but the same is not true for sediment studies. Sediment sampling and analysis require the use of different techniques and equipment. The areal distribution of the samples is not the same, and generally they are taken less frequently in time than for water samples. Nonetheless, sediment analyses often are based on modified procedures of water quality analyses (e.g., Anonymous, 1978a) or on methods developed either in soil science (e.g., Bear, 1964) or for purposes of mineral exploration (e.g., Levinson, 1974; Watterson and Theobald, 1979). After the classic studies by Wright et al. (1965) on coring devices for lake sediments and by Sly (1969) on bottom sediment sampling, it took another 20 years, with increasing interest in sediments acting as a sink and source of contaminants, for sediment sampling and program design to evolve broadly as a special discipline in environmental studies (Keith et al., 1983; Hakanson, 1984; Keith, 1988; Baudo, 1990). Then, in the 1990s, two comprehensive overviews were published: *Handbook of Techniques for Aquatic Sediments Sampling* (Mudroch and MacKnight, 1991, 1994) and *Manual of Aquatic Sediment Sampling* (Mudroch and Azcue, 1995). In the latter book, designed as a field manual and general reference, techniques are described for sediment and sediment porewater sampling that are based on years of experience of many scientists; advantages and limitations of the different techniques and equipment for sampling are pointed out, allowing readers to choose the most adequate sampling technique and equipment to achieve the objectives of the sediment study. Further sections deal with the handling, pretreatment, and storage of sediment samples, and these are important steps prior to analysis because containers and other equipment can be significant sources of contamination. A large number of sediment analyses that have been performed for the inventory, monitoring, and surveillance of pollution in aquatic systems have shown clearly that it is imperative, particularly for river sediments, to base these data on a standardized procedure with regard to particle size. In the final section, the development and application of chemical-numerical sediment quality criteria is described. It seems advantageous to have such a relative simple initial assessment, which

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may then be extended with more complicated procedures, including biological criteria, into an integrated ecological evaluation (see Chap. 16 of this handbook).

OBJECTIVES

Monitoring of sediment contaminants and assessment of sediment quality usually are carried out with the objectives to determine the extent to which the sediments are either a source or a sink for contaminants and to evaluate the effects of these contaminants on the environment of the investigated water body. Such studies either can have regulatory implications, such as dredging and disposal of the dredged material and remediation of the contaminated area, or can be carried out to assess risk to human and environmental health through research on different sediment-water interaction processes (Mudroch and Azcue, 1995, p. 5).

A long-term program of sediment studies normally will consist of a series of objectives of increasing complexity, each drawing part of its information from the preceding database; a typical sequence of objectives may be illustrated as follows, although not all may be required to complete a program (Golterman et al., 1983, pp. 23–26):

1. *Preliminary site characterization.* Low-density sampling with limited analytical requirements to provide a general characterization of an area for which little or no previous information exists.
2. *Identify anomalies.* More detailed sampling and analyses designed to establish the presence and extent of anomalies.
3. *Establish references.* To create reference points in the form of some measured parameters for future comparison.
4. *Identify time changes.* To show trends and variations of sediment data over time by use of sediment cores or other repeated sediment samplings.
5. *Calculate mass balances.* To account for the addition and subtraction of sediment-related components with an aquatic environment (a complex study) by means of accurate and representative sampling and analysis.
6. *Process studies.* Specialized sampling to improve the state of knowledge about aquatic systems (e.g., by supplementary laboratory experiments).

The principal relationships between sampling objectives and types of activities for water-related studies are summarized in Table 14.1. The third column contains the specific objectives of sediment studies just listed. Sediment time-series data (category d) belong to two different types of activities. Suspended-sediment time-series data would be considered as a monitor surveillance activity; sediment core samples represent a highly condensed time series covering relatively long periods between potential samplings, and it may be appropriate to include this sampling objective under survey type activities.

Program objectives largely control the type, density, and frequency of sediment sampling and associated analyses, whereas the type of environment (e.g., rivers, lakes, estuaries, etc.) largely controls the locations and logistics of sampling. Logistic factors include (Golterman et al., 1983, p. 67)

- Local availability of sampling platform or vessel
- Time available
- Access to sampling region
- Suitability of survey system to locate sample position
- Availability of trained personnel and support staff

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SEDIMENT SAMPLING, SAMPLE PREPARATION, GRAIN SIZE CORRECTIONS, AND CHEMICAL CRITERIA

TABLE 14.1 Principal Relationships Between Sampling Objectives and Types of Activities in Water- and Sediment-Related Studies

Type of activity (Anonymous, 1978a)	GEMS water objectives (Anonymous, 1978b)	Sediment objectives (categories in text)
Monitor: Continuous standard measurement and observation	Cultural impact on water quality, suitability of water quality for future use	Establish reference point(s) (category 3)
Surveillance: Continuous specific observation and measurement relative to control and management	Observe sources and pathways of specified hazardous substances	Trace sources (spatial)
Survey: Series of finite duration; intensively detailed programs for specific purposes	Determine quality of natural waters	Identify anomalies (category 2), calculate mass balances (category 5), and study processes (category 6)

Source: Modified from Golterman et al. (1983).

- Availability of equipment
- Storage and security
- Transport systems
- Follow-up capability

The accelerating interest of environmental agencies in adopting sediment analysis as an integral component of their programs substantiates the fact that this type of research has achieved considerable success. It is now possible to outline several useful objectives for sediment sampling programs and to present comments about some of their limitations. The limitations generally are a function of incomplete knowledge or technique, and some of the major aspects will be treated below.

SAMPLING

According to Hakanson and Jansson (1983), as many as 12 different factors might influence the informative value of the sediment samples: type of water system (lentic or lotic), prevailing bottom dynamics, size of the water body, bottom roughness, anthropogenic factors, sediment chemical conditions, sediment physical and biological characteristics, number of samples, type of sampling net, sampling devices, sample handling, and reliability of laboratory analysis. However, "no systematic study has yet been introduced which accounts for even half of these 12 factors" (Baudo, 1990).

It is generally accepted that fine-grained suspended and bottom sediment particles (silt and clay with particle size less than 63 μm) accumulate greater concentrations of contaminants (e.g., Ackermann, 1980; de Groot et al., 1982; Förstner, 1982; Mudroch, 1984; Horowitz and Elrick, 1988), particularly those with low water solubility, than coarse particles (particle size greater than 63 μm). The fine-grained particles exhibit properties suitable for different physicochemical sorption and ion exchange of contaminants than the coarse particles [see the review by Horowitz (1991)]. Further, fine-grained sediments support a large part of the benthic community by supplying the food in sediment organic matter associated

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with the fine-grained particles. Therefore, the assessment of sediment quality must be carried out on the fine-grained sediments sampled in areas of the water body where permanent accumulation of sediments is taking place (Mudroch and Azcue, 1995, p. 8).

Project Planning

At first, the problem to be solved by conducting the project needs to be defined clearly (Mudroch and MacKnight, 1994a): The most common problem in pollution studies is the impact of contaminants on the aquatic environment. In many research-oriented projects, the problem to be solved is a lack of information for validation of a hypothesis. A project to determine the interactions between physical, chemical, and biological processes in water and their effects on marine or freshwater sediments or the influence of bottom fauna on physicochemical properties of sediments can provide a complete data set to confirm the results of preliminary studies or to verify modeling of the processes.

There are particular pieces of data that are relevant to the project planning. These include (Mudroch and MacKnight 1994a)

- General information on the watershed, including quantity and quality of runoff, climatic conditions, general or specific land use, types of industries, effluent, and urban runoff
- Distribution, thickness, and types of sediments, particularly fine-grained sediments (this will assist in assessing the physical extent of sediment accumulation, zones of deposition and erosion, and sediment transport)
- Quantity, particle size, geochemistry, and mineralogy of suspended sediments discharged by tributaries or stormwater runoffs or originating from shoreline erosion (knowledge of the nature and quantity of dissolved and particulate materials entering the area is necessary for the calculation of contaminant and nutrient loading)
- Horizontal and vertical profiles of physical (e.g., porosity, geotechnical properties, water content, bulk density, and grain size) and chemical (e.g., organic matter content and concentrations of nutrients, metals, and organic contaminants) characteristics of bottom sediments
- Biological community structure, composition and diversity, bioaccumulation of contaminants, or bioassay results

An example is presented in Box 14.1 for the project entitled, "Rehabilitation of the Aquatic Environment of a Harbor" (Mudroch and MacKnight, 1994a). The objectives of this project were to evaluate the role of contaminated sediments on the degradation of the ecosystem of the harbor and propose proper treatment of contaminated sediments and to prepare a long-term management plan for the disposal of sediments dredged from the harbor and shipping channel.

BOX 14.1 Rehabilitation of the Aquatic Environment of a Harbor

In this project, it will be necessary to gather information to determine if the sediments are the only source of pollutants or if there are other significant sources that have to be considered before sediment treatment. In addition, any historical information on the extent and type of sediment contamination will help in the preparation of a sediment sampling program for assessment of the quality of sediments in the harbor and to prepare a long-term management plan for dredging and disposal of contaminated sediments from the harbor and shipping channel.

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BOX 14.1 Rehabilitation of the Aquatic Environment of a Harbor (*Continued*)

A. Drainage Basin

- *General information:* Geology, soil type and chemistry, soil erosion, climate (e.g., rain- and snowfall), hydrology (e.g., runoff period), water levels in streams
- *Current land use:* Urban (e.g., population, waste and sewage treatment practices), industrial (e.g., type of industries, products and by-products, processes used in the production), agricultural (e.g., agricultural practices, use of fertilizers, pesticides, and herbicides), landfill sites (e.g., size, type of disposed material, management practices, runoff), historical changes in land use (e.g., changes in population, type of industry, agricultural practices)

B. Inputs to the Harbor

- Industrial facilities, e.g., location, quantity and quality of effluents and discharged solid wastes, historical changes in discharges
- Municipal sewage treatment plants, e.g., location, treatment technology, quantity and quality of effluent, historical changes, variance in flow due to storm waters, discharge of industrial effluents via municipal sewage
- Sewers, e.g., construction and location, sewers combined with other effluent discharges, overflow during storm events, runoff from roads, quantity and quality of effluents
- Tributaries, e.g., quantity and quality of water, quantity and quality of suspended solids
- Landfill runoff, e.g., quantity and quality
- Navigation-related inputs, e.g., from local industries, significance of long-range transport to the harbor
- Occasional spills of contaminants or nutrients in the drainage basin

C. Environmental Conditions in the Harbor

- Bottom sediments, e.g., physicochemical properties such as particle size distribution, geochemistry, concentration of contaminants and nutrients
- Dredging and disposal of sediments, e.g., quality and quantity of disposed material, disposal sites in the harbor or adjacent area
- Water depth and quality, e.g., concentrations of nutrients, contaminants, dissolved oxygen
- Water circulation, e.g., exchange with adjacent waters, residence time of water in the harbor, water column stratification
- Fish, e.g., species found in the harbor, bioaccumulation of contaminants, incidence of tumors/lesions/deformities
- Benthic plants and animals, e.g., community structure, species diversity, bioaccumulation of contaminants.

Source: Murdoch and MacKnight (1994a).

Geophysical Survey (Mudroch and Azcue, 1995, pp. 16–17)

To correctly select the location of sediment sampling stations in studies of sediment contamination, it is necessary to obtain information on the type of sediment, particularly on the location of fine-grained sediments and their extent at the study area. Generally, two methods are available to obtain such information. The first is an acoustic survey of the bottom

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of the water body to be sampled, and the second is limited-scale sediment sampling at selected locations. Preliminary information obtained by one of these methods or a combination of both will provide guidance on the design of appropriate selection of sediment sampling stations in the final sampling program (Mudroch and Azcue, 1995).

Acoustic survey techniques such as echo sounding, seismic reflections, and refraction are able to characterize both the type of surficial sediment layer, such as sand, gravel, or soft silty clay, and the subsurface sediment layers. Acoustic penetration is most effective in unconsolidated sediments consisting of soft, silty clays with high water content. On the other hand, sands or firm, compacted sediments display minimal acoustic penetration. Seismic reflection is based on a principle similar to echo sounding but uses a low-frequency sound and allows a deeper penetration, even into a coarse sediment (Mudroch and Azcue, 1995).

Further information is presented in Chap. 15 of this handbook, including side-scan sonar surveys and high-resolution seismic profiling (sonar transducer techniques, boomer, airgun, sparker, and implosive watergun).

Sampling Stations

In some cases, the objectives of a study of sediment will define the location of the sampling stations (Mudroch and Azcue, 1995, p. 6). For example, if a simple objective of a study is to determine the presence or absence of a specific contaminant in bottom sediment at a given area, then the sediment can be sampled at one or a few sampling stations at fine-grained sediment deposition sites to determine the presence of the contaminant. However, after confirmation of the presence of the contaminant in the sediment, the study may be expanded to determine the extent of sediment contamination by the specific compound or element within the area, the contaminant's sources, history of the loading of the contaminant, its transport, bioaccumulation, and so on. In this case, the objectives of the study become complex and need to be stated clearly before selection of the sampling stations.

- The objective of a *baseline sediment quality survey* is to determine sediment quality within a water body at a fixed point in time against which future surveys may be compared.
- A *monitoring survey,* similar to a baseline survey, involves regular or periodic resampling of sediments. However, the objective of a monitoring survey is to determine the changes in sediment quality over a period of time.

For both the baseline and monitoring sediment surveys, the sediments always need to be sampled from areas of permanent accumulation of fine-grained sediments. Much information has been given on sampling program design (e.g., Green, 1979; Gy, 1979; Keith, 1988). Table 14.2 provides some information on four types of very commonly employed sampling programs and their limitations.

In general, the density of sampling should be as great as possible, bearing in mind time requirements, the capacity of laboratory services, data storage, and handling and processing capabilities. For preliminary or exploratory surveys, the location of survey lines and the position of sample locations depend very much on the size and shape of the water body (Fig. 14.1). For more complex surveys, there are numerous types of sampling patterns from which to choose, e.g., spot samples, random grids, square grids (including nested and rotated grids), parallel-line grids and transverse-line grids (with equal or nonequal sampling), and ray grids or concentric arc sampling, each of which offers some particular advantage (Golterman et al., 1983, pp. 76–79).

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SEDIMENT SAMPLING, SAMPLE PREPARATION, GRAIN SIZE CORRECTIONS, AND CHEMICAL CRITERIA

TABLE 14.2 Examples of Commonly Employed Sampling Designs

Simple random sampling. Sites are selected such that every possible sample has an equal chance of being chosen. This method is very efficient in homogeneous areas; however, it may be ineffective in heterogeneous areas and could lead to overlooking important sites or data. This method is used commonly in reconnaissance surveys where little is known about local conditions.
Stratified random sampling. This entails dividing a heterogeneous area into homogeneous subareas within sampling locations that are randomly selected. This often permits the elucidation of subtle but real differences. This method requires some knowledge of local conditions.
Systematic sampling. This entails establishing a constant interval of distance between sampling sites determined by the number of planned samples. Randomness is introduced through selection of the initial sampling site. The advantage of this method is its ease of application; the disadvantage is that it can produce very biased results.
Fixed transect. Sampling occurs at fixed and predetermined sites that need not be at constant intervals. This method, while extremely simple, has a major statistical drawback: Since sites do not have an equal chance of being selected, any inferences or conclusions are associated only with the selected sites. This area's conclusions may not be valid.

Source: Horowitz (1991).

Sampling Devices

Corers and bottom samplers are used for fine-grained sediments. An extensive review of devices for bottom sediment sampling is presented by Mudroch and MacKnight (1994b). Figure 14.2 lists a selection of devices that have been applied successfully in different aquatic environments. For source reconnaissance analysis, fine- to medium-grained bottom deposits from a depth of 15 to 20 cm can be collected, for example, with an Ekman grab sampler. Material of the upper, flakey, light brown, oxidized layer is generally dissimilar to the layers below it. It is suggested that the chiefly dark layers directly underneath (approximately 1–3 cm in depth) are more representative of the pollution situation over the last few years, especially in river deposits exhibiting rapidly fluctuating sedimentation rates, and should be given priority for subsequent investigations. To complement this, surface sediment (current contamination) as well as a sample from deeper sections (10–20 cm in depth) could be examined. In environments with a relatively uniform sedimentation, e.g., in lakes and in marine coastal basins, where the deposits are fine-grained and occur at a rate of 1 to 5 mm per year, a more favorable procedure involves the taking of vertical profiles with a gravity or valve corer. A core profile of approximately 1 m covers a historical period of at least 200 years, and its development can be traced by virtue of the pollutant content in the individual layers. Table 14.3 through 14.5 list some sample devices and provide a comparison of their characteristics.

Suspended sediment can be used for a variety of geochemical and water quality studies (Allan, 1986; Horowitz, 1991), such as (1) geochemical exploration reconnaissance surveys, (2) regional geochemical surveys, (3) determining pollutant spatial distributions, (4) determining medium- and short-term temporal changes in pollutant concentrations, (5) establishing local baseline concentrations, (6) identifying point and nonpoint sources of pollution, (7) monitoring aquatic disposal of wastes, (8) determining biological effects, (9) determining pollutant transport, and (10) establishing pollutant fluxes. Suspended sediment, along with the sampling and analysis of dissolved samples, may represent the only available means of determining short-term temporal changes in water quality (Horowitz, 1991). Therefore, in water quality studies, the collection of a representative sample is of extreme importance because it is almost impossible to sample and analyze an entire water

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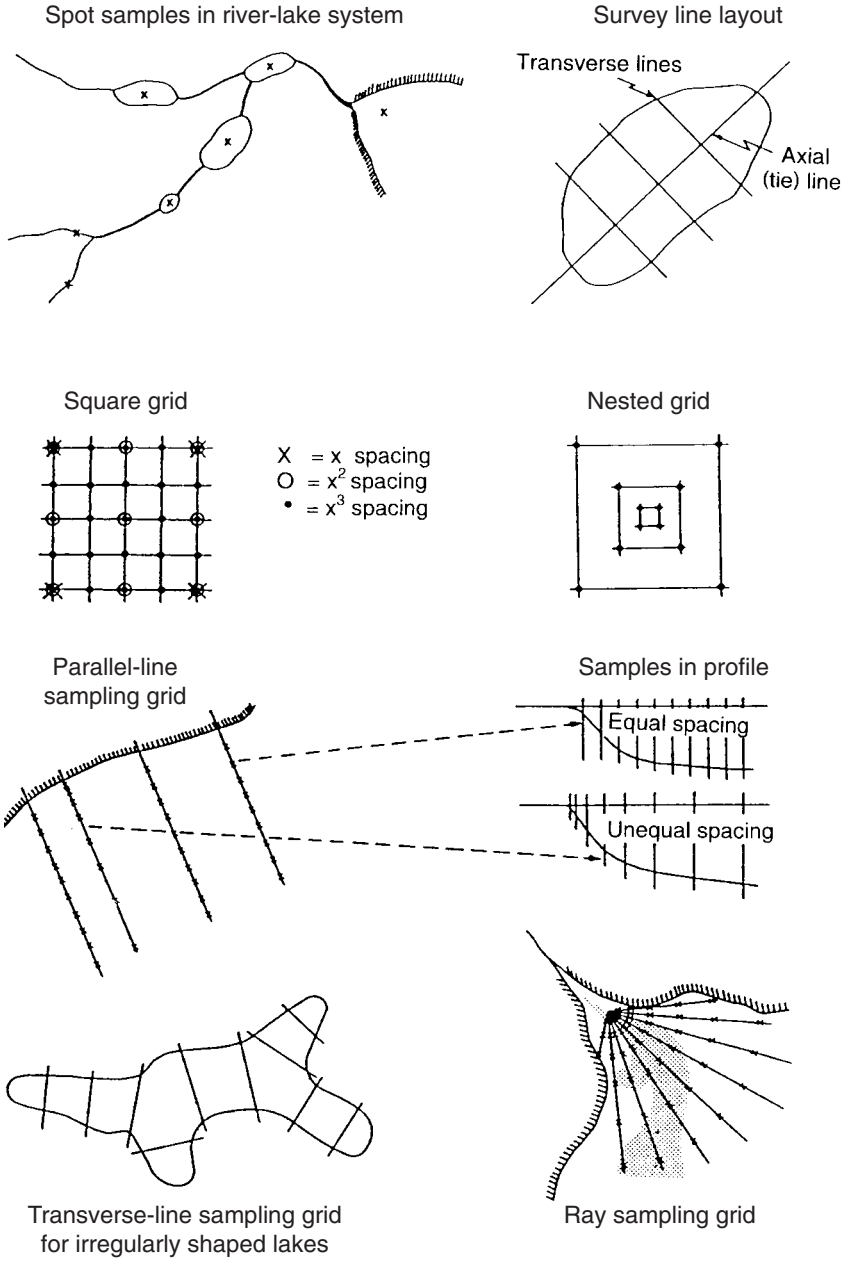

FIGURE 14.1 Examples of different types of sampling grid designs. *(Golterman et al., 1983.)*

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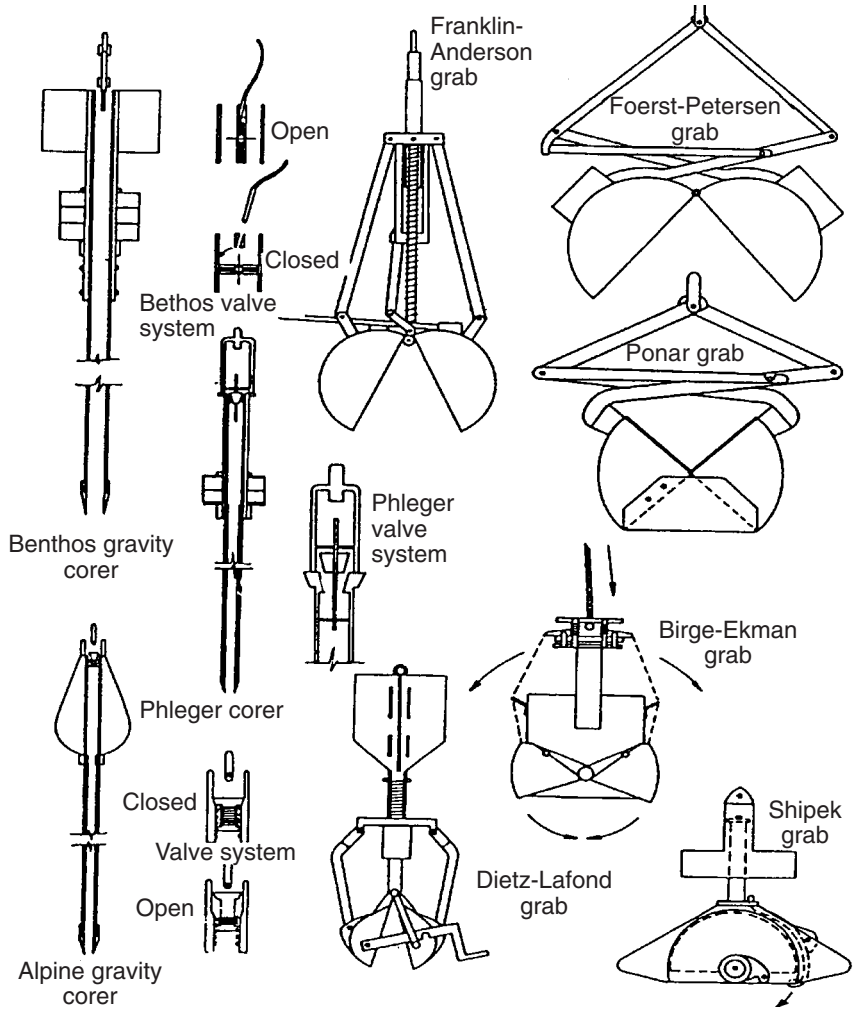

FIGURE 14.2 Examples of corers and bottom samplers. *(Sly, 1969.)*

body adequately (Horowitz et al., 1989). A review of sampling settling and suspended particulate matter is presented by Rosa et al. (1994).

The composition of interstitial waters in sediments is perhaps the most sensitive indicator of the types and extent of reactions that take place between pollutant-loaded sediment particles and the aqueous phase that contacts them (see Chap. 16). Interstitial waters are recovered from sediments by leaching, centrifugation, or squeezing. Most important, oxidation must be prevented during these procedures. Overviews of sediment porewater sampling were presented by Adams (1994) and by Mudroch and Azcue (1995, pp. 81–113).

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TABLE 14.3 Partial Listing of Commonly Used Core Sampling Devices

Free-fall gravity corers. These are used without a wire or line for short-length corers in very soft fine-grained sediment.
Standard gravity corers. These are used with a wire or line for short- to medium-length corers in soft fine-grained clay to fine-grained sand.
Box corers. These are used with a wire or line for short-length undisturbed corers with a large surface area in soft fine-grained clay to coarse-grained sand.
Kastenlots. These are used with a wire for medium-length undisturbed corers in soft fine-grained clay to medium-grained sand.
Piston corers. These are used with a wire for medium- to very-long-length relatively undisturbed corers in soft fine-grained clay to medium-grained sand.
Vibrocorers. These are used with a wire for medium- to long-length corers in soft fine-grained clay to indurated coarse-grained sand.

Source: Horowitz (1991).

TABLE 14.4 Partial Listing of Commonly Used Grab Sampling Devices and the Types of Sediments Where They Are Most Effective

Franklin-Anderson grab. Bulk samples of soft clay, mud, silt, sand, rarely gravel.
Dietz-LaFond grab. Small samples of soft clay, mud, silt, sand.
Petersen grab. Bulk samples of soft clay, mud, silt, sand, gravel.
Ponar grab. Bulk samples of indurated or soft clay, mud, silt, sand, gravel.
Birge-Ekman grab. Small and bulk samples of soft clay, mud, silt, silty sand.
Shipek grab. Bulk samples of indurated or soft clay, mud, silt, sand gravel.

Source: Data from Sly (1969) and Horowitz (1991).

Core Sampling Devices. Coring devices fall into three major categories (Horowitz, 1991): (1) gravity corers, (2) piston corers, and (3) vibrocorers. Selection of core samples invariably involves subsampling, especially when there are obvious physical differences (e.g., texture, color) between various sections of an entire core.

Gravity corers use the force of gravity to penetrate into the sediment. Generally, the heavier the corer, the greater is the degree of penetration. These devices also require a minimum amount of water depth to achieve sufficient velocity to obtain maximum penetration. Box corers and Kastenlots are special types of gravity corers that do not require rapid rates of descent to penetrate a sediment column deeply; the former scoop out a section of the sediment column through the operation of a set of springs, whereas the latter are extremely heavy and wide barreled, involving less frictional resistance due to the thin walls of their barrels (See Fig. 14.2 and Table 14.3).

Piston corers are used to obtain long cores in relatively soft sediment. They are set up so that the piston, which is inserted inside the barrel, stops at the sediment-water interface, whereas the core barrel continues to penetrate the sediment column. The piston creates a vacuum that reduces frictional resistance to barrel penetration.

The length of the cores are quite different (Horowitz, 1991). Typical gravity cores do not exceed 2 m, although Kastenlot cores up to 6 m have been recovered. Under the right conditions, piston cores of more than 30 m have been collected. Length of vibrocores,

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TABLE 14.5 Comparison of the General Characteristics of the Different Sampler Types

Characteristic	Dredges	Grabs	Corers
Free water passage	Yes	Yes	Yes
Wall thickness/sample area	Low	Low	Low
Closing on retrieval	No	Yes	Yes
At top	No	Lid	Lid
At bottom	No	Jaw	No
Transparent side(s)	No	Yes	Yes
Subsampling			
From Sampler	No	Top	No
Extrusion	No	No	Yes
Exchangeable weight	Yes	Yes	Yes
Handling			
Use	Ease	Less easy	Difficult
Weight	Low	Medium	Low/medium
Safety	High	Low	Medium
Sample			
Area	Large	Large	Small
Depth	Small	Medium	High
Cost	Low	Medium	Medium/high
Studies on			
Physics	No	Yes	Yes
Chemistry	?	Yes	Yes
Biology	Yes	Yes	Yes/no
Porewater	No	Yes/no	Yes

Source: Baudo (1990).

which tend to be more disturbed than piston cores, is controlled by the size of the system being used and typically does not exceed 12 m.

Grab Sampling Devices. Grab sampling devices of various design have different advantages and disadvantages depending on the nature of the sediment to be sampled, the water depth, the amount of sediment required, the size of the area to be sampled, local energy conditions, sampling platform, and the availability of lifting equipment. Generally, the selection of a particular type of grab for the collection of a sediment-pollutant sample depends on evaluations against four criteria (Horowitz, 1991; see Fig. 14.2 and Table 14.4): (1) degree of physical disturbance during sampling, (2) loss of material during recovery of the sampler (washout), (3) the efficiency of the grab for collecting sediments of varying textures, and (4) potential for sample contamination.

Suspended-Sediment Sampling. Suspended-sediment samplers fall into three general categories (Anonymous, 1982; Horowitz, 1991): (1) integrating samplers that accumulate a water-sediment mixture over time, (2) instantaneous samplers that trap a volume of whole water by sealing the ends of a flow-through chamber, and (3) pumping samplers that collect a whole-water sample by pump action. Integrating samplers usually are preferred because they appear to obtain the most representative fluvial cross-sectional samples (Table 14.6).

Extraction of Porewater. The sampling requirements and methods for porewater extraction are summarized in Table 14.7; there is no particulate method for porewater sampling

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TABLE 14.6 Types of Fluvial Suspended-Sediment Integrating Sampling Procedures

Point integration. The flow area is divided into lateral increments, with samples collected isokinetically at various depths along a vertical in each increment; incremental widths and sampling intervals are selected such that concentration and velocity differences between adjacent points are sufficiently small as to meet desired accuracy.

Depth integration. An isokinetic sample is collected while the sampler is moved vertically at a uniform speed; sampling can be continuous or discontinuous over the entire depth.

Equal-discharge increment vertical (EDIV). One of several vertical depth integrated isokinetic samples is collected at the centroid of an equal-flow segment in a riverine cross section.

Equal-discharge increment sample (EDI). A suspended-sediment collection technique designed to obtain an isokinetic discharge-weighted sample at a riverine transect by (1) performing vertical depth integration at the centroids of equal-flow segments across the transect and by (2) using a vertical transect rate at each vertical that provides equal sample volumes from each flow segment.

Equal-width increment sample (EWI). A suspended-sediment collection technique designed to obtain an isokinetic discharge-weighted sample at a riverine transect by (1) performing vertical depth integration at a series of vertical sites equally spaced across the transect and by (2) using the same vertical transit rate at all sampling verticals.

Composite sample. An actual sample, formed by combining collected EDIV samples, that is representative of the vertical and horizontal distributions of suspended sediment in a riverine cross section.

Source: Anonymous (1982) and Horowitz (1991).

that seems to be ideal for all objectives or that is problem-free (Mudroch and Azcue, 1995). In situ methods are considered particularly promising because of their inherent simplicity, and they appear to be well adapted to the study of trace metals at the sediment-water interface under field conditions. Initially, the technique described by Mayer (1976) consists of a dialysis bag filled with distilled water, which is displaced into the sediment, allowing equilibrium to take place over a period of some days to weeks. Another in situ sampler for close-interval porewater studies as presented by Hesslein (1976) was made from a clear acrylic plastic panel with small compartments predrilled in 1-cm steps or less. The development and application of the peeper technique is described by Mudroch and Azcue (1995, pp. 101–108).

HANDLING, PREPARATION, AND STORAGE OF SEDIMENT SAMPLES

Measurement and Handling of Samples in the Field

The measurements and handling of sediment samples that should be carried out in the field are outlined in Fig. 14.3. A review by Mudroch and Azcue (1995, pp. 115–138) covers the major operations, such as (1) measurement of pH and Eh (including a detailed description of equipment and solutions used in the measurements), (2) subsampling for determination of cation exchange capacity, (3) subsampling under an oxygen-free atmosphere, (4) sample mixing and subsampling into prepared containers, and (5) sampling of hazardous sediments and safety requirements. Regarding the latter theme, Table 14.8 provides a list of typical hazards encountered when sampling sediments from hazardous waste sites or spills.

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SEDIMENT SAMPLING, SAMPLE PREPARATION, GRAIN SIZE CORRECTIONS, AND CHEMICAL CRITERIA

TABLE 14.7 Advantages and Disadvantages of Techniques Commonly Used for Porewater Sampling

Method	Advantages	Disadvantages
Squeezing	Simple equipment	Oxygen contamination
	Portable	CO_2 degassing that will change porewater composition
	Inexpensive	Temperature-induced changes
	Sediment composition available	Pressure-related additions of metabolites
Centrifugation	Simple	Risks of sampling artifacts
	Sediment composition available	Pressure artifacts
	Easy to obtain large volumes	Effects of oxidation and elevated temperatures
Dialysis	Minimal manipulation of sample	Disturbance of the sediment structure
	No induction of interstitial water flow	Needs of scuba divers or submersibles
	Allows maximal replication	Timing (minimum 12 days)
	Analysis of dissolved gases is possible	Risks of incomplete equilibration
	Temperature- and pressure-related artifacts are avoided	Risks of membrane breakdown
Suction	Simple and easy to use	Fine particles could be collected (reduction of mesh size may cause clogging)
	Allows sampling at fairly well-defined depth	Oxidation effects are hard to prevent

Source: Mudroch and Azcue (1995).

Many of the prevention measures can be applied to remediation activities on abandoned contaminated soils (see Chap. 13).

Wet Sediment Sample Preparation

A general scheme for handling samples for tests and analyses on wet sediments is presented in Fig. 14.4.

Handling of Samples for Determination of Particle Size Distribution. Samples for this purpose should not be frozen but stored at 4°C. Tightly sealed plastic bags, glass jars, or other containers can be used to store samples prior to particle size analyses. Sediments with a high iron content should be stored in airtight containers to avoid precipitation of iron oxides on particle surfaces and should be analyzed as soon as possible after collection.

Handling of Samples for Geotechnical Tests. Sediment samples for geotechnical studies can be stored at 4°C in a humidity-controlled room without any large changes in sediment properties for several months. Long cores, such as those collected by piston coring, can be cut into lengths suitable for storage, wrapped to preserve their original consistency, and stored in a refrigerated room.

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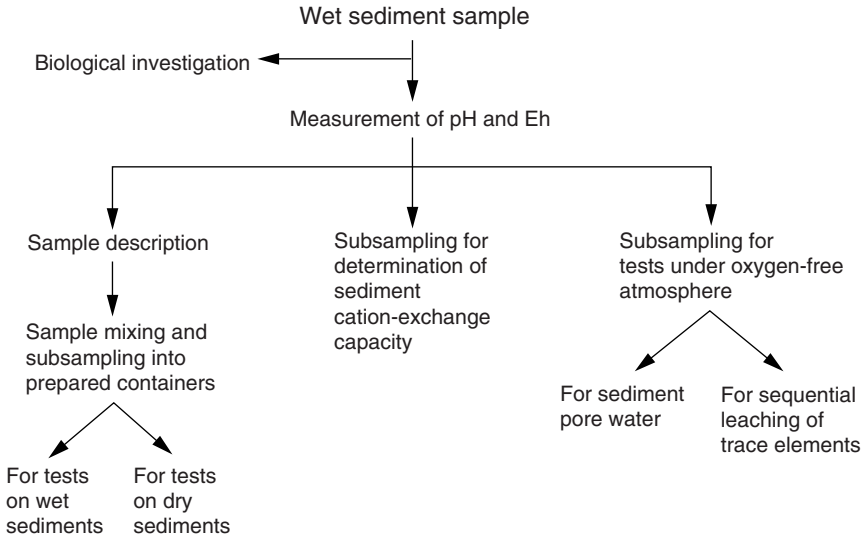

FIGURE 14.3 Sample handling and measurements in the field. *(After Mudroch and Azcue, 1995.)*

Freezing of Wet Sediment. Freezing has long been an acceptable preservation method for sediments collected for the determination of organic and inorganic constituents. It has been shown that rapid and deep freezing can best maintain sample integrity and thus enable investigation for concentrations of contaminants. The lower the temperature of deep freezing, the better; a temperature of −80°C is the suggested maximum.

Handling of Samples for Biological Analyses and Bioassays. Samples collected for investigations of benthic organisms usually are processed in the field by wet sieving through different sized sieves. If for any reason the samples cannot be processed in the field, they should be stored at 4°C in the dark and processed in the laboratory as soon as possible.

Dry Sediment Sample Preparation

Handling operations for dry sediments include drying, sieving, grinding, mixing, and homogenization. Three types of drying are used commonly to prepare solid samples prior to analysis (Mudroch and Bourbonniere, 1994):

Air drying. This is used rarely for the preparation of sediments for pollution studies because it may generate undesirable changes in sediment properties. For example, changes in metal availability and complexation were shown for samples that were air dried. In some cases, air drying has been used to avoid losses of components, such as mercury, that are volatile at temperatures above 50 to 60°C.

Oven drying. This is usually carried out on samples collected for the determination of inorganic components, such as major and trace elements. Oven drying is not acceptable for sediments that contain any volatile or oxidizable components, whether they be organic or inorganic, and may contribute to the alteration of even nonvolatile organics.

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TABLE 14.8 Typical Hazards Encountered When Sampling Sediments from Hazardous Waste Sites or Spills

Hazard type	Exposure route or causes	Prevention
Chemical exposure	Inhalation, eye/skin contact, ingestion, puncture	Use remote sampling devices when possible
Ionization radiation	Sediments containing radioactive materials Exposure radiation burns, ingestion	Perform radiation survey early in investigation Wear protective clothing and dust masks
Physical safety hazard	Steep grades Slippery surfaces Uneven terrain Sharp objects	Perform visual inspection and monitoring Wear better-fitting clothing Wear hard hats, boots with good gripping soles
Biologic (etiologic) hazards	Sediments containing wastes from hospitals and research facilities Poisonous plants, insects, animals, and indigenous pathogens	Wear gloves, respirators, protective clothing Decontaminate with desinfectant Immunize if agent is known
Heat stress or cold exposure	Work done in clothing designed to protect against chemicals but not against weather conditions	Take frequent rest breaks Monitor body temperature Drink fluids Wear appropriate clothing for weather conditions
Fire and explosion	Unstable chemicals Incompatible reactions Vapor buildup	Use nonsparking tools Use fire-proximity suits or blast suits

Source: Mudroch and Azcue (1995).

Freeze drying. This can be used for drying sediments collected for the determination of most organic pollutants, as well as for analyses of inorganic components, such as the major and trace elements. The principal advantages of freeze drying for sediments are (1) low temperatures avoid chemical changes in labile components, (2) loss of volatile constituents, including certain organic compounds, is minimized, (3) most particles of dried sediments remain dispersed, (4) aggregation of the particles is minimized, (5) sterility is maintained, and (6) oxidation of various minerals or organic compounds is minimized or eliminated.

Anoxic Sediment Treatment

Anoxic sediment samples require different sampling preservation techniques such as oxygen exclusion. Drying and freezing (also freeze drying) of the samples should be avoided for material designated for extraction procedures. If total analyses or strong acid digestion is planned, the sediment is dried at 60°C, crushed, and stored; for mass calculations, reweighing after drying at 105°C may become necessary. For a more differentiated approach, in

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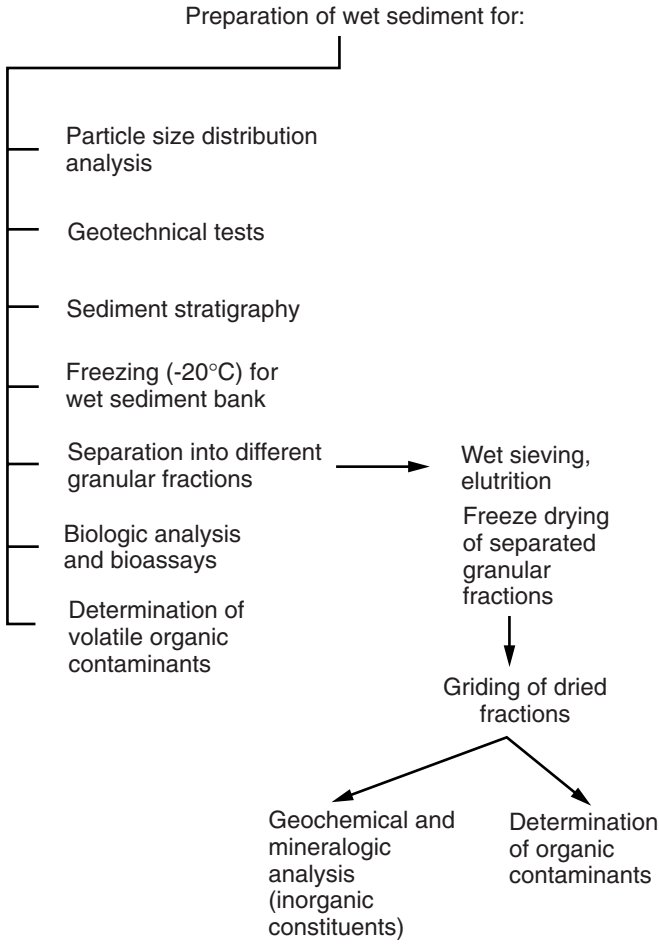

FIGURE 14.4 Handling samples for tests and analyses on wet sediments. *(After Mudroch and Bourbonniere, 1994.)*

particular for solid speciation studies on anaerobic samples, the following pretreatment scheme was developed (Kersten and Förstner, 1987): Samples are taken immediately from the center of the material (collected with a grab or corer) with a polyethylene spoon and placed into a polyethylene bottle up to the top. Immediately after arriving at the laboratory, the sediments are inserted into a glove box prepared with an inert argon atmosphere. Oxygen-free conditions in the glove box are maintained by purging continuously with argon under slight positive pressure. Extractants are deaerated prior to the treatment procedure.

Containers for Sediment Samples: Sampling Protocol

Containers and other equipment used in handling sediment samples after retrieval can be a significant source of contamination (Mudroch and Azcue, 1995, pp. 139–143). For exam-

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ple, plastics contain plasticizers that can be potential contaminants in the determination of organic compounds. Glass, porcelain, stainless steel, Teflon, or Teflon-coated instruments should be used in handling sediment samples to be analyzed for organic components. Wide-mouth amber or clear glass jars and bottles with aluminum foil– or Teflon-lined caps are the best containers, but certain compounds (e.g., phenols) can adsorb to these surfaces (Luepke, 1979). Metal containers, spoons, or other equipment may contaminate samples that will be analyzed for metals and trace elements. If both organic and metal analyses are required for a given sediment sample, a Teflon container is recommended.

Examples of cleaning procedures for containers, as applied at Environment Canada's Water Research Institute (NWRI), are described by Mudroch and Bourbonniere (1994).

Quality Control in Sediment Sampling

Quality control (QC) procedures in environmental analysis reduce and maintain random and systematic errors with tolerable limits, whereas quality assurance (QA) is the management system that ensures that an effective QC system is in place and working as intended (Keith, 1991). As mentioned in the introductory paragraph, standard sampling and preparation techniques are not available for sediments. Results from sediment analyses and in particular their application for sediment quality criteria, therefore, depend in a special way on a high level of QC and QA both in field and in laboratory. Among the few compilations on QC of sediment sampling, the review by Mudroch and Azcue (1995, pp. 181–203) is based on a broad spectrum of experience in the relevant steps outlined in this chapter, i.e., project planning, preliminary surveys, selecting of sampling stations and sampling devices, and handling, preparation, and storage of sediment samples. The initial step, the preparation of a sediment sampling protocol, is exemplified in Box 14.2.

BOX 14.2 Example of a Sediment Sampling Protocol

1. Define the character of the samples to be collected to meet the objectives of the sediment sampling program and the study objectives, e.g., in the collection of surface sediments, the depth of surface sediments to be collected, and in the collection of sediment cores, the length of the sediment cores is to be defined.
2. Confirm available funds and number and availability of trained and nontrained personnel needed for the sediment sampling program.
3. List all physical, biological, and chemical analyses (including bioassays) that will be carried out on collected sediment samples in the laboratory as well as observations and tests that will be carried out in the field.
4. Discuss and confirm with the laboratories a list of individual analyses and assays of sediments collected in the study area. Estimate and compile the quantity (i.e., volume, weight) of wet and dry samples necessary to carry out all listed analyses and assays. In the estimation, consider analyzing duplicate samples, banking collected sediment samples for future analyses, and performing other QA/QC procedures that will require an additional volume or weight of samples.
5. Collect information on various parameters in the study area relevant to the sediment sampling program, such as water depth, morphometry (shape) of the water body, hydrological conditions, sediment distribution, accumulation areas of fine-grained sediments, climatic conditions, etc.
6. Select sampling stations within and outside the study area, e.g., for collection of sediments outside the study area at a selected control site. Plot the sampling stations on a chart containing the study area. Number the sampling stations in the most logical sequence relevant to the sediment sampling program and objectives.
7. Select the time frame of the sediment sampling program. Consider the optimal use of the time spent on the sediment sampling in the study area.

(*Continued*)

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BOX 14.2 Example of a Sediment Sampling Protocol (*Continued*)

8. Consider the safety of the personnel carrying out the sampling program, such as weather conditions expected during the sampling period (wind speed and direction, air and water temperature) and severity of contamination of the sediments and water to which the sampling personnel will be exposed.
9. Select and list all sediment sampling equipment and other materials that will be used in support of the sediment sampling program in the study area, such as tools an spare parts for emergency repairs and maintenance of the sampling equipment in the field, maps, charts, notebooks, sediment logging sheets, equipment for measuring sediment properties in the field such as pH and Eh meters, equipment for homogenization and subsampling of the sediment samples, sample containers, extruders for sediment cores storage boxes, and other equipment specific to the sediment sampling program.
10. List the last date the sediment sampling equipment was tested together with any problems encountered during the testing and repairs of the equipment. List all necessary spare parts and tools that must accompany the sediment sampling equipment for emergency repairs during the sampling program.
11. Select and compile appropriate sediment sampling and subsampling procedures, sample handling, sample preservation, field storage, transport from the site to the laboratory, and storage after samples delivery including required temperature, freezing of the samples, etc.

Source: Mudroch and Azcue (1995, pp. 25–26).

Quality control in *planning* includes choice of (1) sampling locations, (2) sampling procedures, and (3) material; quality control in *field sampling* covers (1) sample collection, (2) sample handling, (3) cleaning procedures, (4) transport, (5) preservation, and (6) storage.

Two techniques can be used for QC in sediment sampling (Mudroch and Azcue, 1995):

1. Collection of more than one sediment sample at selected sampling sites using identical sampling equipment, such as multicorers, as well as using identical field subsampling procedures, handling and storage of the samples, and methods for sediment analyses.
2. Subdivision of the collected sample into a few subsamples and treatment of each subsample as an individual sample. The results of chemical analyses of all subsamples indicate the variability due to the sampling and analytical techniques and sediment heterogeneity within a single collected sample.

The control samples used in sediment studies include sampling, transport, sampling equipment, and control samples for laboratory procedures. Contrary to water sampling, sediment sampling generally does not require the use of blanks. However, several types of blanks are used commonly in *sediment porewater* sampling (Mudroch and Azcue, 1995):

- *Field blanks* are samples of laboratory reagents or reference materials that are carried to the field and exposed to the same procedure, such as transfer into containers or field physicochemical measurement, as the actual samples.
- *Transport blanks* are samples free of contamination that are transported from the laboratory to the field and back to the laboratory without being opened. This kind of blank is important when the sample is stored for several weeks prior to analysis.
- *Equipment blanks* are samples of water that have been used to rinse the sampling equipment. These blanks are critical when sampling sediment porewaters, and they are collected before and after cleaning the sediment porewater sampling devices.
- *Spiked samples* in the field are samples to which a known amount of a certain element or compound of interest is added in the field. These samples are used to identify possible interferences of complex matrices or time-related losses by volatilization.

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A considerable proportion of the review by Mudroch and Azcue (1995) is devoted to the preparation of reference materials. Reasons for this preference are (1) sediment type and mineral composition play an important role in the distribution of elements in the sediment, (2) the lack of matrix matching between sediment samples and analytical standards can cause generation of biased data and erroneous conclusions, and (3) because of the high price of commercially available standard reference materials, it is advantageous for laboratories involved in performing many analyses of sediments to prepare an in-house set of reference materials for different analyses. Regarding the latter point, however, it is also recommended that commercial standard reference materials be used on a weekly basis at least as an aid to monitoring analytical quality assurance.

CORRECTION FOR GRAIN SIZE

One of the most significant factors controlling both suspended and bottom sediment capacity for concentrating and retaining organic and inorganic contaminants is grain size. For example, there is a very strong positive correlation between decreasing grain size and increasing trace element concentration [see review by Horowitz (1991)]. This correlation results from a combination of both physical (e.g., surface area) and chemical factors (e.g., geochemical substrates). However, in many instances, it is impossible to differentiate between effects caused by such factors as surface area, cation exchange capacity, surface charge, and the increasing concentration of various geochemical substrates and effects due to grain size.

A large number of sediment analyses that have been performed for the inventory, monitoring, and surveillance of pollution in aquatic systems have shown clearly that it is imperative, particularly for river sediments, to base these data on a *standardized procedure* with regard to particle size [see review by Förstner (1989)]. However, selection of certain grain size fractions—in particular, for tracing of pollution sources—remains controversial for the following reasons:

1. Since the *larger sediment fractions* are less affected by scour and transport, they may "reflect the effect of urbanization on the distribution of heavy metals over an extended period of time at a given location" (Wilber and Hunter, 1979).
2. The *fine-sand fraction* (approximately 20–200 μm in diameter) seems to be of particular interest for the differentiation of natural and pollutant metal transport because it comprises most of the total sediment.
3. The *silt and clay fractions* comprise the major carriers for both natural and anthropogenic compounds (although in relatively small proportions); they are widely distributed with the sedimentation area and are least affected by grain-size effects.

Different *methods* for grain-size correction are compiled in Table 14.9. These methods will mostly reduce (not eliminate) the fraction of the sediment that is largely chemically inert, i.e., mostly the coarse-grained, feldspar, and carbonate minerals, and increase the substances active in pollutant enrichment, i.e., hydrates, sulfides, and amorphous and fine-grained organic materials.

Separation

Separation of grain size is advantageous because only a few samples from a particular locality are needed. However, it has been inferred that the decrease of pollutant concentrations in the medium grain size range should be even more pronounced if mechanical

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TABLE 14.9 Methods for the Reduction of Grain-Size Effects in Sediment Samples

Method		Reference (example)
Separation of grain-size fractions (mechanical)	204 μm (sieving)	Thornton et al. (1975)
	175 μm (sieving)	Vernet and Thomas (1972)
	63 μm (sieving)	Allan (1971)
	20 μm (sieving)	Jenne et al. (1980)
	2 μm (settling tube)	Banat et al. (1972)
Extrapolation from regression curves	Metal/percent 16 μm	De Groot et al. (1971)
	Metal/percent 20 μm	Lichtfuss and Brümmer (1977)
	Metal/percent 63 μm	
	Metal/specific surface area	Smith et al. (1973) Oliver (1973)
Correction for inert mineral constituents	Quartz-free sediment	Thomas (1972)
	Carbonate/quartz-free	Salomons and Mook (1977)
Treatment with dilute acids or complexing agents (determination of mobile fraction)	0.1 *M* hydrochloric acid	Gross et al. (1971)
	0.3 *M* HCl	Malo (1977)
	0.5 *M* HCl	Agemian and Chau (1976)
	25% acetic acid	Loring (1977)
	EDTA, DTPA, NTA	Gambrell et al. (1977)
Comparison with conservative elements	Metal/aluminium	Bruland et al. (1974)
	Sediment enrichment factor (Al_x/Al background)	Kemp et al. (1976)
	Relative atomic variation	Allan and Brunskill (1977)
	Metal/Cs, Sc, Eu, Rb, Sm	Ackermann (1980)
	Al_x/standard Al	Li (1981)
	Sc_x/standard Sc	
		Schoer et al. (1982), Thomas and Martin (1982)

Sources: Förstner and Wittmann (1979), DeGroot et al. (1982), Salomons and Förstner (1984), Förstner (1989).

fractionation would more accurately separate individual particles according to their grain size. One has to consider that coatings, for example, of iron/manganese oxides, carbonates, and organic substances on relatively inert material with respect to sorption act as substrates of pollutants in coarser grain size fractions (Förstner and Patchineelam, 1980). Nonetheless, the less than 63-μm fraction has been recommended for the following reasons (Förstner and Salomons, 1980):

- *Pollutants* have been found to be present mainly on clay/silt particles.
- This fraction is nearly equivalent to the material carried in *suspension,* the most important transport mode by far.
- *Sieving* mostly does not alter pollutant concentrations (for metals even by wet sieving, when water from the same system is used).
- *Numerous pollutant studies,* especially with respect to heavy metals, have already been performed on the less than 63-μm fraction, allowing better comparison of results.

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SEDIMENT SAMPLING, SAMPLE PREPARATION, GRAIN SIZE CORRECTIONS, AND CHEMICAL CRITERIA

On the other hand, it has been argued by Ackermann (1980) that separation of the less than 20-μm fraction, which also can be performed with nylon sieves, should be favored at least for coastal sediments, where the correlation with conservative elements has been found to be better with this fraction than with less than 63-μm fraction (see below). In addition, for organic pollutants, separation of the less than 20-μm fraction seems to compare favorably with other grain-size fractions (Hellmann, 1983).

Extrapolation

Extrapolation techniques both for the grain size and for specific surface area require a relative large number of samples (10–15). Further complicating is the fact that calculation of the regression line is a tedious and mostly inaccurate procedure. The *quartz-correction method* involves fusion with potassium pyrosulfates, which preferentially removes the layered silicates (clay), organic and inorganic carbon, and sulfides with a residue made up of quartz plus feldspar and resistant heavy minerals such as zircone (Thomas et al., 1976). Extraction of environmentally active trace metals (Bopp and Biggs, 1981) should consider the more mobile fractions of elements, which are introduced by human activities and are bound to the sediment in sorbed, precipitated or coprecipitated, or organically complexed form.

Generally, five types of elements have been distinguished according to their distribution in sediment cores from Lake Erie (Kemp et al., 1976): (1) *diagenetically mobile* elements, such as iron, manganese, and sulfur, (2) *carbonate* elements, carbonate-C, and calcium, (3) *nutrient* elements, organic carbon, nitrogen, and phosphorous, (4) *enriched* elements, such as copper, cadmium, zinc, lead, and mercury, and (5) *conservative* elements, such as silicon, potassium, titanium, sodium, and magnesium. Comparison of group (4) elements of environment concern with conservative elements (group 5) seems to be particularly useful for the reduction of grain-size effects because no separation step is required.

The suitability of *reference elements* has been tested by Ackermann (1980) on sediment samples from the Ems River estuary in northern Germany. Table 14.10 summarizes the correlation coefficient r between the contents of conservative elements and the percentage of grain-size 20- and 63-μm fraction, respectively, and the slope of the regression line, the quotient $s(100\%)/s(0\%)$ from the ordinate values extrapolated for 100 and 0 percent of the two grain-size fractions (Fig. 14.5*a*). According to Table 14.10, cesium appears to be the preferred reference element for two reasons. First, it is particularly well correlated ($r = 0.987$) with the percentage of the less than 20-μm fraction, and second, the quotient $s(100\%)/s(0\%)$ is greater than for the other elements. A test for the *applicability* of the correction procedure was made on a 140-cm-long sediment core from the brackish water zone of the Ems River estuary near Emden (Fig. 14.5*b*). The curve of bulk Zn concentrations (broken line) in the samples varies with depth and does not give an indication of the zinc pollution, whereas the zinc data corrected for grain size (solid line) clearly indicate the very significant increase in zinc pollution during the last 100 years (dating performed with ^{137}Cs activity).

Geochemical Substrates versus Grain Size

Grain size typically influences the concentrations of contaminants because most surface-active sediment components are enriched in the fine-grained fractions. The relative capacity of collectors (e.g., for trace elements) has been arranged by Horowitz and Elrick (1987) in the sequence: amorphous iron oxide > total extractable iron > total organic carbon > reactive iron > clay minerals > total extractable manganese > manganese oxides. This

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TABLE 14.10 Correlation Coefficent r and Concentration Ratios $s(100\%)/s(0\%)$, for Some Potential Reference Elements

	Cs	Sc	Fe	Rb	Eu	Th	Sm
Fraction <20 μm:							
r	0.987	0.982	0.858	0.958	0.945	0.32	0.878
$s(100\%)/s(0\%)$	14.0	7.3	6.4	3.4	3.1	3.2	3.1
Fraction <60 μm:							
r	0.919	0.937	0.789	0.900	0.947	0.944	0.911
$s(100\%)/s(0\%)$	>20	15	9.0	3.7	3.8	3.8	3.9

Source: Ackermann (1980).

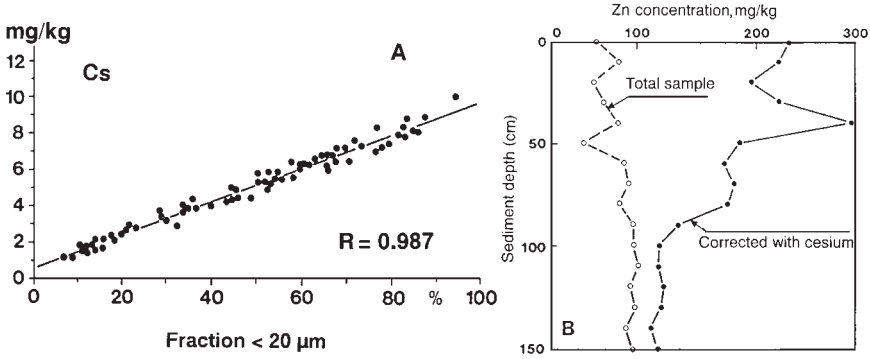

FIGURE 14.5 Correction of grain-size effects by conservative element content in relation to cesium. (*a*) Regression line and correlation to percentage of fraction < 20 μm in sediment samples from Ems estuary. (*b*) Correction of zinc contents in a sediment core from Ems estuary. *(Ackermann, 1980.)*

relatively simple picture is complicated by the fact that, for example, aquatic organic matter exists in two physical forms: surface coating that tends to concentrate in the finer size fractions and separate particles that tend to be associated with the coarser size fractions (Horowitz, 1991). The major role of clay minerals is not direct sorption of trace elements but rather to act as mechanical substrates for the precipitation and flocculation of organic matter and secondary minerals (e.g., hydrous iron and manganese oxides) (Jenne, 1976). Alterations of the grain-size spectrum of some characteristic components of sediments are presented in Fig. 14.6 for Lake Constance and Lower Rhine River samples.

The relatively insignificant differences in the grain-size distribution curves do not imply that material inhomogeneities sometimes cannot be very large. Since the greater majority of the particles range in grain size from 2 to 20 μm (Fig. 14.6*a*), the increased values for the specific surface area (Fig. 14.6*b*), for example, climb in this grain-size spectrum in Rhine River sediments to a value that is clearly higher in the overall sample of the Lower Rhine (223–3 m^2/g) compared with 7.2 m^2/g in the Lake Constance sample. Two especially important carriers for trace metals are shown in Fig. 14.6*c* and *d.* Iron oxihydrates are distinctly enriched in the Rhine River sediment compared with the sample from Lake Constance. The iron oxides prefer the fine-grained particle surfaces, and the humic substances apparently tend more to collect fine- to medium-sized silt grains.

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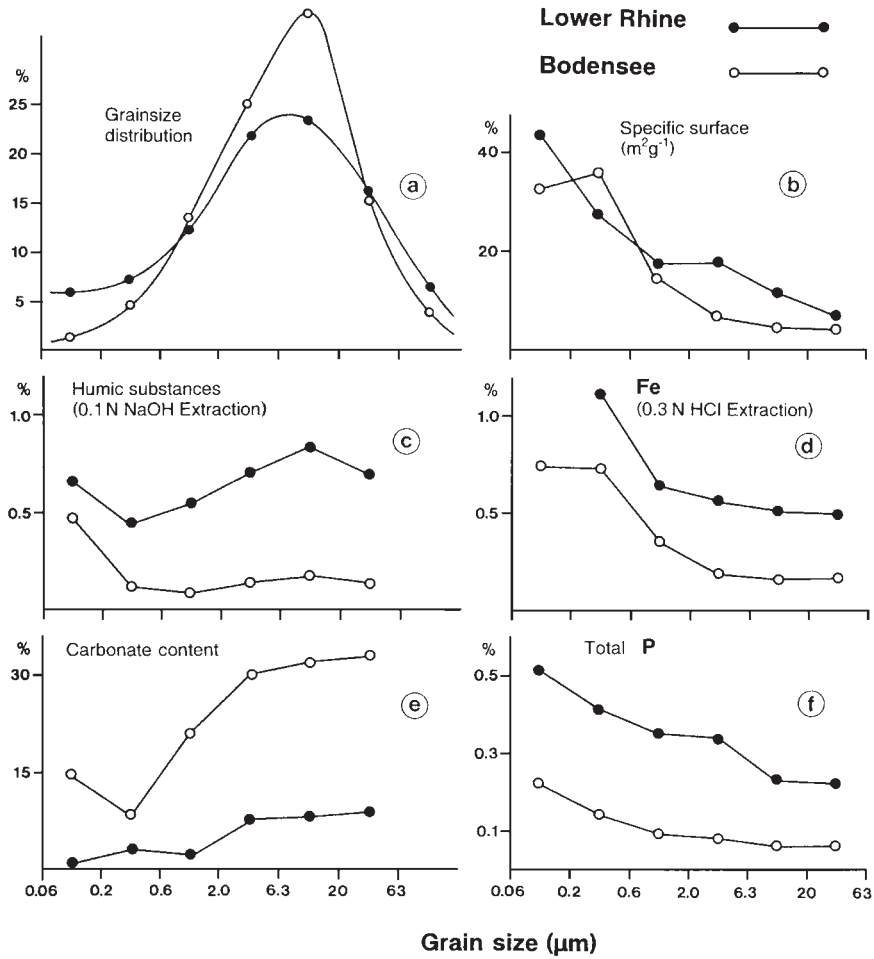

FIGURE 14.6 Grain-size spectrum of some components in sediments from Lake Constance and the Lower Rhine River.
(Salomons and Förstner, 1984; partly after Förstner and Patchineelam, 1980.)

For phosphate compounds (Fig. 14.6*f*), there is a preference toward the fine-grained fractions. In the latter case, the strong enrichment in Lower Rhine River sediments occurs as nonapatitic inorganic P associations. Detrital carbonates (Fig. 14.6*e*) generally possess a diluting effect on metal concentrations in the coarser sediment fractions of Lake Constance, where they are four to five times more prevalent than in the sample from the Lower Rhine River.

It has been stressed by Horowitz (1991) that patterns from normalized data can have same drawbacks and that each pattern must be evaluated in terms of potential pollutant sources and potential geochemical processes. This especially has to be considered in the survey of areal distributions of sediment-associated contaminants on lakes and coastal seas, which is an important field of application of sediment studies.

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CHEMICAL SEDIMENT CRITERIA

Two major reasons were given for the establishment of sediment quality criteria:

- In contrast to the strong temporal and spatial variability in the aqueous concentrations of contaminants, sediments integrate contaminant concentrations over time and therefore can reduce the number of samples needed in monitoring, surveillance, and survey activities.
- Long-term perspectives in water resource management involve integrated strategies in which sediment-associated pollutants have to be considered.

During the 1980s, efforts were undertaken mainly by the U.S. Environmental Protection Agency (EPA) to develop standard procedures and criteria for assessment of the environmental impact of sediment-associated pollutants. Initial discussions (Anonymous, 1984, 1985) suggested five methodological approaches that merit closer consideration: (1) the background approach, (2) the water quality/porewater approach, (3) the sediment-water equilibrium-partitioning approach, (4) the sediment-organism equilibrium approach, and (5) the bioassay approach. Further discussions led to the differentiation of chemical-numerical and biological approaches (Chapman, et al., 1987). While the latter eventually will dominate the decision-making processes in the future (see Chap. 17 on biological sediment and soil quality criteria), chemical-numerical approaches are still in use due to their simple application and easy interpretation. In the following subsections, a short overview is presented of the development of chemical sediment criteria, including examples of former and actual applications.

Background Approach

Standard Values. An example of standard values for sediment quality criteria is given by a former Dutch sediment quality draft (Van Veen and Stortelder, 1988). Dutch environmental pollution standards traditionally have been based on contaminant concentrations. The advantages, particularly for monitoring this type of standard, are simplicity and the absence of ambiguity. The lack of consideration of the ecological impact is a disadvantage. In a draft for developing sediment standards—aimed at the disposal of contaminated sediments on land—the pollutant concentrations are normalized to a standard sediment (underwater soil) consisting of 10 percent organic matter and 24 percent clay content (particle size < 2 μm). The level for the target value is based on field observations of sediments in surface waters not affected by industrial or other discharges. The level for the standard value is based on observations of sediments that are slightly contaminated but with no known ecological effect. The levels for the limit value do not have any ecological background; they are based on existing standardization in the Rotterdam area. These three levels are defined for many toxic compounds, some of which are given in Table 14.11. Integration of standards for terrestrial and aquatic soils is under discussion and could be of great importance in, for example, the case of disposal of contaminated sediments on land.

Pollution Indices. A quantitative measure of metal pollution in aquatic sediments has been introduced by Müller (1979) and is called the *index of geoaccumulation:*

$$I_{geo} = \log_2 C_n/1.5 \times B_n$$

where C_n is the measured concentration of element n in the pelitic sediment fraction (<2 μm) and B_n is the geochemical background value in fossil argillaceous sediment (average shale) ; the factor 1.5 is used because of possible variations in the background data due to lithogenic effects. The index of geoaccumulation consists of seven grades, whereby the highest grade (6) reflects 100-fold enrichment above background values ($2^6 = 64 \times 1.5$) . Table 14.12 provides

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TABLE 14.11 Draft Standards for Contaminated Sediments in the Netherlands

	Cr	Cu	Zn	Cd	Hg	Pb	As	Oil	PCB	PAH
Target value	100	25	180	0.8	0.3	50	25	—	1	50
Standard value	125	70	750	4	1	125	40	2000	10	500
Limit value	600	400	2500	30	15	700	100	5000	100	3500

Note: Data in mg/kg, except PCB and PAH (μg/kg).
Source: van Veen and Stortelder (1988).

TABLE 14.12 Comparison of IAWR Water Quality Indices (Based on Biochemical Data) and Index of Geoacccumulation (I_{geo}) of Trace Metals in Sediments of the Rhine River

IAWR index	IAWR water quality (pollution intensity)	Sediment accumulation (I_{geo})	I_{geo} class	Metal examples	
				Upper Rhine	Lower Rhine
4	Very strong pollution	>5	6		Cd
3–4	Strong to very strong pollution	>4–5	5		
3	Strongly polluted	>3–4	4		Pb, Zn
2–3	Moderately to strongly polluted	>2–3	3	Cd, Pb	Hg
2	Moderately polluted	>1–2	2	Zn, Hg	Cu
1–2	Unpolluted to moderately polluted	>0–1	1	Cu	Cr, Co
1	Practically unpolluted	<0	0	Cr, Co	

Source: After Müller (1979).

an example for the River Rhine, and a comparison of these sediment indices with the water quality classification of the International Association of Waterworks in the Rhine Catchment (IAWR) has been made. It should be mentioned that (similar to the sediment standards in Table 14.11) no further consideration is given to the ecological relevance of the values.

Ecological Risk Indices Derived from Enrichment Factors. A sedimentological approach to an ecological risk index was introduced by Hakanson (1980) and tested on 15 Swedish lakes representing a wide range in terms of size, pollution status, trophic status, etc. These estimations are based on four requirements that are determined in a relatively rapid, inexpensive, and standardized manner from a limited number of sediment samples. Contrary to the before-mentioned approaches, a special term is introduced for estimating the ecotoxicological significance of the individual contaminants. The *toxic requirement* differentiates the various contaminants according to an *abundance principle,* i.e., saying that there exists a proportionality between toxicity and rarity, and to their *sink effect,* i.e., their affinity for solid substrates. After a normalization process, the *sedimentological toxic factor* is calculated in the following sequence:

$$Zn = 1 < Cr = 2 < Cu = Pb = 5 < As = 10 < Cd = 30 < Hg = PCB = 40$$

The *toxic response factor,* as formulated by Hakanson (1980) from a complex matrix of assumptions, possibly can be defined much easier from direct measurements of the relative toxicity of typical pollutants in aquatic systems, e.g., from bioassays on water samples. We propose a toxicity factor based on the standardized microtox test system, where the individual concentrations are determined from comparable EC_{50} values (Förstner et al., 1990). According to Walker (1988) the following factors could be used for metallic elements: Pb = 1, Zn = 5, Cu = 5, Cd = 10, and Hg = 35.

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Equilibrium Partitioning

Porewater Approach. It was mentioned in Chap. 13 that in the more science-based regulations, such as the U.S. EPA's sediment quality criteria (SQCs), sediment quality advisory levels (SQALs) and chemical-specific fate scores are derived directly or indirectly on the basis of the linear equilibrium model (Anonymous, 1997). The purpose of SQCs is to ensure that the porewater concentration of a certain compound does not exceed the final chronic water quality criteria (FCVs).

While the direct recovery and analysis of water-borne constituents can be seen as a major advantage of this approach, there are several disadvantages, particularly arising from sampling and sample preparation, that are not yet routine procedures and usually involve a number of precautionary measures, such as exclusion of oxygen. Generally, interpretation of profile data may be difficult, as demonstrated in the review of porewater studies by Song and Müller (1999). There are strong gradients for redox-sensitive constituents, such as iron, arsenic, and sulfate; the question is which position in the core profile is the most typical with respect to uptake by benthic organisms.

Sediment/Water Equilibrium Partitioning. This approach is related to a relative broad toxicological basis of water quality data. The distribution coefficient K_D, which is determined from laboratory experiments, is defined as the quotient of equilibrium concentration of a certain compound in sediment (C_s^x, e.g., in mg/kg) and in the aqueous phase (C_w^x, e.g., in mg/liter). Since, in particular, water quality management is requesting such simple calculation bases, the problematic nature of these relations—as evidenced from various references (Table 14.13)—should be indicated clearly.

In practice, three categories of compounds can be distinguished:

- *Nonpolar organic compounds.* These are dominantly correlated with the content of organic carbon in the sediment sample. The partition coefficient K_D can be normalized from this parameter and the octanol-water coefficient (K_{OW}): $K_D = 0.63\ K_{OW}$/content of organic carbon in total dry sediment (0.63 is an empirical value). For these substances, such as PCB, DDT, and PAH, reliable and applicable data can be expected with respect to the development of sediment quality criteria.

TABLE 14.13 Factors and Mechanisms Influencing the Distribution of Pollutants Between Solid and Dissolved Phases

Factor/mechanism	Example*	Reference
Sample preparation (e.g., drying)	Metals*	Duursma (1984)
Separation (filtration/centrifugation)	Metals*	Calmano (1979)
Grain-size distribution	Metals*	Duursma (1984)
Suspended matter concentration	DDT/Kepone, PCBs	Connor and Connolly (1980), Voice et al. (1983)
Kinetics of sorption/desorption	Metals*	Schoer and Förstner (1984)
Nonreversibility of sorption	Metals, PCBs, chlorophenols	Lion et al. (1982), DiToro and Horzempa (1982), Isaacson and Frink (1984)
Effect of bioconcentration	1,4-DCB	Oliver and Nicol (1982)

*Experiments with artificial radionuclides.
Source: Förstner et al. (1990).

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- *Metals.* The K_D values of metals are correlated not only with organic substances but also with other sorption-active surfaces. Toxicological effects often are inversely correlated with parameters such as iron oxyhydrate. Quantification of competing effects is difficult, and thus the equilibrium partition approach for sediment quality assessment of metals still exhibits strong limitations.
- *Polar organic substances.* These substances (e.g., phenols, polymers with functional groups, tensids) are widely unknown with respect to their specific sorption behavior. Partition coefficients are influenced by anion and cation exchange capacity and surface charge density as a function of pH and other complex properties, so the K_D approach at present cannot be taken into consideration.

In the sediment quality criteria of the U.S. EPA, equilibrium partitioning models were mainly applied for the distribution of functionally diverse hydrophobic organic compounds such as PCBs, PAHs, DDT, chlorobenzenes, etc. (Anonymous, 1997). However, these models (derived from laboratory sorption studies and mainly based on partitioning with bulk organic carbon) may lead to a significant overestimation of risks, which is due to a wide spectrum of aging processes (see Chap. 13).

Sediment-Biota Equilibrium Partitioning. A very important aspect of the assessment of the environmental fate of chemicals is prediction of the extent to which these substances will achieve concentrations in biotic phases. For organic chemicals, it has been suggested by Mackay (1982) that the bioconcentration factor K_B can be regarded simply as a partition coefficient between an organism consisting of a multiphase system and water; if the dominant concentrating phase is a lipid that has similar solute interaction characteristic to octanol, a proportional relationship between bioconcentration factor K_B and K_{OW} is expected ($K_B = 0.048\ K_{OW}$). This correlation must be used with discretion, particularly for very low-K_B compounds, where the amount of solute in nonlipid phases may be appreciable, and for high-K_{OW} compounds (e.g., Mirex, octachlorosterene, and higher chlorinated biphenyls).

Elution Approach

Single and Sequential Extraction. Solvent leaching—apart from characterization of the reactivity of specific metals—can provide information on the behavior of pollutants under typical environmental conditions. Common single-reagent leachate tests (e.g., U.S. EPA, ASTM, IAEA, and ICES) use either distilled water or acetic acid (Theis and Padgett, 1983). A large number of test procedures have been designed particularly for soil studies; these partly used organic chelators such as EDTA and DTPA (Sauerbeck and Styperek, 1985).

Single-extractant procedures are restricted with regard to prediction of long-term effects (e.g., of highly contaminated dredged materials) because these concepts involve neither mechanistic nor kinetic considerations and therefore do not allow calculations of release periods. This lack can be avoided by controlled significative intensivation of the relevant parameters such as pH value, redox potential, and temperature combined with an extrapolation on the potentially mobilizable pools that are estimated from sequential chemical extraction before and after treatment of the solid material.

Several aspects of metal speciation in sediments were reviewed by Förstner (1993):

1. Due to the instability of polluted solid materials, sample handling and storage prior to analysis are problematic. In particular, changes from reducing to oxidizing conditions, which involve transformations of sulfides and a shift to more acid conditions, increase the mobility of critical metals.

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2. Simple standard leaching tests can be used for easily soluble components such as halides or sulfates but in most cases are not adequate for assessing mobility of trace metals. With sequential extraction procedures, rearrangements of specific solid phases can be evaluated prior to their actual mobilization.
3. Partitioning studies on materials from core profiles are particularly useful because they provide information on relative variations of elemental phases irrespective of the method applied and thereby an insight into diagenetic processes taking place after deposition of the sediment components.
4. The leachable fraction does not necessarily correspond with the amount available to biota. Studies on the prediction of trace metal levels in benthic organisms have shown that the prognostic value of sequential extraction data is improved when the trace metal concentrations are normalized with respect to the iron (hydrous oxide) and/or organic content of the sediments (Tessier and Campbell, 1987).

In a series of investigations and collaborative studies initiated by the Community Bureau of Reference (BCR) of the Commission of the European Community, both single-extractant and sequential-extraction procedures were subjected to interlaboratory trials (Ure et al., 1993). For these trials, a simple three-step extraction procedure that evolved from that of Salomons and Förstner (1984) was used (Table 14.14). Sediments certified for metal contents extracted by a sequential extraction procedure were prepared by the BCR.

Acid-Producing Potential. Both pH and redox potential in sediment-water systems are significant parameters for mobilization and transformation of metals. Many investigations have shown that pH decreases during oxidation of sediments (Förstner, 1995), and this process will significantly mobilize toxic metals (Calmano et al., 1994). Criteria for prognosis of the middle- and long-term behavior of metals therefore should include the abilities of sediment matrices to produce acidity and to neutralize such acid constituents.

Effects of redox processes on acid-producing potential (APP) and metal mobility in sediments were reviewed by Hong et al. (1994). S, Fe, and N are the most important elements in redox processes of a sediment-water system. This is due not only to their chemical reactivity but also to their abundance in natural waters and sediments. For example, in tidal marsh sediments, pyrite contents (FeS_2) are often present on the order of 1 to 5% on a mass basis or higher (Postma, 1983). If chemical components in the sediment are known, APP can be calculated. For example, 1 mol of FeS_2 can produce 4 mol of hydrogen ions. Because of its high acid-producing coefficient and its abundance in anoxic sediments, this oxidation reaction has been discussed extensively (Sullivan et al., 1988).

TABLE 14.14 Three-Step Sequential-Extraction Procedure for the Sediment Trial (BCR Sequence)

Step 1: 0.5 g sediment extracted for 5 hours with 20 ml of acetic acid 0.11 mol/liter centrifuged and supernatant decanted for analysis by AAS or ICPOES.
Step 2: Residue from step 1 extracted overnight (16 h) with 20 ml of hydroxylammonium chloride ($NH_2OH{\cdot}HCl$ 0.1 mol/liter) acidified with nitric acid to pH 2, centrifuged, and the supernatant decanted for analysis.
Step 3: Residue from step 2 treated twice with 10 ml of hydrogen peroxide 8.8 mol/liter and the dry residue extracted overnight with 50 ml of ammonium acetate 1 mol/liter adjusted to pH 5 with acetic acid; the supernatant, separated by centrifugation, is retained for analysis.

Source: Ure et al. (1993).

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The concept of APP has been used in the prediction and calculation of acid mine drainage and waste tailing management (Rahn, 1992). Experimental approaches for calculating APP and acid-consuming capacity (ACC) for sulfidic mining residues were summuarized by Ferguson and Erickson (1988). A test described by Sobek et al. (1978) involves the analysis of total pyritic sulfur; potential acidity is then subtracted from neutralizing potential, which can be obtained by adding a known amount of HCl, heating the sample, and titrating with standardized NaOH to pH 7. Bruynesteyn and Hackl (1984) calculated APP from total sulfur analysis; here, APP was then subtracted from ACC, obtained by titration with standardized sulfuric acid to pH 3.5.

For determining the acid-producing potential (*maximum APP*) in anoxic sediments, both the FeS pool (*actual APP*) and the maximum ferrous sulfide (worst case, pyrite) producing potential on disposal have to be taken into consideration. The latter is expressed by the *sulfide-binding capacity,* which can be predicted from the reactive metal concentrations—predominantly reducible Fe^{3+}—available to form sulfide minerals (*available sulfide capacity,* or ASC) (Williamson and Bella, 1980).

As demonstrated from an example of Hamburg Harbor mud (Kersten and Förstner 1991), simultaneous application of standard sequential leaching techniques (BCR version; see Table 14.14) on critical trace metals and matrix components can be used for geochemical characterization of anoxic sulfide-bearing sediments in relation to the mobility of these metals. In Table 14.15, the ASC value was calculated from the Fe concentration in step 2 of the sequential leaching results. The stoichiometry of the oxidizable S and Fe fractions of step 3 indicate that the ferrous sulfide extracted in this step was in the FeS form. The sum of both the ASC and the actual APP gives the maximum APP for the sample, as shown in Table 14.15. The ACC value for the sample was determined more simply from the Ca concentration released from reactive carbonates by the Na-acetate solution of step 1, which has to be multiplied by a factor of 0.5 to account for the stoichiometric ratio between pyrite and calcite within the redox reaction. The negative balance between the APP and ACC indicates that the mud sample from Hamburg Harbor has a significant acidification potential.

Extractable Metal/Acid Volatile Sulfide. One of the major chemical components that controls metal activities in the interstitial water of anoxic sediments is *acid volatile sulfide* (AVS). AVS is operationally defined as the sulfides that are liberated from a sediment sample to which acid has been added at room temperature under anoxic conditions. This operational definition includes most of the amorphous and moderately crystalline monosulfides (e.g., FeS) and lesser percentages of other sulfides. A closely related term is *simultaneously extractable metals* (SEMs), which can be operationally defined as "metals…[that] form less soluble sulfides than Fe or Mn and [that] are at least partially soluble under the same test conditions in which the AVS content of the sediment is determined" (Allen et al.,

TABLE 14.15 Balance Between APP (Acid-Producing Potential) and ACC (Acid-Consuming Capacity) Values for an Anoxic Sediment Sample from Hamburg Harbor

Compound	Function	Value	Parameter (mmol/kg[1])	
Ca in step 1	base potential	(× 0.5 =)	ACC	90
Fe in step 2	ASC	(335)		
S in step 3	sulfide sulfur	(+ 85 =)	max. APP	420
Balance			ACC − APP =	− 330

Note: For definitions of steps 1, 2, and 3, see Table 14.14.
Source: Kersten and Förstner (1991).

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1993). The chemical basis for the primacy of the sediment sulfide phase for metal binding is assumed to be that at equilibrium, S^{2-} successfully outcompetes all other common dissolved or particle-associated ligands for metal ions and forms insoluble metal sulfides (Di Toro et al., 1990).

It has been demonstrated that if the molar concentration of AVS that is extracted from a sediment exceeds the molar sum of the simultaneously extracted metals (∑SEM) that form more insoluble sulfides than iron sulfide (that is NiS, ZnS, CdS, PbS, and CuS), any one of which is denoted by MS, then those sediment metals will not be toxic to sediment-dwelling organisms (Di Toro et al., 1991: Berry et al., 1996, Hansen et al., 1996).

There are several concerns about using the ∑SEM/AVS ratio (Meyer et al., 1994). First, the replacement reaction, that is, $Me^{2+} + FeS(s) = Fe^{2+} + MeS(s)$, has not been unequivocally established in nature. Although experiments were conducted to address this question, no one has yet reported an equimolar increase in Fe^{2+} concentration as sediment that contains FeS is titrated with a trace metal ion that would replace the Fe^{2+}.

Second, results of chemical analysis of homogenized sediment collected with grab samplers do not necessarily indicate the bioavailability of trace metals in intact, in-place sediments. If the sediment is oxic or weakly reducing, SO_4^{2-} will not be reduced to S^{2-}, and most of the previously formed sulfides (if any are present) will be oxidized to SO_4^{2-}, allowing the trace metal ions to be released and possibly associate with other dissolved or particulate components.

Third, AVS is not likely to be present at a uniform concentration in the sediment environment. An instantaneous measurement of AVS represents, at best, an ephemeral state that depends on the rates of supply of reactive C_{org}, SO_4^{2-}, and trace metals. These rates will be affected by periodic and episodic events.

Fourth, and most important, in an established sediment, the biota create microenvironments in which the chemistry differs from the bulk sediment. Burrowing organisms, which occur more commonly in marine systems than in freshwaters, pump oxic water into their burrows, causing a localized high redox potential that affects the local concentrations of AVS and trace metals regardless of the bulk content of AVS in the surrounding sediment.

In summary, the ratio ∑SEM/AVS appears to be a useful concept to explain toxicity of organisms exposed to homogenized bulk sediments in laboratory test systems. However, it remains to be demonstrated whether that ratio is appropriate for predicting bioavailability of metals to organisms inhabiting oxic or partially reducing regions of in-place sediments. Tests with homogenized bulk sediments may be suitable to mimic the exposure conditions that might occur during a dredging operation before the AVS is oxidized (Hong et al., 1994). However, in this situation, the potential toxicity of trace metals probably will be overshadowed by the catastrophic effects of the dredging operations on the physical habitat of the organism.

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CHAPTER 15
SEDIMENT PHYSICAL PARAMETERS AND TECHNIQUES

Alex Zeman and Timothy Patterson

INTRODUCTION

From a geotechnical viewpoint, aquatic sediments can be viewed as soils deposited underwater, and thus onshore geotechnical methods can be used to determine sediment physical properties. Most sediments are characterized by high water content and, in the case of cohesive sediments, by low values of shear strength and high compressiblity. Due to variable hydrodynamic conditions in both space and time, sediments vary in texture. Usually, in normally consolidated cohesive sediments, the shear strength increases while the compressibility decreases with the depth below the sediment-water interface.

Reliable measurements of sediment shear strength and compressibility require relatively undisturbed samples. This requirement is more severe than the one for onshore soil sampling procedures. Besides mechanical disturbances and disturbances due to transportation, storage, and preparation, aquatic sediments are disturbed by changes in hydrostatic stress, temperature, release of gases, and sediment oxidation. Increased temperatures and exposure to air may result in decomposition of organic matter and a growth of bacteria. These miscellaneous disturbances can reduce or, conversely, increase the sediment strength and alter other geotechnical properties. The prevailing opinion is that all sediment samples are significantly disturbed (Monney, 1971).

Coarse (granular) sediment fractions consist of rock fragments that are composed of one or more minerals either fresh or weathered. Sandy sediments typically consist of rock fragments, quartz, feldspars, mica, and heavy minerals. Clay minerals predominate in fine-grained (cohesive) sediments, and they are usually subdivided into three subgroups known as the *kaolinites, illites,* and *montmorillonites.* Sediments usually contain a mixture of clay minerals, amorphous (iron, silicon, and aluminum) oxides, and organic matter. The interactions among sediment particles, porewater, and dissolved constituents in porewater are primarily responsible for physical properties of fine-grained sediments. The pronounced influence of clay mineralogy on most physical properties of cohesive sediments is reflected, for example, in the Casagrande plasticity chart (Terzaghi and Peck, 1968).

Offshore sediments consist of a three-phase system of solid particles, porewater, and gas. Microbiological degradation of organic matter is responsible for the presence of gases. Sediment gases contain methane (CH_4) and nitrogen (N_2) in dominant amounts and carbon

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dioxide (CO_2) and hydrogen (H_2) in trace quantities (Fendinger et al., 1992). Henry's law describes the continuous balance between gas existing in the sediment as free bubbles and gas dissolved in sediment porewater. A substantial decrease in hydrostatic pressure occurs when sediment samples are brought to the surface, which produces gas ebullition and sample volume change. Changes in hydrostatic pressure and temperature and subsequent rapid gas expansion are known to produce severe disturbance of samples, particularly in sediments with high organic carbon content.

Bioturbation can change the physical properties of sediments considerably, and changes in geotechnical properties due to bioturbation of sediments are related to fabric changes. A direct comparison between bioturbated and nonbioturbated deposits is difficult because sediment physical properties are also affected by conditions that prevent bioturbation, e.g., rapid sedimentation and oxygen-depleted bottom waters. It is possible, nevertheless, to evaluate the effect of bioturbation indirectly by analyzing different sediment cores and vertical trends in a single core. Bioturbation usually increases porosity and decreases compressibility. Sediment mixing and reworking further affect sediment water content, grain size, and permeability. Deeper in the sediment, physical properties are more controlled by sediment composition and porewater chemistry than by fabric. For this reason, the influence of bioturbation is most pronounced in sediments close to the sediment-water interface, and this influence is obliterated in more compacted sediments (Wetzel, 1990).

American Society for Testing and Materials (ASTM) Standard D422 uses the hydrometer method for the determination of sizes smaller than 74 μm. Geologists measure grain size of sediments using other laboratory procedures, e.g., the pipette method (Royse, 1970), the sieve and sedigraph method (Duncan and LaHaie, 1979), and the Coulter method (Mudroch et al., 1997). Note that in the geological literature the boundary between silt and clay sizes is 4 μm (8 phi) as opposed to the boundary of 2 μm used in the geotechnical literature.

For environmental concerns, sediments near the sediment-water interface are of importance. These sediments are typically of very low consistency, and therefore, the disturbance of these samples due to sampling should be taken into account. The issue of sample disturbance is particularly important for strength and consolidation testing. For this reason, in situ testing is often preferred over tests on cored samples.

OFFSHORE SOIL MECHANICS

In Situ Testing Methods

The difficulty in obtaining undisturbed samples for laboratory testing of very soft cohesive sediments favors the use of in situ testing methods. However, these in situ tests frequently are complemented by laboratory geotechnical tests because sediment samples often are collected for geological and geochemical reasons and because in situ tests without groundtruth data frequently are difficult to interpret.

Cone-Penetration Tests. Various types of cone penetrometers have been designed over the years, and standard testing procedures have been developed in Europe and North America (Richards and Zuidberg, 1985). The penetrometers equipped with a pore pressure-measuring system are referred to as *piezocones.* Piezocone testing procedures should follow ASTM Standard D344-1 and ISSFME1989.

The cone-penetration test (CPT) can be used for both granular and cohesive sediments to obtain shear strength parameters both for drained and undrained conditions. Measured parameters are cone point resistance, friction sleeve resistance, and pore pressure. Other

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SEDIMENT PHYSICAL PARAMETERS AND TECHNIQUES

geotechnical parameters, such as sediment geotechnical classification, relative density, undrained shear strength, drained shear strength (cohesion and friction), deformation moduli, preconsolidation pressure, and coefficient of consolidation, can be derived from recorded values (Senneset and Janbu, 1985). Pore pressure-dissipation tests may provide additional information on sediment permeability. A competent interpretation of measured values requires a solid grasp of advanced soil mechanics and a comparison of penetrometer tests with other field and laboratory measurements.

Specialized cone penetrometers can be equipped with electrodes and measuring probes to measure sediment temperature, electrical conductivity, resistivity, and shear-wave velocity. Research penetrometers have been designed for porewater geochemical sampling and outflow hydraulic conductivity testing (Campanella et al., 1993).

A free-fall impact penetrometer with a capability of testing the surficial ocean sediment up to a depth of 10 m was developed at Memorial University, Newfoundland, with a 45-cm^2 nominal cross section (Chari, 1981). The test results were compared with similar tests on a standard 10-cm^2 Fugro type of penetrometer. The effects of the penetrometer size, cone angle, sediment-cone friction, and penetration rates in cohesive and granular sediments were studied.

Two light penetrometers have been used to map the properties and thickness of contaminated freshwater sediments at the National Water Research Institute of Environment Canada (Rukavina and Trapp, 2000; Zeman et al., 2000). A weighted tripod equipped with an underwater video camera and echosounder records the depth to refusal with a precision of about 5 cm. The second instrument is a dynamic penetrometer (Sting), which is lowered from a boat to a predetermined depth and then allowed to fall freely and penetrate into the bottom sediment to refusal. On retrieval, electronically recorded deceleration data are downloaded to a notebook computer and converted to dynamic bearing-capacity values. Penetrometer measurements of soft (usually contaminated) sediments have been found more reliable than determinations using gravity coring, where the results are influenced appreciably by unavoidable shortening of sediment cores.

Standard Penetration Tests and Field-Vane Tests. The standard penetration test (SPN) is used in conventional geotechnical investigations in combination with split-spoon sampling. The test consists of counting the number of blows of the drop weight required to drive the sampling spoon into the sediment for a distance of 0.3 m. This test is very rapid, and it is particularly useful for investigations of stiff clays (e.g., overconsolidated till deposits), silts, and sands. Offshore applications require a stable support, e.g., a drill ship or a jackup platform.

The field vane test is used for determinations of the undrained shear strength and sensitivity of soft cohesive sediments. Offshore applications are quite analogous to onshore procedures, which have been in use for at least a half century (Terzaghi and Peck, 1968). The vane shear apparatus, usually consisting of a four-bladed vane fastened to the bottom of a vertical rod, is pushed gently into the sediment. The apparatus is then rotated, and the relationship between torque and angular rotation is recorded. The undrained shear strength can be calculated from measured torque and vane dimensions. The sensitivity is determined from comparison of values obtained for undisturbed and fully remolded sediment conditions. In offshore applications, the field vane apparatus usually is installed on a bottom-resting platform that is controlled remotely from a supporting vessel. In shallower waters, the field vane frequently is used with standard onshore drilling rigs that operate from a fixed (spudded) platform or from a drill ship.

Porewater Pressure and Seepage Measurements. Since the hydrostatic pressure increases linearly by about 10 kPa per meter of water depth, it is difficult in deeper water to measure absolute pressures close to hydrostatic values. However, it is relatively easy

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to measure small differences between sediment pore pressures and the hydrostatic pressure. Differential piezometers are used to measure the extent of underconsolidation in soft fine-grained sediments. The degree of underconsolidation is expressed by the presence of the excess pore pressures (i.e., above the hydrostatic value). These instruments may be deployed at an offshore site for several months in order to monitor long-term fluctuations in excess pore pressure. Fluctuations may be produced by the passage of a large storm, or in the case of shallow water depths, they may reflect the effect of surface waves, tides, and currents. Effective shear-strength parameters can be computed from pore-pressure measurements. Results may be affected by the presence of gas, and the recorded excess pore pressure may reflect porewater pressure, pore-gas pressure, or both (Hirst and Richards, 1977).

Seepage meters of different designs (tubes, inverted barrels, and sample bags, pressure transducers) are installed in near-shore sediments to monitor the interaction between groundwater and open-water bodies. These instruments have been used to determine the horizontal and vertical sediment permeability, as well as the direction, quantity, and quality of groundwater flow (Lee, 1977; Cooke et al., 1993).

Laboratory Testing Methods

Laboratory geotechnical tests are identical in principle to those carried out with onshore soil samples. Since sediments typically are of very soft consistency, appropriate testing equipment and procedures have to be selected. These departures from standard laboratory geotechnical testing will be emphasized in detail in the following paragraphs. Laboratory investigations start with a thorough inspection of sediment samples submitted to the laboratory. Apart from visual examination and sample description, examination of samples by x-rays provides information on sediment stratigraphy, sediment structure, and the degree of sample disturbance prior to sample extrusion.

Information on sediment texture (particle size) and sediment plasticity is used for sediment classification. Sediment samples can be classified according to their physical properties using the well-established Unified Soil Classification System adopted in 1952 by the U.S. Corps of Engineers and the Bureau of Reclamation (Terzaghi and Peck, 1968; ASTM Standard D2487). According to this system, sediments can be divided into three major groups: coarse-grained, fine-grained, and highly organic (peaty). The boundary between coarse-grained and fine-grained sediments is taken to be the 200-mesh sieve (74 μm). The coarse-grained sediments (gravels and sands) are classified according to their grain size and size distribution. The results of plasticity tests are used for the classification of silts and clays.

Geotechnical parameters are measured according to pertinent ASTM standards. These include the natural water content (D2216), the Atterberg limits (liquid limit, plastic limit, and plasticity index; D4318), grain-size distribution (D422), and various procedures to measure the shear strength (Chaney and Demars, 1985) and consolidation testing (standard oedometer test; D2435). The standards for common geotechnical tests used in Germany are provided by the German Institute for Standards (DIN 1988; Kern and Westrich, 1999).

Moisture (Water) Content. The natural water content is the ratio of the weight of water to the weight of sediment. In sedimentology it is common to use the weight of wet-saturated sediment (total-water content or wet-water content), whereas in soil mechanics the weight of dry sediment (dry-water content) is used. Since weight measurements rather than volume measurements are used, this test is not very sensitive to sediment disturbance of fine-grained sediments (in contrast to free-draining coarser sediments). The loss of water is determined by drying a sample at 105°C. If dryng is carried out at a higher temperature,

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which is not recommended, higher water losses will be measured, particularly in samples containing swelling clay minerals and organic matter.

The natural water content can be measured directly using precise weighing and oven drying according to a standardized procedure. Indirect measurements by methods such as time-domain reflectometry and gamma-ray attenuation (Mudroch et al., 1997) are seldom used in routine investigations of aquatic sediments.

Unit Weight and Bulk Density. *Unit weight* is the ratio of the total weight to the total volume of a sediment sample. *Bulk density* is the mass of a sediment sample divided by its volume; i.e., the same sediment property is measured, but it is expressed in different units. Unit weight or bulk density measurements allow a conversion of water percentages by weight to water content by volume and can be used for calculating porosity and void ratio when particle density is known. *Porosity* is defined as the ratio of the volume of voids to the total volume. *Void ratio* is defined as the ratio of the volumes of voids to the volume of solids. The use of porosity is preferred in sedimentology, whereas void ratio is used commonly in soil mechanics. Functional relationships of various sediment quantities can be found in many textbooks (e.g., Jumikis, 1962; Das, 1983).

ASTM Standard D2937 describes the gravimetric and volumetric determination of bulk density. A cylindrical metal sampler or a syringe is used for volume determinations. For hard sediments and rock pieces, a density balance, a pycnometer, or a direct comparison with heavy liquids can be used (Mason and Berry, 1968; Mudroch et al., 1997). Gamma-ray attenuation techniques are used for nondestructive and rapid determinations of bulk density (ASTM Standard D2922; Mudroch et al., 1997). Gamma-ray attenuation techniques have been used for nondestructive bulk density measurements of sediment cores and for vertical profiles of artificially sedimented laboratory columns used in studies of sediment deposition and consolidation (Kern and Westrich, 1999).

Undrained Shear Strength. In measurements of shear strength, a distinction is made between undrained and drained testing (Terzaghi and Peck, 1968). In drained tests, the changes in stress are applied slowly to allow pore pressures to dissipate, and the shear stress is expressed in terms of effective stresses. Drained shear strength can be determined only in the laboratory using direct shear tests and triaxial tests, which can be time-consuming for low-permeability sediments. In undrained tests, the stresses are determined so rapidly that no dissipation of pore pressures occurs, and the shear stress is expressed in terms of total stresses. Relatively rapid undrained testing, in which no dissipation of pore pressures is assumed, is described in the following paragraphs.

Tests used to determine undrained shear strength include the minivane, the torsional vane, the fall cone, and the pocket penetrometer. If draining of samples is possible, tests must be conducted rapidly enough so that undrained conditions prevail. All these tests are carried out only on fine-grained sediments that display clear plastic characteristics. Results obtained on sandy sediments are difficult to interpret due to dilation and partial drainage.

The miniature vane test is based on the same principle as the field vane test, and testing is carried out in accordance with ASTM Standard D4648. These tests can be run quickly, require little skill, and are similar to a common in situ testing technique. In the test, a vane is inserted into a soft sediment and rotated until the sediment fails. The measured torque is then converted to the undrained shear strength. Since the shear strength depends on the vane rotation rate, the vane is rotated at a recommended constant rate of 90° per minute using the motorized vane shear apparatus. The lower measurement limit is about 5 kPa.

The torsional vane test (Torvane) is similar to the laboratory vane test, but the vane is hand held and rotated. Poor repeatability of this test has been reported (Lee, 1985).

The Swedish fall-cone device (Hansbo, 1957) is used for rapid measurements of the undisturbed and remolded (undrained) shear strength. The advantage of the fall-cone test

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over the vane test is more rapid testing and better applicability to sediments with very low shear strength (0.5–5 kPa). The fall-cone test determines the depth to which a cone of given apex angle and weight penetrates the sediment under its own weight. The undrained shear strength is obtained from empirical correlations. An automated fall-cone device for testing of extremely soft sediments, with shear strength values as low as 1.5 Pa, was developed at the Massachusetts Institute of Technology (MIT) (Zreik et al., 1995). A pulley and a counterweight system enables the use of very low cone weights. The new device also records cone penetration versus time throughout the test.

The pocket penetrometer (Lee, 1985) is a small, flat-footed, cylindrical probe that is pushed 6.4 mm into a sediment surface. It is particularly convenient for very firm sediments that cannot be tested by other rapid techniques. The penetration is related to the unconfined compressive strength, and the value must be divided by 2 to obtain the shear strength.

In general, there is little correlation between the strengths of comparable samples using different testing methods. Therefore, the testing method used always should be stated clearly. Rapid determinations, particularly using the Torvane and the pocket penetrometer, do not provide more than a rough comparative index of the shear strength.

Consolidation Measurements. When freshly deposited on the bed of a water body, fine-grained sediments have very high water content, void ratio, and porosity values. As sedimentation continues, the overburden weight will cause the sediments to consolidate. It has been recognized clearly by Terzaghi (1923) that compaction is a function of the effective pressure, i.e., the total pressure minus the pore pressure.

A sediment deposit is normally consolidated if it has never been under a pressure greater then the existing effective overburden load. In many offshore sediments, especially where sedimentation is rapid and sediment permeability is low, excess pore pressures cause sediments to be underconsolidated. Sediments are regarded as overconsolidated if the present effective overburden pressure is less than the maximum to which the sediment was subjected in its depositional history. The two most common reasons for overconsolidation are the removal of overburden due to erosion and the subaerial exposure and consequent desiccation of the sediment.

Consolidation problems involving very soft and highly compressible sediments are encountered in predicting behavior of hydraulically placed fills in mine tailings and dredged material disposal. A further application is in predicting sediment behavior due to dredged material capping and in situ capping of contaminated sediments (Zeman and Patterson, 1995; Rollings, 2000).

The standard one-dimensional consolidation test (ASTM Standard D2435) is carried out on saturated samples. The rate and magnitude of consolidation of the sediment are determined under the conditions of lateral restraint, axial loading, and axial drainage in a consolidometer. The load on the sample usually is applied through a lever arm, and the compression is measured by a micrometer dial gauge or an electronic deformation gauge. The load usually is doubled every 24 hours. For each load increment, the sample deformation and the corresponding time are recorded to obtain void ratio versus effective pressure relationships. Prescribed procedures are used to obtain 0 and 100 percent consolidation as well as the coefficient of consolidation for each load.

Laboratory consolidation testing of soft sediments often requires a lighter loading sequence or a self-weight test to provide information on sediment compressibility at higher void ratios (Rollings, 2000). Self-weight consolidation can be studied in laboratory settling columns, where density profiles are obtained using an x-ray apparatus and pore pressures are measured by transducers or standpipes (Been and Sills, 1981). Slurry consolidation consolidometers were built for measurements of sediment consolidation under very low stresses (Monte and Krizek, 1976). Large odometer tests with pore-pressure measurements using the Rowe cell (Rowe and Barden, 1966) were found suitable for primary and sec-

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ondary consolidation under low stresses, as well as for creep tests under sustained low loads (Zeman and Patterson, 1997).

The classic one-dimensional theory of consolidation (Terzaghi, 1943) is restricted to problems for which vertical strains are small. In the classic theory, strain is assumed to be infinitesimal, and the hydraulic conductivity and the coefficient of compressibility are assumed constant for a given load increment. However, soft fine-grained sediments may undergo vertical strain on the order of 50 percent during the consolidation process (Rollings, 2000). Recognition of the limitation of the classic theory for highly compressible sediments led to the development of finite-strain theories of consolidation (Gibson et al., 1967, 1981; Schiffman et al., 1984). In addition to treating large strains, variations of sediment compressibility and hydraulic conductivity during consolidation are taken into account, as is self-weight in some cases.

In general, finite-strain theories of consolidation result in a highly nonlinear partial differential equation problem that can only be solved by a numerical technique (finite differences of finite elements), or analytical solutions can be used that employ some linear-form approximations. Although comparative studies are available, a single formulation has not gained universal acceptance (Fox, 1999).

Viscosity. Rheological properties of cohesive sediments sometimes are measured to determine sediment behavior under hydrodynamic action, and the results can be used for the prediction of sediment erodibility under applied shear stresses. So far no standardized measurement of sediment viscosity has been developed, and therefore, comparisons of existing data are difficult (Kern and Westrich, 1999).

Freshwater, marine, estuarine, and human-made cohesive sediments were investigated by Migniot (1968), who used a viscometer to measure the dynamic viscosity and the initial rigidity of the sediments. In this comprehensive study, the hydraulic shear velocity was related empirically to the mean particle concentration and the initial rigidity of the sediments using tests in a 12-m-long tilting flume. Comparisons of viscometer measurements with any conventional geotechnical tests were not attempted in this study. Migniot's experimental results showed clearly that the water content is not a sufficient parameter to characterize the hydrodynamic behavior of a cohesive sediment. At the same water content, the values of initial rigidity were found to range over several degrees of magnitude. The data showed significant influence of mineralogical composition on the initial rigidity values. Viscosity measurements were used by Robertson et al. (1965) to make a rough determination of sediment mineralogical composition.

Faas (1981) measured viscosity behavior of sediment samples taken from the upper, middle, and lower reaches of an estuary. Viscosity measurements were carried out with a conventional rotational viscometer. Significant differences in apparent viscosity between each of the estuarine segments were reported. Apparent viscosity was found to decrease down-estuary with increasing salinity in bottom sediments. Viscosity measurements with a vane viscometer were used in a study by Kelly et al. (1982), who correlated the critical shear stress (obtained from water tunnel tests) and the Bingham yield stress (obtained from viscometer measurements) with sediment solids concentration and water salinity. More recent experience with various viscometers has been reviewed by Jones (1997).

Recently developed methods using the Nautisonde probe (Kern and Westrich, 1999) allow in situ determinations of viscosity of the water column and soft sediment. Four rheological regions subsequently are measured: (1) the water column, (2) the suspended sediment layer, (3) very soft mud, usually removed during maintenance dredging, and (4) consolidated sediment that is usually not reached during maintenance dredging. From several viscosity profiles, cross sections with "isoviscs" (lines of equal viscosity) can be constructed in the region of interest. This in situ technique is very useful for optimization of maintenance dredging operations in marine and estuarine areas.

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Particle Size Distribution. Particle size distribution has been used for the classification of sediments for sediment transport, geotechnical investigations, and geological and geochemical interpretations. The particle sizes range from less than 1 μm to greater than 1 m in diameter. A geometric scale is used to separate sediments into size classes, in which class limits increase from a base of 1 mm by a factor of 2 or decrease from this base by a factor of $^1/_2$. The standard classification of sediments into Wentworth size classes, phi scale classes, and sieve numbers is used commonly (Royse, 1970). The MIT classification has been used commonly in the geotechnical literature, in which particles finer than 2μm are classified as clay-sized particles (Terzaghi and Peck, 1968), whereas in sedimentology the boundary between silt and clay is 4 μm. It has to be emphasized that particles defined as clay on the basis of their size are not necessarily clay minerals.

Pretreatment of samples for particle size analysis is commonly required to avoid interference from flocculation and binding of individual particles by salts, Mn and Fe oxides, and carbonates. Freeze drying is recommended for fine-grained sediments. In the classic analysis, dry sieving is used for segregating particles coarser than silt sized (0.063 mm). Wet sieving is used to separate fine particles from surfaces of coarser particles or to recover the fine fractions ($<$0.063 mm) for analysis. If the sample contains significant amounts of silt- and clay-sized particles, it is necessary to perform e.g. pipette or hydrometer analysis in conjunction with the sieving. The standard testing method, as outlined in ASTM Standard D422-63, uses the hydrometer for determination of the silt- and clay-sized fractions. Both the pipette method and the hydrometer method are considered inaccurate and time-consuming and have been replaced by automated methods (Mudroch et al., 1997).

The Coulter method of sizing and counting particles (Coulter counter, the electrical sensing zone technique) measures the volume of electrolyte displaced by sediment particles that pass between electrodes. Volume displaced is measured as a voltage pulse, and the height of each pulse is proportional to the volume of the particle. Several thousand particles per second are counted and sized individually. The method is independent of particle shape, color, and density. The automatic data processing provides number, volume, and surface-area distributions in one measurement. Particles in the range of 0.4 μm (fine clay) to 1.2 mm (very coarse sand) can be measured.

The Sedigraph (x-ray sedimentation technique; Micromeritics Instrument Corporation) measures the velocity of a particle falling through a viscous medium. This technique is used for measurements of particle size distributions of fine-grained sediments (0.1 μm to 0.3 mm). The sample is mixed with a viscosity-specific fluid that allows the particles to go into suspension while being stirred with a magnetic stirrer or a peristalting pump. X-ray intensity is then related to the settling rate and the particle size distribution using Stokes' law.

Commercially available laser instruments that measure the particle size distribution are based on the time of transition theory (Bringman particle size analyzer) and laser diffraction spectrometry (Malvern Instruments, Ltd.), where the size distribution is computed using the Frauenhofer diffraction theory. A submersible laser particle size analyzer (Krishnappan, 2000) can be used for in situ measurements of flocculated sediment particles in a riverine environment.

Electron microprobes and scanning electron microscopes are used for detailed image analysis (physical properties and chemical composition) of individual particles of extremely fine-grained sediments (Mudroch et al., 1997).

Specific Surface Area. The *specific surface* of a sediment particle is defined as the surface area per unit mass of sediment and is expressed in square meters per gram. Differences in surface area result from particle size, clay mineral type, and organic matter content. The surface area is highly correlated with cation-exchange capacity and inversely proportional to particle size. Clay-sized particles contribute the most to the specific surface of an inorganic sediment. Some clay minerals have extensive internal surfaces. The specific surface

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for clay minerals varies from 5 to 20 m^2/g for kaolinite to 700 to 800 m^2/g for smectite group minerals with expandable internal surfaces.

Methods used to determine specific surface area of sediment particles include gas adsorption (the BET method), the ethylene glycol monoethyl ether method, and the methylene blue method. When sediment samples do not contain expandable clay minerals, each of these methods should yield comparable results. The Brunauer, Emmett and Teller (BET) method, which is time-consuming and requires highly specialized equipment, should not be used for analyzing sediments containing expandable clay minerals because only external surface areas are measured (Mudroch et al., 1997).

MAPPING OF OFFSHORE SEDIMENTS

Mapping the distribution and thickness of offshore sediments is carried out by offshore coring and grab sampling using a variety of sediment sampling devices (Mudroch and MacKnight, 1994). Divers sometimes are used for collecting samples where access to the sediment otherwise would be difficult or where a high priority is put on retrieving undisturbed samples. Diver-retrieved samples are more costly and time-consuming than regular core or grab samples.

In recent years, novel mapping techniques have been used for the mapping of contaminated, mostly fine-grained sediments. Since contaminated sediments typically are of very similar grain size as clean sediments, it is often difficult to determine the volume of contaminated sediments from sedimentological or geotechnical properties.

Due to the complex pattern of contamination occurring in sediments, the use of geophysical techniques is helpful to complement the information obtained from isolated cores and samples.

Echosounder systems provide information on water depth and morphology of a sediment surface. There are three main groups of echosounders currently in use: single-channel echosounders, multiple-channel echosounders, and multibeam echosounders (Kern and Westrich, 1999). The multibeam echosounder can be used in shallow waters, and its surveys produce accurate and continuous maps of the sediment surface. Very often echosounding is combined with subbottom profiling (see below).

Side-scan sonar surveys (Rukavina and Versteeg, 1996; Kern and Westrich, 1999) are useful for mapping bottom disturbances due to shipping, dredging, and dumping that would not be detected by an underwater camera or television due to poor visibility at the bottom of a water body. The vertical resolution is on the order of several centimeters, whereas the horizontal resolution is not substantially better than 1 m.

Marine high-resolution seismic profiling has been used extensively in the last 20 to 30 years for quaternary mapping, seabed process investigation, engineering applications, exploration for aggregates and placers, and habitat studies. There are four broad categories of marine seismic sources for high-resolution studies in common use today (Mosher and Simpkin, 2000). These are (1) controlled waveform (sonar, e.g., 3.5-kHz sounder, parasound, chirp), (2) accelerating water mass (e.g., boomer, airgun), (3) explosive (e.g., sparker), and (4) implosive (e.g., watergun).

Sonar transducers, which have been in common use for nearly four decades, range from high-frequency bathymetric echosounders to the modern chirp profiler. The 3.5-KHz subbottom profiler has been used in marine high-resolution reflection profiling for decades. The chirp sonar is the latest advance for subbottom profiling, sweeping through a range of frequencies anywhere between about 400 Hz and 20 kHz.

Electrodynamic sources known as *boomers* usually operate in the 1- to 5-kHz range. They provide higher penetration (between 50 and 100 m) than the chirp sonar but are of

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lower vertical resolution (between 0.5 and 1.0 m). Compressed-air sources (airguns, sleeve guns) explosively release compressed air into the surrounding water. The airguns used in high-resolution profiling are smaller in size but otherwise similar to those used in conventional exploration seismic reflection surveys.

The most common explosive for high-resolution marine surveying is the sparker, which generates a steam bubble by discharging electrical energy through a point electrode. Other explosive sources include dynamite, blasting caps, and gas exploders.

Implosive sources are those which use the implosion of a bubble or vacuum to create an impulsive pressure wave. A more recent development is the water gun, which projects a slug of water at high speed into the surrounding water mass. The cavity produced in the wake of this slug is near vacuum, which implodes and produces a measurable signal.

Each of these basic categories of seismic sources for high-resolution profiling has its advantages and limitations. In a seismic survey, the geometric configuration of the source and receiver and the receiver design are also important considerations (Mosher and Simpkin, 2000).

Another geophysical tool that has proven to be very useful in mapping contaminated sediments is an acoustic bottom-classification system called RoxAnn, which uses the character of bottom echoes to identify the bottom sediment type. This can be viewed in real time on a computer monitor as the information is being saved. The procedure is combined with ground-truth data from sediment samples and underwater television observations (Rukavina and Caddel, 1997).

The acoustic system DSLP (Detection of Sediment Layers and Properties) is based on a special multiple-frequency echosounding combined with a differentiated complex numerical signal analysis (Eden et al., 1999; Kern and Westrich, 1999). The DSLP method is independent of the acoustic frequencies used and provides high-resolution analysis of the stratification of suspended sediments and individual sediment layers of unknown physical and sedimentological properties. The depth of interfaces can be estimated with a vertical resolution of 3 to 5 cm. The DSLP method also can be used for accurate determinations of volumes of sediments to be dredged, which is of great importance for maintenance dredging and for sediment remediation projects.

Positioning instrumentation for mapping of offshore sediments has become much more accurate in the last decade. Where reference to more than one shore station through line of sight once was necessary, global positioning systems (GPS) technology now allows for more precise positioning with greater ease. This is especially true where a fixed antenna of known coordinates is used in conjunction with a GPS unit to produce differential GPS (DGPS). Under optimal conditions, positioning with DGPS results in a horizontal accuracy of ± 10 cm and a vertical accuracy of ± 1 cm (Zeman and Patterson, 1997). Positioning readouts of the vessel's antenna can be displayed on a computer monitor and updated automatically every second.

EROSION AND TRANSPORT OF COHESIVE SEDIMENTS

Introduction

Cohesive sediments are made up of the finest eroded particles, which usually are classified as silt and/or clay. They have physical, erosive, and transport characteristics that not only are different from those of coarse sediments but also are much more complex. To understand erosion and transport processes in both freshwater and marine environments, it is important to understand the distinction between cohesive and coarse sediments.

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With coarse sediments (primarily sand and gravel), the erodibility and transport processes, in addition to flow conditions, are primarily a function of particle shape and weight. The number of particles deposited per unit area per unit time equals the number of particles eroded. The concentration of the coarse suspended bed material in the water column thus depends solely on flow conditions. Cohesive sediments, in contrast, can remain in suspension in little or no flow conditions for hours and even days. It is thus much easier to calculate or model erosion and deposition tendencies of coarse sediments in both river and coastal environments.

The boundary between cohesive and granular sediments is not clearly defined and often varies with the type of sediment. Generally, silts and especially clays are cohesive. Coarse sediments often will erode into finer sediments over time, which in turn usually will become cohesive.

Particles of finer sediments tend to form flocs rather than act independently of each other (i.e., there are interparticle forces of both attraction and repulsion). This fact can cause the clumped particles of cohesive sediments to fall into the size category of coarse sediment and to take on coarse sediment transport characteristics until particle breakup recurs.

There are several different forces involved in the interaction of cohesive sediment particles. The attraction between molecules and atoms (van der Waals forces) consists of short-range forces inversely proportional to the seventh power of the distance between atoms. The forces thus decrease very rapidly as distance between the particles increases. The magnitude of the force depends on sediment surface properties. In some circumstances, there are forces that act between clays that are inversely proportional to the square of the distance (Coulomb forces). Kaolinite clay, for example, develops positive charges under acidic conditions. There are also bonds due to nonclay (e.g., silt) material bonding to surfaces of more than one clay particle. Iron oxide, aluminum oxide, and carbonates are examples of bonding materials. Organic matter in surface soils forms interparticle bonds. Organic molecules are held at the clay surface by hydrogen bonding or electrical bonds and aid in the bonding of clays to coarse sediments (Yong, 1966).

Knowledge of the erodibility and transport processes of cohesive sediment is important from both the engineering and environmental perspectives. Annual erosion rates of land adjacent to rivers and coastlines under various flow conditions must be determined in dealing with erosion control measures. Determining the stability of shoreline structures such as hydrotowers or nearby buildings relies on knowing sediment type, erodibility, and flow patterns. Most contaminants within soil or sediment usually bind to the finer or cohesive particles and thus will be transported with these particles.

Numerous experiments on cohesive sediments have been conducted both in the field and in laboratories where flows and wave action are measured carefully. Despite these experiments, there is still much information that is unknown regarding relationships between chemical bonds, flow patterns, and erosion rates. The following subsections draw on the information gleaned from such studies involved with cohesive sediment research. Flume designs commonly used for simulating flow conditions in this field of research are also described briefly.

Erodibility of Cohesive Sediments

Cohesive sediment can be eroded only when the electrochemical bond existing between the sediment particles is broken. This means that the force required to break or shear the sediment (critical shear stress) must be exceeded before erosion can occur. There are two forms of erosion that exceed the critical shear stress of cohesive sediments, namely, surface erosion and bulk erosion. Surface erosion (i.e., fluid shear stress) is the entrainment of particles at the bed surface through the breaking up of the electrochemical bonds due to shearing

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under turbulent bed shear stresses. Bulk erosion is the undercutting of sediment masses, causing the eventual fall and collapse of these masses into smaller clumps. These smaller clumps are eroded more readily though surface erosion. Typical values for critical shear stress of soft estuarine sediments measured in laboratory tests are around 0.1 to 2 Pa (Berlamont et al., 1993).

Silt and clay particles suspended in water often have a tendency to clump together due to various factors such as particle mineralogy, electrochemical bonds, bacteria, and the hydrodynamic properties of the flow field (Krishnappan, 1996). This clumping or coalescing of the particles forms larger aggregates or clumps of sediment called *flocs,* which then settle out of suspension. This process, known as *flocculation,* causes an effective increase in particle size and increases the rate of sediment settlement. Hunt (1980) identified three prominent processes that result in the collision of particles: Brownian motion, velocity gradients (laminar and turbulent), and differential settling of particles (i.e., fast-settling particles colliding with slower-settling particles). Four processes result in cohesion, namely, electrochemical bonds induced by salt, chemical coatings affecting charge characteristics of the particles, bioflocculation due to polymers secreted by bacteria and other microorganisms, and pelletization after sediment has been ingested by filter feeders and other animals (Krishnappan, 1996).

For most cohesive soils, the particle-floc contact is considered to be the only significant area between particles where normal stresses and shear stresses can be transmitted (Mitchell et al., 1969). Fluid shear stress imposed on a soil surface can be related to the velocity of flow (Partheniades and Paaswell, 1970). For cohesive sediments, however, correlations between the erosive force of fluid shear stress and sediment shear strength have been hard to obtain in laboratory measurements. Previous attempts to relate erosion resistance to undrained shear strength have met with only limited success (Kelly and Gularte, 1981). On average, there is a slight increase in the resistance to erosion with increasing soil density and shear strength for medium- to high-strength clays. Despite this fact, however, critical fluid shear stresses for cohesive soils of similar shear strength may differ by several orders of magnitude. In addition, cohesive soils with low shear strength may resist fluid shear stresses that are much higher than what other cohesive soils of higher shear strength can withstand. It is thus concluded that the mechanism of failure of a cohesive soil by fluid shear stress is different from the mechanism of mass shear stress failure from external forces (Partheniades, 1972). Research has been ongoing in trying to explain this phenomenon.

The swelling of cohesive sediment particles by saturation in water causes a weakening of the electrochemical bonds and thus increases the sediment erodibility. The amount of swelling depends on factors such as the shape of the particles, salinity of the water, sediment load, and the sodium adsorption ratio (SAR) (Grimshaw, 1971). The SAR is expressed as

$$\frac{0.043 \times \text{sodium concentration})}{(0.025 \times \text{calcium concentration} + 0.04 \times \text{magnesium concentration})^{0.5}}$$

Swelling decreases with a lower SAR and also decreases with greater salinity (Sargunam et al., 1973). The spacing between particles in the sediment will increase with greater water content, thus increasing erodibility of the sediment.

Measurement of the erodibility of a cohesive sediment bed depends first on defining or delineating the bed. Often there is a gradual transition from muddy water, with a high concentration of suspended cohesive sediment, to watery mud, to firm mud. This transition varies in thickness and provides a challenge in determining the plane of the bed. For measurement of erodibility of the bed, the plane is considered to be where resistance to fluid shear stress occurs below the water flow. This is called the *hydrodynamic bed,* and its depth

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is called the *hydrodynamic depth.* The resistance that defines the hydrodynamic bed depends on bed density (Mehta et al., 1989).

Erodibility of a cohesive bed depends on how consolidated the bed is. Consolidation can be ongoing as cohesive sediments gradually settle into the hydrodynamic bed. Typically, the susceptibility to erosion of a bed is reduced the more consolidated it is. The more consolidated the bed, the more dense it is, which means a greater fluid shear stress is required to erode the same volume of sediment than a less consolidated bed of equal volume.

Organisms, or benthos, can affect the erodibility of a cohesive sediment bed by either increasing or decreasing the potential for erosion. Organisms decompose organic matter and consequently alter sediment pH, redox potential, and porewater chemistry (Montague, 1986). The production of organic coatings, or extracellular polymeric substances (EPS), by organisms has been known to hold sediment together (Decho, 1990). Decreased erodibility by organisms have been measured in subtidal mats of algae in marine environments, where the mats have been measured to be five times more resistant to erosion than bare sediment (Neumann et al., 1970).

Bioturbation, or the burrowing action of benthos in the sediment bed, is the most common way benthos increases erodibility (Meadows and Tait, 1989). The aerating and loosening of the sediment by benthos weaken the sediment. The concentration of benthos in the sediment is in turn largely affected by the redox, or oxygen-reduction, potential. The redox potential depends on the electrochemical properties and depth of sediment, as well as on oxygen levels in the water column.

Seasonal fluctuations must be considered when attempting to determine erosion rates of any specific site. The environmental conditions that affect the mortality or population of benthos, such as oxygen content in the water (i.e., redox conditions), will affect their impact on eroding the sediment. Water temperature has a very significant influence on the erosive characteristics of cohesive sediments. Erosion rates in water at 35°C are about twice as much as those in water at 20°C (Partheniades, 1971). Higher pH values in water also increase erodibility and will destroy positive charges in the electrochemical bonds of the sediment (Nielson, 1973). The growth of aquatic plants and their root structures in warmer seasons may create more stability within the sediment while slowing down flows. Ice scouring may occur during colder seasons.

Transport of Cohesive Sediments

Understanding of sediment transport requires a knowledge of various hydromechanical parameters, such as grain size, flocculation, turbidity (concentration of suspended sediment), bedforms, wave action, and littoral transport. There are so many variables in nature, however, that it is virtually impossible to have an understanding of flows and sediment transport that is completely accurate for all natural flow conditions. Research into sediment transport patterns has been ongoing for decades. Basic principles known at present are discussed in this subsection.

The grain size of particles obviously will be a factor in their movement in varying flow velocities. Likewise, but to a lesser extent, the size of particles in aquatic environments directly affects flow conditions. While the transport tendencies of coarse sediment generally are well known, the movement of finer particles is more complex because the finest suspended sediments can remain in suspension in little or no flow, creating turbid conditions. The velocity at which cohesive sediment settles cannot be predicted because particle size and densities change with flocculation (Krishnappan, 1996), which also affects their erodibility and transport. Settling velocities of cohesive sediments in a natural suspension are considered to be around 0.01 to 10 mm/s. This value will increase with concentration due to flocculation to reach a maximum concentration of 2 to 10 g/liter. At higher

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concentrations, flocs are broken, and the settling velocity decreases rapidly (Berlamont et al., 1993).

Turbidity is a factor for deposition of eroded cohesive sediments. The amount of sediment that can be maintained in suspension at steady state depends not on the flow condition but on the available initial quantity of suspended sediment. This fact contrasts with the transport process for coarse cohesionless sediments, where the bed material transport is governed by an exchange of the sediment particles between the bed and the suspension (Mehta and Partheniades, 1975).

Rivers. Transport processes in rivers, with the absence of significant waves, rely mainly on flow mechanics. The varying shapes of riverbeds, the type of sediment, and the drag on flows in the river channel have a large influence on flow velocities and sediment transport.

For cohesive sediments, flow conditions have an effect on sediment suspension that is not a linear relationship. There appears to be a critical flow limit above which sediment can be maintained in suspension at high concentrations, but just below this limit all the suspended sediment deposits rapidly (Partheniades, 1972).

For steady, uniform flow in regularly shaped river channels, total flow resistance may be divided into grain resistance and form resistance. Grain resistance is the result of shear and pressure forces acting on the grains comprising the boundary of the watercourse, whereas form resistance is due to the drag of larger obstructions that protrude from the boundary into the flow (Yen, 1992). Total shear stress likewise may be separated into grain shear stress and form shear stress. Partitioning shear stress in this manner is significant because it is widely believed that in river flows the transport capacity of bed sediments is controlled by grain shear stress rather than by total shear stress (Atkinson et al., 2000).

Cohesive sediments can erode by their gradual deterioration and flaking off into thin flakes. This process is known as *slacking* and is significant in river flow erosion. Slacking is not a completely understood phenomenon, but it is known that one of the causes of slacking is air entrapment in the sediment voids if the sediment becomes compacted.

Where fast fluid velocities overflow an irregularly shaped river bed, severe erosion or scouring of the bed can occur. Cohesive sediments are more scour resistant than coarse sediments; therefore, a cohesive river bed is more stable than a bed of coarse material. Scouring of a river bed tends to lessen with time. It has been found in open flume testing (Abdel-Rahman, 1962) that the maximum depth of erosion increases as both bed shear stress and bed roughness increases and as the shear strength of the bed decreases.

Cohesive river beds under steady, uniform flow have been shown by Parker and Izumi (2000) to produce a series of raised bedforms or steps that migrate slowly upstream and create hydraulic jumps. The upstream region of each step has subcritical flow, whereas the downstream region has supercritical flow ending with a hydraulic jump.

River flow mechanics vary quite a bit from flows and currents along coasts. Likewise, suspended cohesive sediments in river flows are significantly affected where rivers flow into saltwater estuaries along coastlines. Saltwater tends to underlie freshwater in an estuary. This produces a unique movement of sediment. The lower, denser saltwater moves toward the head of the estuary and replaces the surface-flowing freshwater. Some of the suspended sediments a river transports downstream are carried away as a result, and they are dispersed over a wider area in the estuary. If the river is polluted, the contaminants carried in the sediment will follow this pattern of deposition, where they may bioaccumulate in estuarine organisms (Oberrecht, 1997). The concentration of suspended cohesive sediments in an estuary can be as high as 100 g/liter (Mehta et al., 1989).

Coastal Areas. Depths of water along coastal areas can vary to a much greater degree than in rivers. This means that much of the drag in coastal flows is induced by the upward rise to the shore, especially where onshore breezes exist. The mechanics involved in wave

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creation involve orbital flow patterns below the water surface that can reach down to depths of several meters. These depths are decreased toward shore with the rising lake or marine bed. Where the shallowness of the bed interferes with these orbital flows, pressure is induced on the bed by these flows in the form of normal stress.

The surface sediment often oscillates and moves in a mass as wave forces push down and release on the sediment bed. This type of movement is known as a *mud wave.* The height of the mud wave depends on the geotechnical properties of the sediment and the amplitude and wavelength of the bottom pressures. Heights of mud waves range from a few millimeters to about a meter under storm conditions. Surface waves lose a lot of energy when mud waves are generated. The wave height can decrease by 10 percent in a distance of about 20 or 30 m (Suhayda, 1986). The erosive action of the surface waves are thus decreased because an energy transfer to the sediment bed occurs. This transfer of energy to the sediment is mainly from the normal stress induced by wave action rather than through shear stress (Li and Mehta, 1997).

Wave action has an effect on cohesive bottom sediments in shallow areas off coasts. Since surface wave action affects lower water column flow over the sediment, entrainment of cohesive sediments occurs. This dense suspension of sediments above the bed layer along coastal areas is known as *fluid mud.* The formation of fluid mud has been described to occur by the gradual sinking of suspended sediment as well as by wave action. Winterwerp and Kranenburg (1997) state that fluid mud can be formed when floc particles become highly concentrated and sink so that they settle above the surface of the bed. Toorman (1992) claims that both fluidization (an increase in porewater pressure due to wave action) and liquefaction (sediment suspension resulting from shear force) produce fluid mud. Feng (1992) states that fluid mud formation occurs when the effective normal stress on the bed surface is almost nonexistent.

The processes involved in the generation of fluid mud affect the reaction of a muddy bed to waves and currents and play a major role in the transport of cohesive sediments (De Wit and Kranenburg, 1997). If currents are present during wave action, the combined fluid shear stress from the two forces can be significant, causing the fluid mud to be carried away by the currents (Mehta et al., 1989). If currents are minor, or nonexistent, deposition tends to take place. With continuing deposition, the mud layer moves from a loose, mobile state to a grounded state and becomes less erodible as it settles into the bed. The porewater is squeezed out, and the weight of the mud layer becomes supported by electrochemical bonds. This process is called *self-weight consolidation* (Teisson et al., 1993). The viscosity boundary between fluid and plastic mud was measured at 3 Pa (Migniot, 1989), although there is no established theory for calculating erodibility of mud deposits (Teisson et al., 1993).

Seasonal variations in erosion along coastal areas occur. This is due to weather conditions such as seasonal wind storms, differences in water temperature affecting organism growth, water current trends, and other factors. The difference in seasonal erosion affects the amount of sediment transport along coastlines for each season. The overall movement of this sediment can be measured over the course of a year or for a longer period to determine the overall trend of sediment transport.

The transport of sediments by waves and currents along a coastline is known as *littoral transport.* Much of the sediment that is moved by littoral transport is newly eroded, often from exposed shoreline bluffs. Where the soil around such bluffs has been contaminated, the potential exists for a fresh supply of contaminated sediments to enter the adjacent water body simply by the act of erosion. Littoral transport of contaminated sediments can cause a continuous supply of contaminants along a coastline. This is especially true where long-term movement of wind and wave action transports the greater portion of eroded sediment in one direction (littoral drift). Cohesive sediments that are flocculated will coincide with the littoral transport patterns of coarser sediments. In addition to eroded sediments, effluent from

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industries, sewers, streams, and agricultural runoff may add more contaminants to the littoral sediments.

The process of flocculation is largely affected by salinity levels. Consequently, flocculation characteristics can change along coastal inlets, such as estuaries. In freshwater, clay particles are kept in suspension by their molecular motion and often are negatively charged, thus decreasing flocculation. In an estuary, however, where freshwater meets and mixes with ionically charged saltwater, negative charges are neutralized, and sediment particles flocculate even more so than in freshwater. More finer sediment particles, in the form of flocs, thus settle out of suspension. Variations in flocculation may occur due to tides and seasons or due to runoff fluctuations and storm surges. Incoming tides and storm surges deposit ocean sands in many estuaries. This often produces sediment gradients ranging from coarse sand at the mouth of an estuary to extremely fine or cohesive sediment at the head (Oberrecht, 1997).

Flumes

Modeling flows to test for sediment erosion and transport usually is done with a laboratory flume. Specific soil or sediment types are laid out along the base of the flume, and a continuous flow of water is induced over the sediment for varying periods of time from several minutes to several days. Measurements and observations of flocculation, settlement, and so on are taken at various intervals. There are two basic types of flumes, namely, laboratory and in situ. Of these, flumes can be either straight or in a circular or looped pattern.

There are significant limitations to flume tests because they fail to duplicate field conditions in several ways. One notable example is the misrepresentation of induced stratification effects (Teisson et al., 1993), which are small in flume tests but often found to be larger in field conditions. Kuijper et al. (1989) noted that erosion measurements of cohesive sediment beds in a straight flume appeared to be more severe than in a circular flume with similar sediment and velocities.

Straight Flumes. Straight flumes are typically long, rectangular glass or acrylic designs that allow for straight flow simulation. They are used commonly for experimental research on noncohesive sediments such as sand and gravel but are not considered to be suitable for cohesive sediments such as silt and clay. This is due to the tendency of the silt and clay particles to floc together. Straight flumes tend to disrupt the flocs when the flocs pass through the return pipe and diffusers that are common on straight flumes (Mehta and Partheniades, 1975). The flocs usually are fragile and are susceptible to breakage by the forced flows of the recirculating pumps. Cohesive sediment transport processes are also time dependent, ranging from hours to days for completion, creating the need for excessively long flumes (Krishnappan, 1993). Volume flows in straight flumes tend to be large. Because of this, it is more difficult to determine erosion rates from the concentration of suspended sediment due to the length of time required for complete mixing of the sediment and the subsequent changes in the overall suspended concentration (Berlamont et al., 1993).

Circular Flumes. Circular flumes generate a flow that is theoretically uniform at every section and is free from any floc-disrupting elements. Circular flumes thus are used commonly for fine sediments. A disadvantage of circular flumes is the centrifugal force created by their rotation, which tends to push the flowing water and suspended sediments toward the outer section within the flume. Natural straight flows thus are virtually impossible to simulate. It has been noted by Berlamont et al. (1993), however, that circular flumes give a good general idea for the erosion and deposition properties of cohesive sediments.

A common circular flume design (for indoor use) rests on a rotatable circular platform and houses an annular cover plate (ring) inside the flume that makes contact with the sur-

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face water in the flume. A king-post configuration may be used to support the flume, where the weight of the entire structure is supported by two tapered roller bearings housed within the king post. The two bearings are held in a rotating hollow shaft that supports the lower rotating platform on which the flume is mounted. The hollow shaft also supports an inner solid shaft connected to the upper turntable for the ring assembly. The two shafts are fixed axially and are driven independently by two separate drive systems (Krishnappan, 1993). The flume and the ring thus can be rotated in opposite directions, as is usually done. This counterrotation is important in offsetting the centrifugal force that otherwise would produce uneven flow patterns within the circular flume.

In situ Flumes. Where laboratory conditions are deemed to be insufficient or inaccurate for calculating field conditions, in situ flumes sometimes are used. An in situ flume is designed to be lowered underwater and embedded into the sediment. The flume consists of a bottom-open channel that sinks into the sediment and has paddles that push and circulate water around the channel. A roof isolates the inside of the channel from external disturbances. Sampling ports are incorporated into the design to allow for water sampling or measuring devices such as sensors. Flumes can vary in shape, e.g., being circular (Amos et al., 1992) or raceway-shaped (Black and Cramp. 1995).

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CHAPTER 16
SEDIMENTS AND SOILS: INTEGRATED PROCESS STUDIES

Ulrich Förstner

INTRODUCTION

Both for establishing sediment-related quality objectives and for developing and implementing technical problem solutions, a set of practical process knowledge is needed that uses a wide range of simulation techniques as well as models in different spatial and temporal scales. In practice, specific information on interacting hydromechanical, biological, and geochemical processes will be required for two reasons:

1. *Sediment quality assessment* is considerably more complex than water quality assessment due to the many site-specific parameters that need to be considered that are not a factor for water. Bioavailability of a contaminant, for example, depends on sorption kinetics, sediment characteristics (capacity-controlling properties), and sediment deposition and erosion. The methodologies developed to date do not deal adequately with the complex nature of sediments.
2. *Remediation techniques* for contaminated sediments generally are more limited than for other solid waste materials. Considering the worldwide dredging activities—more than 1 billion m^3 per year—only a very small percentage of these materials can undergo treatment in the closer sense—solvent extraction, bioremediation, thermal desorption, vitrification, etc. Here, geochemical mechanisms such as concentration, stabilization, and other forms of long-term self-containing barriers could reduce the mobility and biological availability of critical pollutants.

The position of *integrating process studies* between ecotoxicological risk assessment (see Chap. 17) and remediation technologies in the management of aquatic sediments and dredged materials (see Chap. 13) is presented in Fig. 16.1.

In the following section an overview is given of the major in situ processes and mechanisms of pollutant transfer in various compartments of the aquatic system. Then an interdisciplinary process approach relating to the release of dissolved organic carbon, nutrients, and pollutants into the open water is derived from the evaluation of the international state of the knowledge with three major themes: experimental techniques, processes and properties, and development and validation of models. This approach forms the basis of a coordinated research project entitled, "Fine Sediment Dynamics and Pollutant Mobility in

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Rivers," funded by the German Ministry of Education and Technology and scheduled to start in early 2002.

BEHAVIOR OF PARTICLE-ASSOCIATED POLLUTANTS

Due to the strong interactions with particulate matter, the behavior of contaminants such as heavy metals and organic chemicals in surface waters is regulated by the transport, dispersal, and sedimentation of aquatic solid materials. Chemical processes therefore are strongly influenced by the suspended matter concentrations and, due to the shallowness of the waters, by the deposited sediments.

Origin of Pollutant Substrates

Particles as substrates of pollutants originate from two major sources: (1) endogenic fractions of particulate matter that include minerals that result from processes occurring within the water column and (2) authigenic (or diagenetic) fractions that include minerals that result from processes within deposited sediments (Jones and Bowser, 1978). Enrichment of minerals generated by endogenic processes may be influenced by settling of particulates, filtering organisms, and flocculation. Endogenic processes exhibit a distinct temporal character, often as a result of variation of the organic productivity. In lakes, the total particulate concentration of trace metals generally is lowest in the hypolimnion due to the decomposition of organic matter. Consequently, net biogenic flux, for example, of metals depends on the lake's capacity to produce organic particulate matter and to decompose it before it is buried definitely in the sediment (Salomons and Baccini, 1986). Authigenic or diagenetic formations mostly relate to decomposition of organic matter, which is mediated by microorganisms. These processes generally follow a finite succession in sediments depending on the nature of the oxidizing agent. The successive events are oxygen consumption (respiration), nitrate reduction, sulfate reduction, and methane formation. The composition

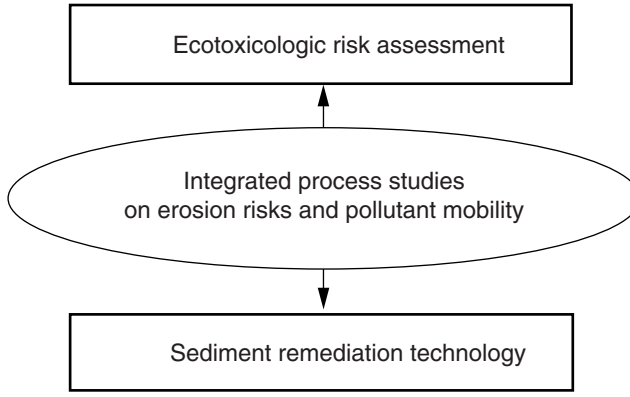

FIGURE 16.1 The position of integrated process studies between ecotoxicologic risk assessment (see Chap. 17) and remediation technologies in the management of aquatic sediments and dredged materials (see Chap. 13).

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of interstitial waters in sediments is perhaps the most sensitive indicator of the types and extent of reactions that take place between pollutant-loaded sediment particles and the aqueous phase that contacts them. The large surface area of fine-grained sediment in relation to the small volume of its trapped interstitial water ensures that minor reactions with the solid phases will be shown by major changes in the composition of the aqueous phase. Thus the theoretical assessment of the nature, for example, of trace-metal phases via the equilibrium solution composition can be used for evaluation of sediment quality data.

Pollutant Transfer Between Inorganic and Organic Substrates

The following factors influence the distribution of pollutants between solution and particulates in soils and sediments (Salomons and Stigliani 1995):

1. The form of dissolved inputs of chemicals from both natural and civilizational sources
2. The types of interactive processes, i.e., either sorption/desorption- or precipitation/dissolution-controlled mechanisms for metals (Salomons, 1985)
3. The concentration and composition of particulate matter mainly with respect to surface-active phases and grain-size distribution

For specific adsorption of metals, binding strength typically depends on adsorbend concentration because there exists a range of site-binding energies (Leckie, 1986). High-energy adsorption sites, because they are fewer in number than lower-energy sites, become limiting first; as lower-energy sites are gradually filled, the overall binding constant decreases. Particularly in systems containing organic substances, a reduced reversibility of metal sorption has been observed (Lion et al., 1982).

With respect to the modeling of metal partitioning between dissolved and particulate phases in a natural system, e.g., for estuarine sediments, the following requirements have been listed by Luoma and Davies (1983):

1. Determination of binding intensities and capacities for important sediment components
2. Determination of the relative abundance of these components
3. Assessment of the effect of particle coatings and of multicomponent aggregation on binding capacity of each substrate
4. Consideration of the effect of major competitors (Ca^{2+}, Mg^{2+}, Na^{+}, Cl^{-})
5. Evaluation of the kinetics of metal redistribution among sediment components

It seems that models are still restricted for various reasons: (1) adsorption characteristics are related not only to the system conditions (i.e., solid types, concentrations, and adsorbing species) but also to changes in the net system surface properties resulting from particle-particle interactions such as coagulation, (2) influences of organic ligands in the aqueous phase rarely can be predicted as yet, and (3) effects of competition between various sorption sites and reaction kinetics of the individual constituents cannot be evaluated in a mixture of sedimentary components.

Mobilization of Pollutants

Mobilization, in a wide sense, comprises changes in the chemical environment that usually affect lower rates of precipitation or adsorption—compared with "natural" conditions—rather than active releases of contaminants from solid materials. With respect to particle-bound

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metals, their solubility, mobility, and bioavailability can be increased by five major factors in terrestrial and aquatic environments, as noted in the following subsections.

Acidification. Acidity imposes problems in all aspects of metal mobilization in the environment: toxificity of drinking water, growth and reproduction of aquatic organisms, increased leaching of nutrients from the soil and the ensuing reduction of soil fertility, increased availability and toxicity of metals, and the undesirable acceleration of mercury methylation in sediments. On a regional scale, acid precipitation probably is the prime factor affecting metal mobility in surface waters—by changing solid/dissolved equilibria in the atmospheric precipitation, by creating washout effects on soils and rocks in the catchment area, by enhancing groundwater mobility of metals, and by active remobilization from aquatic sediments.

Acidic drainage from coal and ore mines has been recognized as a serious environmental pollution problem for a long time. Transformations of sulfides and a shift to more acid conditions are particularly enhancing to the mobility of elements such as Mn, Fe, Zn, Pb, Cu, and Cd. A simple chemical mechanism could not explain the rapid production of acidic mine drainage by the oxidation of metal sulfides. According to Singer and Stumm (1970), ferric iron is the major oxidant of pyrite in the complex natural oxidation sequence, and it is mainly *Thiobacillus ferrooxidans,* an iron-oxidizing acidophilic bacterium that accelerates metal sulfide oxidations 10^6 times over the abiotic rate.

Salinity Increase. The effect of higher salinity seems to be particularly critical for resuspended cadmium-rich sediments in estuaries (Salomons and Förstner, 1984). As a result of biological or biochemical pumping, the tidal flats may act as a source of dissolved metals. Release of trace metals from particulate matter has been reported from several estuaries (Scheldt, Gironde, Elbe/Weser, Savannah/Ogeechee) and has been explained by oxidation processes and by intensive breakdown of organic matter (both mediated by microorganisms), after which the released metals become complexed with chloride and/or ligands from the decomposing organic matter in the water. According to experimental data given by Salomons and Mook (1980), these effects can even be found in salt-polluted inland waters; at chloride contents of 200 mg/liter—for example, the Lower Rhine River—the "normal" adsorption rate of cadmium would be reduced by approximately 20 percent; at 1000 mg/liter Cl^-—for examples, the Weser River in Germany—this rate would be only half compared with the sorption of Cd under natural salt concentrations.

Complexing Agents. Significant effects on the mobility of heavy metals can be expected by strong synthetic chelators such as nitrilotriacetate (NTA), a substitute for polyphosphate in detergents, and ethylenediamintetracetate (EDTA), which is used as well for replacing phosphate but also is used in metal processing, galvanotechnology, and the photoindustry. The extent of metal mobilization depends on the concentration of complexing agent, its pH value, the mode of occurrence of heavy metals in the suspended sediment, and competition by other cations. Active remobilization seems to exhibit reliable results at NTA concentrations above approximately 1 to 2 mg/liter; such concentrations of NTA could be expected rarely in normal river waters but may occur at even higher levels in sewage treatment plants. Passive effects of NTA (where the complexing agent may negatively influence the natural adsorption processes) are starting at lower values, at NTA concentrations of 200 to 500 μg/liter, and it has been found by Salomons (1983) that zinc adsorption is already significantly affected at NTA concentrations of 20 to 50 μg/liter at pH 8 conditions.

Biomethylation. Organisms not only accumulate metals from the abiotic reservoirs, but they are also able to interact with metals and modify processes affecting them, e.g., by pH increase, reduction of sulfate, redox conversions of inorganic forms, and release of extracellular material. Methylation of inorganic metal compounds is an important and well-

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known biogeochemical phenomenon in natural systems and has been shown to occur for a number of trace elements, including Hg, As, and Sn (Craig, 1986). Mercury is the best-studied example of an element that undergoes a complex cycle in the biosphere and for which there is evidence of the biochemical and molecular basis of the transformations. The product is mainly monomethylmercury under neutral and acidic conditions and (volatile) dimethylmercury under basic conditions. Conversion of organic mercury to methylmercury in anaerobic sediments is negatively correlated with salinity; as an explanation, the theory is advanced that sulfide, derived from sea salt sulfate by microbial reduction, interferes with Hg^{2+} methylation by forming highly insoluble HgS (Compeau and Bartha, 1983). Estimates for net methylation rates in sediments range from 15 to 40 ng/g per day to 137 ng/g per day, the latter in organic-rich salt marsh sediments (Windom, 1976).

Oxidation-Reduction Processes. Under oxidizing conditions, the controlling solid may change gradually from metallic sulfides to carbonates, oxyhydroxides, oxides, or silicates, thus changing the solubility of the associated trace metals. The major process affecting the lowering of pH values (to pH 2–3) is the exposure of pyrite (FeS_2) and other sulfide minerals to atmospheric oxygen and moisture, whereby the sulfidic component is oxidized to sulfate and acidity (H^+ ions) is generated.

Field evidence for changing cadmium mobilities was reported by Holmes et al. (1974) from Corpus Christi Bay Harbor. During the summer period when the harbor water was stagnant, cadmium precipitated as CdS at the sediment-water interface. In the winter months, however, the increased flow of oxygen-rich water into the bay resulted in a release of the precipitated metal.

In the St. Lawrence estuary, Gendron et al. (1986) found evidence for different release mechanisms near the sediment-water interface. The profiles for cobalt resemble those for manganese and iron with increased levels downward, suggesting a mobilization of these elements in the reducing zone and a reprecipitation at the surface of the sediment profile. On the other hand, cadmium appears to be released at the surface, probably as a result of the aerobic remobilization of organically bound cadmium.

Biological activities typically are involved in these processes. Remobilization of trace metals has been explained by the removal of sulfide from porewaters via ventilation of the upper sediment layer with oxic overlying water, allowing the enrichment of dissolved cadmium that would otherwise exhibit very low concentrations due to the formation of insoluble sufides in reduced H_2S-containing sediments. Emerson et al. (1984) suggest a significant enhancement of metal fluxes to the bottom waters by these mechanisms. It was shown by Hines et al. (1984) from tracer experiments that biological activity in surface sediments greatly enhances remobilization of metals by the input of oxidized water. These processes are more effective during spring and summer than during the winter months.

From enclosure experiments in Narragansett Bay, Hunt and Smith (1983) estimated that by mechanisms such as oxidation of organic and sulfidic material, the anthropogenic proportion of cadmium in marine sediments is released to the water within approximately 3 years. For remobilization of copper and lead, approximately 40 and 400 years, respectively, is needed, according to these extrapolations.

An important and long-term source of metals is the sediments reworked from the flood plain, mainly by repeated oxidation and reduction processes. High concentration factors were found in inland waters affected by acidic mine effluents.

Mobility of Organic Pollutants. Compared with the wide experience with mobilizing processes on trace metals, knowledge on desorption of organic contaminants from solid substrates is still relatively poor. Regarding at first the before-mentioned parameters controlling sorption/desorption processes of inorganic pollutants, it can be expected that pH and ionic strength of leachates predominantly should affect partitioning of ionic organic compounds.

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One measure of the degree of bonding strength, i.e., the mobility of an organic chemical, is the distribution coefficient K_d of the solute and the solid. Table 16.1 provides several examples of pesticide groups that are of interest with respect to the activity of synthetic organic compounds in soils and sediments. The spectrum of K values from high (e.g., organochlorine pesticides) to low distribution coefficients (e.g., heterocyclic nitrogen pesticides such as triazine) not only is indicative of increasing solubility but also represents, more generally, the transition from nonpolar to semipolar to polar properties. The more soluble pesticides, which are degraded more easily and whose bonds are hydrolyzed more easily, such as methylcarbamate and the organophosphate insecticides, generally do not bioaccumulate as do the organochlorine compounds. On the other hand, the chlorinated phenols (commonly used for wood preservatives), which are weak hydrophobic acids and have octanol-water coefficients of 10^2 to 10^5, are being viewed with increasing concern because they can be mobilized, with their overall relatively low bonding strength, under changing pH values and other little known environmental factors (Farrington and Westall, 1986).

IN SITU PROCESSES IN AQUATIC SYSTEMS

Table 16.2 lists the major processes influencing the cycling of contaminants in aquatic systems according to the primary research discipline involved and phase (dissolved or particulate). There are characteristic interactions between chemistry and biology in the case of bioturbation of sediment deposits and between chemistry and photodegradation. Biological activity is involved in physical cycling of particulate matter both in the water column and at the sediment-water interface. Organic excretions may produce fecal pellets and may enhance aggregation and thus hasten settling of particles (Honjo, 1980). There are well-documented effects of reworking and resuspension of sediments by benthic organisms such as tubifid worms but also by amphipods, shrimps, and clams. Bioturbation is a major postsedimentation process affecting the fate of particle-associated toxic metals and persistent organic chemicals that are not affected primarily by volatilization, photolysis, or bio- and photodegradation (Allan, 1986).

TABLE 16.1 Estimated Sediment-Water or Soil-Water Distribution Coefficients for Various Pesticides

Pesticide group	K range
Organohalide	
Aromatic	
Aliphatic	10^5–10^3
Organophosphate	
Aliphatic derivative	5×10^2–10^1
Phenyl derivative	10^3–10^2
Heterocyclic	5×10^2–50
Carbamate	
Methylcarbamate	5×10^2–2
Thiocarbamate	5×10^2–50
Nitroaniline	1×10^3–50
Triazine	8–1

Source: Pavlou and Dexter (1980).

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TABLE 16.2 Processes Affecting the Cycling of Pollutants in Aquatic Systems

	Aqueous species	Particulate species
Chemical	Dissolution	Precipitation
	Desorption	Adsorption
	Complexation	Aggregation
	Species transformation	
Biologic	Decomposition	Food web transfer
	Absorption, release	Filtering, digestion
	Cell wall exchange	Pellet generation
	Bioturbation	
Physical	Advection	Resuspension
	Diffusion	Settling
	Photolysis	Burial

INTEGRATED PROCESS STUDIES ON EROSION RISKS AND POLLUTANT MOBILITY

Due to their particular dynamics, three characteristic features of sedimentary processes in rivers should receive special attention:

1. The dramatic effects of stormwater events on particle transport
2. The rapid and far-reaching effects of sulfide oxidation
3. The biological accumulation and potential release of toxic elements

In practice, emphasis has to be given to fine-grained sediments and suspended matter because these materials exhibit large surface areas and high sorption capacities. Organic materials are highly reactive. Degradation of organic matter will induce depletion of oxygen and may enhance formation of flocs and biofilms. Study of variations in sediment and water chemistry predominantly should include changes in pH and redox conditions, competition of dissolved ions, and processes such as complexation by organic substances. Major questions relate to the potential reduction of sorption sites on minerals and degradation of organic carrier materials. All these processes will influence solution-solid equilibrium conditions and have to be studied prior to modeling the overall effects on the water body and aquatic ecosystems.

Depicted in Fig. 16.2, which reflects the initial structural approach of the coordinated research program outlined below, three scientific disciplines are involved, and three study objects can be distinguished: suspended matter, sediment, and porewater or open water. Special study targets are the formation of aggregates in turbulent water, flocs and biofilms from organic reactions, and the formation of new surfaces for readsorption of dissolved pollutants. The main focus is on the degradation of organic matter, which affects both hydrodynamic processes—here, erosion versus sedimentation—and geochemical redox cycles. The crucial question of the whole program, after all possible interactions between both existing and newly formed solid and dissolved phases, refers to the net release of dissolved organic carbon (DOC), nutrients, and pollutants into the open water.

The program scheme shown in Fig. 16.3, with three major themes, experimental techniques, processes and properties, and development and validation of models, has been

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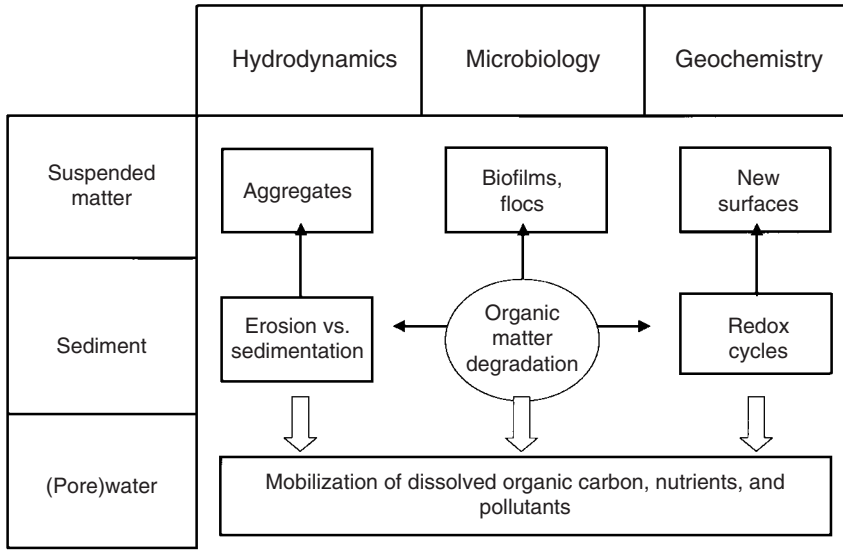

FIGURE 16.2 Scientific disciplines and study objects in a coordinated research program on fine *se*diment *dy*namics and pollutant *mo*bility in rivers (SEDYMO).

derived from an evaluation of the international state of knowledge and is presented in the following subsections.

Experimental Techniques

Fine-particle transport and related relocation of particle-bound pollutants take place, in the long-term and large-scale perspective, as events in zones that are either predominantly depositional or also can include erosive processes. The transport and transformation of pollutants at the interface between the water column and the bottom zone are controlled, on the one hand, by biogeochemical processes within the bottom sediment layer and, on the other hand, by hydrodynamic and biogeochemical processes within and from the flowing water. The quantification of flow rates, including the transport direction of particle aggregates, microorganisms, and dissolved and adsorbed substances, needs an integration of various experimental and modeling techniques for the determination of hydrodynamic, chemical, and (micro)biological parameters. In these fields, research at various institutions has led to new perceptions and a working hyptheses, which—for the first time—allows quantification of the above-mentioned relocation and flocculation/aggregation processes. The development of new systems can be based on the following research work (see also Chap. 15).

- Clarification of the interrelations among mineralogical, microbiological, and porewater parameters in erosion devices with the precise control of bottom hydrodynamics (Amos et al., 1992; Booij et al., 1994; Wiltshire et al., 1998)
- Investigation of erosion characteristics and sediment stabilities in relation to composition and mixing proportions of cohesive and granular particles and aggregates, respectively

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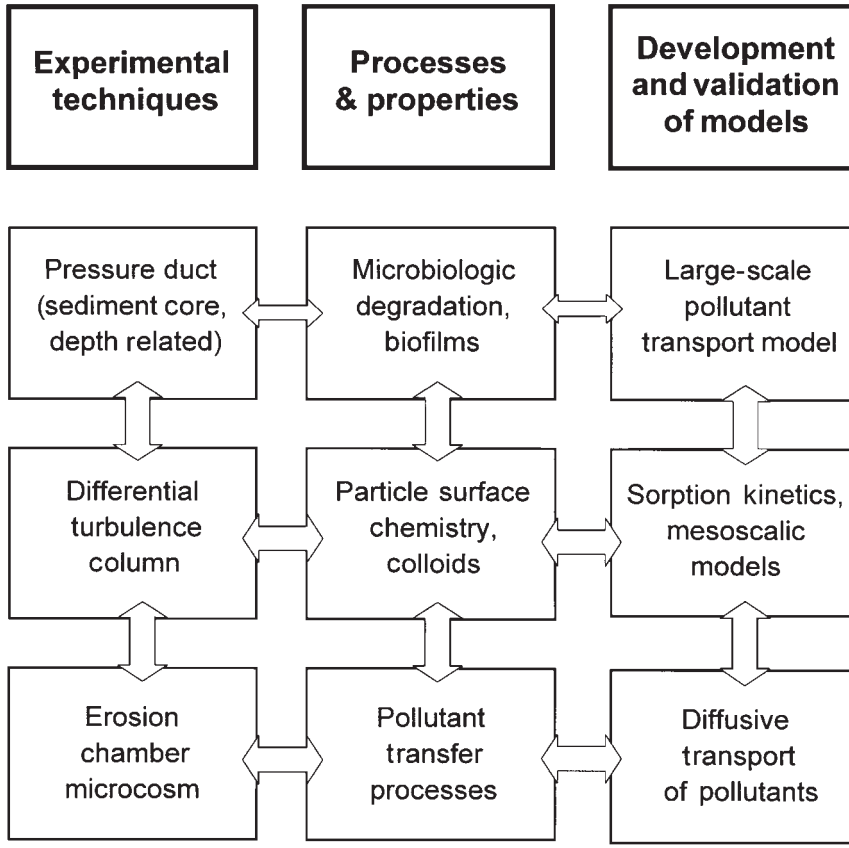

FIGURE 16.3 Structure of the SEDYMO program. In total, 20 subprojects are involved in the coordinated project (2002–2005).

- Determination of the dependence of erosion stability from consolidation and mechanical properties of bottom sediments, including biogenic stabilization by microorganisms (Spork, 1997)
- Studies on the types of flocs and aggregates in the water column in (1) turbulent, (2) oscillating (waves), and (3) slowly cyclic (tidal) flows (Gust and Müller, 1997)
- Investigations of the erosion and deposition behavior of particles and respective vertical mass flows in different hydrodynamic characteristics of simulators, such as erosion chambers, differential turbulence columns, and so on.

Key factors and processes in these interactions are degradation of organic matter, sorption and mobilization of pollutants, and the effect of turbulence. Since hydraulic effects are the primary input factor, most experiments need basic equipment for simulating reproducible hydraulic conditions. In the framework of this main theme, a combination of methods should be achieved that, on the one hand, will cover relevant deposition and erosion mechanisms and, on the other hand, will include the newest simulation and measuring techniques for both laboratory and field performance.

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Erosion Risk Assessment: Pressure Duct Experiments on Sediment Cores

Measurement of the critical shear stress of erosion is performed by Haag et al. (2000) with the SETEG flume, a straight rectangular pressure duct similar to the one developed by McNeal et al. (1996). It allows the measurement of erosion as a function of sediment depth at shear stresses of up to 15 Pa. Flow and corresponding shear stress are increased incrementally until the critical shear stress of mass erosion is reached; i.e., the sediment surface is disturbed instantaneously. Then the sediment material remaining within the tube is moved upward, and the procedure is repeated.

This experimental setup was applied to sediment cores from a lock-regulated reach of the River Neckar in Germany. The spatial pattern of contamination in the river reservoir was found to be remarkably heterogeneous. At some sites, very high heavy metal concentrations were detected at the sediment surface. The presence of an erosional unconformity that sharply separates young sediments from old ones strongly indicated that old and highly polluted sediments were remobilized from the reservoir in the past. The comparison of bottom shear stress in the river and critical shear stress also showed that, in principle, buried and fully consolidated old sediments can be eroded during major discharge events.

Simulating Natural Hydrodynamics with a Differential-Turbulence Column

The differential-turbulence column was developed at Cornell University in the framework of a doctoral thesis by Brett Brunk and was used initially to simulate the homogeneous turbulent kinetic energy and sediment-loading profiles for open-channel flow (Brunk et al., 1996). The reactor consists of five vertically spaced grids that oscillate to simulate turbulence in natural hydrodynamic systems. Spatial distribution of turbulence is measured using an acoustic Doppler velocimeter. In situ sampling can be done for introducing chemical species and monitoring chemical dynamics. Under homogeneous and open-channel-flow turbulent conditions, sediment profiles obtained in the differential-turbulence column accurately followed conventional theory (Brunk et al., 1996).

Using this device, Brunk et al. (1997) studied the enhancement of sorption of phenanthrene to particles in an estuary because these locations have been reported to be sinks for hydrophobic pollutants, and sorption has been attributed commonly to be an important mechanism responsible for the observed pollutant trapping. The sorption enhancement caused by salt effects and dissolved organic matter (DOM) coatings was both measured and modeled. The polycyclic aromatic compound phenathrene, an extracellular polymer from a soil bacterial isolate, and a low-organic-carbon kaolinite were used as models for the hydrophobic pollutant, DOM, and suspended sediment, respectively. Both salt effects and DOM coatings induced increased sorption, the former approximately 50 percent and the latter approximately 10 percent. These experiments showed that equilibrium sorption of phenanthrene cannot explain the full extent of pollutant trapping in estuaries. It seems that some sediment-bound phenanthrene, perhaps associated with atmospheric soot particles, may not be available for an aqueous-phase equilibrium distribution.

Erosion Chamber (Microcosm) in Combination with Skin-Friction Probe

The principal operational settings of the erosion chamber designed by Gust (1991) are to generate a spatially homogeneous skin friction at the sediment surface. It is achieved (1) by the variable rotational speed of a stirring disk placed at 6 cm over the sediment-water interface and (2) by the volume of recirculated suspension sucked through the rotating axis. The resulting suspension, of which concentration is indicative of the phase

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with erosion/deposition cycles, is monitored online in the concentration range of 0 to 20 g/liter by using a two-channel turbidity meter and a mass flowmeter (Fengler et al., 1998). Specially adapted online microsensors for the detection of oxygen, redox, and pH were integrated into the path of the recirculated suspension, as well as profiling probes to the sediment-water interface.

The special merits of this approach lie in the fact that natural conditions can be transferred directly into the micrososm system. For this purpose, measurements of hydrodynamic field data at the sediment-water interface such as the skin-friction velocity were done by running a constant-temperature hot-film anemometer for field application with high precision and accuracy (Gust, 1988). Continuous measurements at 20 Hz for up to 6 channels at a 12-bit resolution with a simultaneous collection of temperature and pressure make the system usable for long-term measurements such as the evaluation of tidal cycles.

Investigation of the release of trace metals from model sediments by Akkiparambath (1999) indicates that during simulation of a tidal cycle by increased skin-friction velocities, the initially resuspended particles of organic bottom sediment typically exhibit higher concentrations of copper and cadmium compared with the subsequent resuspension phases. In another experimental series, an increase in erosion stability was observed in the sequence of resuspension events. As a result, a decrease of metal mobilization by resuspension takes place particularly in the organic-rich model sediments. During the resuspension experiments of model sediments similar to real sediment composition, an increase of inorganic carbon was observed, accompanied by a reduction of calcium in solutions. It is suggested that the precipitation of calcium carbonate occurs in this sequence. During oxidation of sulfidic components, i.e., during resuspension of anoxic sediments, the carbonate content is steadily depleted. Oxidation of ammonia to nitrate, during a batch experiment using artificial sediments, induced a drastic pH decrease and effected—in the course of three redox cycles—a continuous increase of dissolved cadmium concentrations.

Comparison of Different Methods for the Study of Erosion Behavior

A comparison of different methodological approaches to the experimental study of the erosion behavior of aquatic sediments was made by Kern and Westrich (1999), as shown in Table 16.3. With a rotating circular flume, sedimentation/deposition aspects can be studied (Krishnappan, 1993). In some cases, sediment material is mixed prior to the laboratory experiment or is suspended/redeposited in an interim step. Homogenization is performed when stronger heterogeneities of material and erosion properties in the experimental design can be expected. On the other hand, transferability of data from laboratory experiments especially can be restricted if investigations have been made on sediments lacking natural layering. The decisive influence of long-term mechanical and biogeochemical consolidation processes on erosion stability of the sediment thus is frequently neglected. In addition to these problems, it should be kept in mind that the erosion behavior of aquatic sediments may be influenced both by the concentration of suspended matter and by the type and concentration of dissolved constituents in the water used in the laboratory experiments.

In principle, the demand for studying sediments under their natural layering can only be met by conducting erosion experiments directly within the aquatic system. With the actually available erosion measuring devices in most cases, only the erosion behavior at the sediment surface or a few centimeters below can be studied. However, there is a strong need for depth-profiling investigation because the strongly polluted sediments of the past are covered over time by depositions of less contaminated materials. Regarding the depth-profiling investigation, laboratory experiments using sediment cores have been proposed; some inconsistencies may be caused by the potential compression of sediment cores during sampling.

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TABLE 16.3 Methodologic Approaches to the Experimental Study of the Erosion Behavior of Aquatic Sediments

Procedure	Experimental Condition: Flowfield	Experimental Condition: Layering	Target Parameters (B, erosion begins; R, erosion rate; D, depth dependency)
Circular flume (Spork, 1997)	Rotational flow	Disturbed (artificial bed)	B, R
SETEG (Kern et al., 1999) (see text)	Longitudinal flow (pressed duct)	Nearly undisturbed	B, (R) D, up to 150 cm
EROMES (Witte and Kühl, 1996;	Propeller Rotation cylinder	Nearly undisturbed	B, (R) D, with adaption
Microcosm (Gust 1991)		Undisturbed feasible	B, R D, up to 2 cm (greater depth with adaption)
In situ channel (Hartmann 1997)	Longitudinal flow (pressure duct)	Undisturbed (in situ)	B
In situ (EROMES) (Liem et al., 1997)	Propeller	Undisturbed (in situ)	B, (R) D, up to approx. 5 cm

Source: Examples given in the compilation of Kern and Westrich (1999).

PROCESSES AND PROPERTIES

The second main theme comprises the biological and geochemical studies that are needed as a basis for evaluation of priority pollutants in relation to quality standards for sediments and suspended matter. The biological subprojects are aimed mainly at investigating the quantity and quality of particulate and dissolved organic substances, their microbial metabolism using various electron acceptors, and the role of biofilms and colloids on the behavior of pollutants in sedimentary systems. The major objective of the geochemical subprojects is the reality-near description of the transfer of nutrients and pollutants from particulate into dissolved phases (porewater and open-water body), the dynamic and resulting microscalic heterogeneity of material dispersion within the sediment, and the diffusive transfer of pollutants across the sediment-water interface. Most of the micro- and mesoscalic geochemical information will be used in the development of models.

Particulate organic matter is the most important energetic basis for organisms in rivers and plays a key role in the material cycle in these systems (Pusch et al., 1994). The question of whether sedimentation of suspended material is slow or fast is controlled not only by flow velocity but also by the structure of biofilms. More recent findings indicate that macrophytes and sediment ripples and mounds form typical retention mechanisms for both fine-grained particulate matter (FPOM) and coarse organic materials (CPOM) (Pusch et al., 1998). The particulate organic matter may be loosely associated with the bottom structures following their input into the sediment. They may be stored in the deeper parts of the riverbed or bank, and they also may be decomposed (Eisenmann et al., 1997). As for marine sediment, where the sequence of reduction processes is well documented, there are considerable gaps for allocating these processes to physiological groups of microorganisms in freshwater environments. Here, application of molecular-ecological techniques is particularly promising,

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especially in relation to qualitative and quantitative changes of inorganic and organic materials during resuspension of freshwater sediments (Meyercordt and Meyer-Reil, 1999).

Cycles of carbon, iron, manganese, and sulfur are closely coupled in the sediments of aquatic ecosystems, and these interactions may influence the mobility of potential metal contaminants as well. The typical chain of events leading to the release of micropollutants from sediments has been depicted by Salomons (1993) in the concept of the so-called chemical time bomb for soils and sediments. The first cycle—organic matter, sulfur, iron—provides the fuel for the subsequent processes. Capacity-controlling properties include buffer capacity and sorption capacity. These may be limited due to simple overloading or by consumption, e.g., by dissolution of carbonate. In this case, a sudden release of pollutants can occur. A new component in the system is that mobilized pollutant species can be readsorbed, preferentially to organic substances. The effectiveness of such processes has been demonstrated in the multichamber device, where competing effects of metal sorption from solution can be studied (Calmano et al., 1988). Copper in particular showed a distinct tendency to be readsorbed to organic substrates. With this process, even at relatively low rates of mobilization, significant metal accumulation can occur on organic matrices that may be further amplified in the food chain (Förstner et al., 1989).

Microbiological Degradation Studied by Microelectrodes and Optodes

Microelectrodes are useful tools for assessing the distribution of relevant milieu parameters in the immediate neighborhood of microorganisms with high spatial resolutions. For example, microscalic determination of the bioavailable fraction of organic carbon in sediments and biofilms has become possible as a result of the development of a microbial biosensor (Neudörfer and Meyer-Reil, 1997).

Considerable achievements in the simulation of metabolic processes in sediments have been provided by the development of particle-oriented sensor techniques, e.g., by the Max Planck Institute for Marine Biology in Bremen (Jørgensen 1994). Apart from glass-based microelectrodes for measuring oxygen (Glud et al., 1998), and hydrogen sulfide (Kühl et al., 1999) there are light meters with fiberoptic microprobes (optodes), by which the delay time of material-specific pigments of dissolved substances such as oxygen, nitrate, nitrite, and ammonia can be analyzed on a microscale, e.g., at the sediment-water interface (Kühl et al., 1997).

In a practical example, oxygen profiles have been studied in a cross section of 170-mm width and 40-mm depth using microelectrodes with a built-in reference electrode (Ziebis et al., 1996). A 10-mm-high sediment mound in the middle was exposed to a flow velocity of 10 cm/s. In the upstream part of the mound, oxygen was pushed approximately 30 mm into the sediment. In the downstream, where the flushing effect was less intensive, oxygen still reached down to a 17-mm sediment depth. In the low-pressure area on top of the mound, anoxic porewater from deeper layers was transported upward. Consequently, extremely shallow oxygen penetration was measured at the downstream edge. When oxygenated water was forced into the sediment, ammonium-rich porewater ascended from deeper sediment layers. By this process, an anoxic channel was created by which dissolved iron(II) and manganese(II) could reach the surface (Huettel et al., 1998).

Role of Biofilms in Sediments and on Suspended Particulate Matter. Riverine flocs have a complex composition and may be dynamic in both structure and function due to manifold interactive processes that operate between the various physical, chemical, and biological factors. Most flocculated natural aquatic sediments commonly have a living and active biological component in conjunction with inorganic and nonliving biological particles. Flocculation alters the hydrodynamic properties of particles; therefore, it influences

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the fate and effect of sediment-associated contaminants. In a review of these processes, Droppo et al. (1997) suggest that fibrils consisting of extracellular polymers are the dominant agent for both the development and stabilization of flocculated materials. This does not exclude electrochemical flocculation completely, but rather, it appears to be less significant than the biological flocculation in natural systems.

Biofilms are very diverse, and one of their characteristics is their heterogeneity. They consist of various microorganisms and develop on various surfaces and under various conditions (Characklis, 1990). In many cases under natural conditions, mineral surfaces are at least partially covered by a biofilm. Dissolved substances thus will sorb first on this biofilm before they reach the original mineral surface. The sorption properties of the insulating layer therefore are of importance for the dissolved and the sorbed state of pollutants (Flemming et al., 1995). Active binding occurs through the excretion of binding, chelating, or precipitation cell products in response to the presence of the dissolved substance. In addition, active transport systems may allow the uptake of metal ions, for example, into the cytoplasm. Metal binding by bacterial surfaces is considered largely a passive phenomenon within the process of electrostatic interaction between cationic metals and anionic cell surface groups.

Biofilm cells are dynamic and respond to environmental conditions by excreting larger quantities and possibly also different extracelular polymer substances (EPSs). Varying milieu conditions may effect a partial breakoff of biofilms, and thus they can induce an additional mobilization effect of pollutants. This has been confirmed by Schmitt et al. (1992) using Fourier transform infrared spectroscopy (FTIR) with an internal reflection element (IRE) for the monitoring of biofilm formation in a flow cell experiment. In the presence of 5 ppm toluene, compared with a toluene-free assay, increases in the absorption bands of carbon-oxygen-carbon or carbon-oxygen-phosphorous in polysaccharidic molecules were attributed to increased EPS production as a stress response to toluene.

Colloids in River Water and Sediments: Physicochemical Characterization

In the transport of pollutants in surface, subsurface, and porewater of soils and sediments, the colloidal phase, often defined as particles between 0.001 and 1 μm, can play a major role due to the high specific surface area and high mobility (Buffle and Leppard, 1995). From the available information, it appears that submicron particles in oxygenated waters of rivers are mainly made of organic matter (e.g., fulvics, humics, polysaccharides, proteins), silica, iron oxyhydroxides, and possibly small clay particles and that while representing only a small fraction ($<$10 percent) of the total particle mass, their number increases with the decreasing particle size (Buffle and Van Leeuwen, 1992).

A sampling, fractionation, and analysis scheme has been developed and applied for the characterization of submicron particles in the Rhine River near Basle (Switzerland) by Perret et al. (1994). The scheme includes sedimentation, centrifugation, and filtration as fractionation methods and photon correlation spectroscopy (PCS), microelectrophoresis (ME), transmission electron microscopy (TEM), light scattering (LS), inductive-coupled plasma atomic emission spectroscopy (ICP-AES), and total organic carbon (TOC) as analytical techniques. Colloid characterization using flow-field fractionation (FFF) followed by multidetection analysis [UV/VIS, fluorescence, multiangle laser light scattering (MALLS)] has been used by von der Kammer and Förstner (1997) to study changes in redox potential on the constitution of colloid samples.

The results of a comparison of field data with classic coagulation/sedimentation model predictions indicated that the colloidal particle size distribution in the Rhine River—according to the scheme of Perret et al. (1994)—was maintained in a relatively steady-state condition by gravitational sedimentation of particles larger than 3 to 5 μm and by brownian coagulation and association of particles smaller than approximately 100 nm with organic

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matrices (Newman et al., 1994). The size distributions observed did not vary greatly with time or flow rate. Simulation of an initially tridisperse system containing uniform concentrations of 10-nm, 200-nm, and 4-μm particles indicates that small particles disappear rapidly, whereas a stable peak appears at 100 to 300 nm. Although particles smaller than 200 nm made up less than 2 percent of the total particle mass in the Rhine River samples, they contribute significantly to the available colloidal surface area and thus to the fate of both organic and inorganic pollutants (Newman et al., 1994).

Pollutant Transfer Processes: Experiments Related to Resuspension Effects

Acidity, as suggested by Stigliani (1991), is the most important driving force in chemical time bomb effects. In river sediments, acidity can be produced from the process split of sulfate (Van Breemen, 1987): During organic degradation, iron sulfide and calcium bicarbonate are formed. The latter is removed with running water. The (solid) acid-producing potential can come to action during resuspension and oxidation. With each cycle of deposition and erosion, a certain proportion of buffer capacity in the sediment is consumed. In certain cases, when no more buffer—mainly calcium carbonate—is available, a breakthrough of acidity and heavy metals can be expected.

A compilation of the factors controlling mobility of cadmium has been presented by Peiffer (1997) for the case of a well-buffered neutral sediment. Cadmium is relatively mobile and is affected by exchange processes with calcium. Addition of oxygen leads to oxidation of sulfides, ammonia, and organic matter. Acidity in the form of carbonic acid and protons is consumed within the system by dissolution of calcium carbonate and exchange of released Ca^{2+} and protons, respectively, with matrix-bound Cd^{2+}. Further input of protons is provided from oxidation of Fe(II); Fe(III) mediates further oxidation of iron sulfides. It is important to note that the exchange by calcium (or magnesium) is the major mechanism for the release of cadmium into the water phase in such buffered systems.

Resuspension experiments at defined shear stress and related parameters have been undertaken using the erosion chamber device (microcosm) described earlier in this chapter (Gust, 1991). Figure 16.4 presents results on the release of cadmium and zinc from a poorly buffered harbor sediment from the Elbe River at Hamburg during an erosion period of more than 1000 hours. There is a significant difference in the metal release at later stages—after approximately 500 hours—between the condition with no bottom sediment and a situation where the bottom of the chamber is still covered by sediment. In the latter situation, which can be explained by an ongoing supply of buffer capacity, there is practically no pH change and no metal release from the resuspended sediment.

At this stage, the cause of the delayed pH change and metal release is not resolved. The principal observation of such effects goes back as far as the mid-1980s. Interferences with microbial activity (Prause et al., 1985) seem to provide more probable explanations than inorganic complexation Förstner, 1984; Salomons et al., 1987). Detailed analysis of the sequence of processes leading to the nonlinear release of metals from sediments will be in the center of a subproject entitled, "Prognosis of Pollutant Transfer in Sediments and Suspended Matter," in the framework of coordinated research projects outlined in Fig. 16.3.

DEVELOPMENT AND VALIDATION OF MODELS

Analytical and numerical models are indispensable both for connecting and integrating the interdisciplinary study of individual processes and for transferring the findings from laboratory experiments to a natural aquatic system where processes take place on extremely

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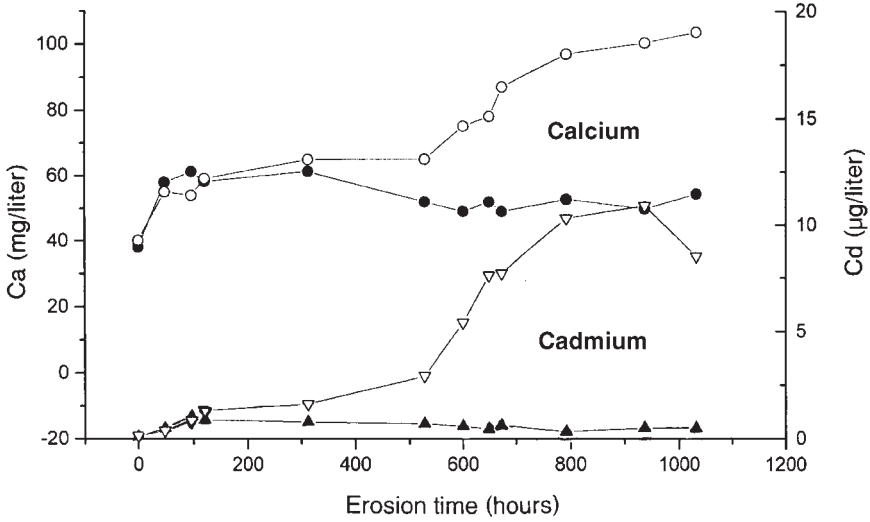

FIGURE 16.4 Mobilization of Cd and Zn in resuspension experiments with poorly buffered harbor sediment from the Elbe River at Hamburg. Open signature: with no bottom sediment. Full signature: with bottom sediment (Fengler et al., 1999).

variable scales in both space and time. For process description, numerical models using different concepts can be applied:

- Transport and reaction modeling considers advective, dispersive, and diffusive transport mechanisms as well as adsorption and desorption processes (e.g., CoTReM) (Landenberger, 1998).
- Hydrodynamic (Johnson and Tezduyar, 1997; Boivin et al., 1998; Ling et al., 1998), statistical (Lick et al., 1992), and/or stochastic (Hesse and Tory, 1996) models operating on the particle level are best suited for the study of fine-scale aggregation/segregation processes and in addition may include biological and chemical processes.
- Continuum mechanical field models (Malcharek, 1995) as well as particle-tracking models (Wollschläger, 1996) are particularly efficient at locally concentrated emissions and for conducting long-term simulations.
- Macroscalic long-term simulation due to limited computer capacities so far can only be performed using simplified model approaches.

Available material transport models are still restricted mainly to the description of transport and dispersion processes of suspended sediments as well as of dissolved and particulate substances. The hydrodynamic interactions between turbulent flow and suspended and bottom sediments, as well as the biogeochemical interaction between particles and pollutants—in particular in the near-bottom layer—are as yet rarely studied and (numerically) modeled. In the project entitled "Particle Interactions in Harbor Basins," high-resolution microscalic models will be developed for near-bottom areas including three-dimensional fluid movements with density gradients, high particle concentrations, and aggregating fine particles. These data will form the basis for evaluating the direct pollutant transfer between different solid matter fractions.

Determinations of bonding parameters in heterogeneous systems principally are affected by many uncertainty factors that are caused by sorptions sites of variable affinity on the adsorbens or by the solubility of amorphous solid phases. In particular, for describing the

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transport of inorganic and organic substances, high priority has to be given to the effects of competing adsorption and replacement desorption; here, the influences of dissolved organic matter (DOM) on sorption processes have not as yet been considered adequately. A possible tool for future prognoses in the three-component system sediment–DOM–hydrophobic organic substance (HOS) could be developed from the thermodynamic theory of the "ideally adsorbed solution (IAS theory) (Hess et al., 1997), and a project is planned in the framework of this interdisciplinary program. Investigations on sorption kinetics will include both the simulation of natural conditions using different reactor types and the experimental analysis of concentration-time curves and loading-time curves for different solid phases (model and natural sediments) and model adsorptives (HOS, DOM).

The calculation of equilibrium speciation in aqueous systems using computer programs such as MINEQL (Westall et al., 1976) or PHREEQC (Parkhurst, and Appelo, 1999) requires exact knowledge of the formation constants of all species under consideration, as well as the total masses of some selected components, which are derived from chemical analyses. Imprecision may arise from uncertainties in experimental parameter determination as well as from inconsistencies in the available data in the literature, sometimes differing by orders of magnitude. These effects are particularly strong in heterogeneous systems such as sediment and suspended matter. Schulz et al. (1999) have presented a method based on fuzzy-set theory to incorporate imprecise thermodynamic parameters into chemical equilibrium calculations of aqueous systems. An application of the proposed method to a cadmium-sulfide system demonstrates the acquisition of membership functions, which are derived from the concept of intervals of confidence with different levels of presumption using four scenarios. In the planned subproject, the fuzzy-logic approach will be incorporated in the numical transport model combining hydrodynamic resuspension data with the distribution coefficients for critical chemicals.

In the final step of the project, the major findings will be interconnected by integrating models. At this stage, the number, type, and structure of these models are still open. On the one hand, they should be complex enough to include as much information as possible; on the other hand, they should be applicable for practical uses.

In the conclusion of his dissertation (1997), Ulrich Kern from the Institute of Hydrology at the University of Stuttgart indicated in a general way how future achievements from chemical and biological research could be implemented in integrated models (Table 16.4). These

TABLE 16.4 Development of Models Coupling Hydrodynamic and Biogeochemical Data for the Prediction of Pollutant Transport in Rivers

Numerical description	Components in water body	Solute-solid interaction	Formulation of transport equation
Distribution coefficient (K_d concept)	Dissolved + particulate	K_d = constant	Two coupled linear differential equations
Extended K_d concept	Dissolved + particulate + milieu factors	$K_d = f$(pH, pE, complexing agents, competing ions)	Additional n linear differential equations for milieu factors
Chemical multi-component model	Chemical individual species	Dissociation and binding constants, solubility products	Coupled differential-algebraic equation system
Biochemical multi-component model	Chemical species + biota	Additional growth and decay rates	Differential-algebraic equation system

Source: After Kern (1997).

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models for predicting pollutant transport in rivers are dominated by hydromechanical parameters; inclusion of chemical terms mainly means constant distribution coefficients. A first step for extending these models could involve consideration of typical ecosystem factors such as competing ions, complexing agents, redox conditions, and—dominantly for metals—pH values. The next tier of sophistication would be the inclusion of binding constants, solubility products, and other factors that can describe solid-solution interactions of critical chemicals in a multicomponent system. The last step, which can be seen so far, would extend the mechanical-chemical model into biology. Such biochemical multicomponent models should at least consider rates of growth and decay of organisms and organic matter.

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CHAPTER 17
SEDIMENT AND SOIL QUALITY CRITERIA

Wolfgang Ahlf, Thomas Braunbeck, Susanne Heise, and Henner Hollert

INTRODUCTION

Compared with water and air, soil and sediments are immobile and spatially heterogeneous components of ecosystems. Although the constituents vary tremendously in their physical and chemical characteristics, they have a great capacity to retain contaminants, especially those with apolar molecules or positively charged ions. Consequently, concentrations of pollutants often are considerably higher than in any other environmental compartment. In the last three decades, it has been shown that many pollutants found in soils and sediments may persist in part in the solid material, whereas the pollutant pool is not totally inert to organisms. Adverse effects of contaminants are discussed commonly in terms of their implications for ecosystems or human health.

The analytical capabilities for documenting the presence of contaminants are well developed. In general, a protection of ecosystems needs quality criteria to reduce the adverse impacts of chemicals that consider the degree of exposure and risk from individual compounds. However, the critical question is how to determine if organisms are adversely affected and how to provide information on the exposure to pollutants. The underlying issue is one of bioavailability, which is a dynamic result composed of complex physical, chemical, and biological interactions. Sediment and soil quality assessments are considerably more complex than water quality assessment due to the many site-specific parameters that need to be considered that are not a factor for water. In the United States, large data sets have been provided to test proposed relationships between sediment chemistry and toxicity. The conclusion was that no chemical measurement reliably predicts sediment toxicity (O'Connor and Paul, 2000). Two main limitations to chemical predictors are obvious. An increasing number of new substances is released to the environment every year and adds up to an amount impossible to monitor on a routine basis, even if appropriate methods existed for their analyses. In addition, chemical contaminants in sediments rarely occur as single substances but instead are found as diverse mixtures. So far only one variation on the Soil Quality Criteria (SQC) for Poly Aromatic Hydrocarbos (PAH) compounds exists that adds up fractional toxicity attributable to each individual PAH (Swartz et al., 1995).

Therefore, a comprehensive sediment assessment approach includes (Krantzberg et al., 2000) (1) benthic community structure, (2) laboratory bioassays for evaluating the toxicity of in-place pollutants, (3) bioaccumulation and biomagnification information, (4) knowledge of site stability, and (5) physicochemical sediment properties. It is well known that

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ecosystems and their interactions with stresses are complex. If we reflect this complexity with data from all the assessment approaches just mentioned, we need an appropriate method for a reliable evaluation. Burton (2001) proposed a weight-of-evidence approach in which possible conclusions could be derived by interpreting typical response patterns.

We agree that multiple end points are necessary to assess sediment and soil quality effectively. However, since the basic question is whether biological impairment exists, why not measure this and develop biologically based quality criteria? We think that understanding the bioavailability of pollutants is the key issue for assessing soil and sediment quality. The goal is to provide a scientific basis for the development of regulatory schemes for sediment and soil management that implies biological hazard but avoids overestimation of ecological risks.

Bioavailabilty of Solid-Associated Contaminants

To environmental scientists, *bioavailability* represents the accessibility of a chemical for binding to organism surfaces. To toxicologists, the term represents the availability for crossing a cell membrane and entering a cell. Of course, to ecotoxicologists, toxic effects and bioaccumulation establish bioavailable pollutants. Although the same geochemical processes cause an accumulation of pollutants on solid surfaces in soil and sediments, the assumption of the ecologically relevant proportion of contaminants is different for soil and sediments found in scientific literature. The transfer of sediment-associated contaminants to biota often was restricted to solubility or uptake with food. However, evidence of bioavailable fractions from particle associated contaminants were demonstrated for different organisms (e.g., Harkey et al., 1994; Liss and Ahlf, 1997). Recently, geochemical influences on assimilation of sediment-bound metals have been evaluated by Griscom et al. (2000) in a series of experiments using the suspension-feeding mussel *Mytilus edulis* and the facultative deposit feeder *Macoma balthica.* The results imply that metals associated with sulfides and anoxic sediments are bioavailable. These findings qualify the supposed dominant role of the sediment sulfides in controlling metal availability.

The unequal spatial distribution of microorganisms and pollutants, in combination with physically retarded substrate diffusion, nowadays is generally accepted as the key limiting factor for efficient biodegradation of hydrophobic contaminants (Wick et al., 2001). This means that most of the particle-associated contaminants are potentially available. In the last decade it has been shown increasingly that the formation of nonextractable residues may contribute to less bioavailability. Initial findings from soil studies indicated that as the residence time of compounds such as phenanthrene and 4-nitrophenol in soil increases, they become increasingly unavailable to microorganisms and resistant to mild extraction (Hatzinger and Alexander, 1995). Subsequently, chemical extraction procedures were developed to predict bioavailability of soil-aged organic chemicals (Kelsey et al., 1997; Tang et al., 1999), and the role of nanoporosity and hydrophobicity in sequestration and bioavailability of typical organic contaminants has been studied with model solids (Nam and Alexander, 1998). The conclusions are that "correlations are needed to assess the role and contribution of organic matter, clay content, nanoporosity, surface area, or other soil properties in governing the rate and extent of decline in bioavailability so that predictions of diminished exposure will be possible" (Chung and Alexander, 1998).

Bioavailability is a complex result of contaminant-particle interaction and can be superimposed on the activity of organisms. In addition, bioavailability is also organism-specific, for that reason it is unlikely that chemists could develop chemical extraction methods that imitate an all-encompassing bioavailability. From biodegradation studies it is observable that bacterial features may enhance the transfer of poorly bioavailable substrates (Wick et al., 2001)

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- By reducing the mean distances between pollutants and bacteria, e.g., by adhesion to sorbents
- By causing active transfer of the pollutant into the aqueous phase
- By using uptake systems with high specific affinity

Thus the application of microorganisms as test organisms in bioassays could be an advantage to assess the biological impacts of solid-associated contaminants.

Biological Assessment Methods

Biological testing and characterization of contaminated soils and sediments are major components of environmental quality assessment. Most frequently this testing is confined to acute and chronic laboratory bioassay protocols. Excellent reviews for sediment testing describe methods, strategies, and open questions (Burton and MacPherson, 1995; Chapman, 1995; Chapman and Wang, 2001). The weaknesses of toxicity testing are as follows:

- The causes of measured effects are not clear.
- No general agreement exists on test species for soils and sediments.
- The ecological relevance of the responses under standard conditions should be confirmed *in situ*.
- Chronic tests are required, but they are time-consuming and expensive.

Benthic bioassessment, which relies on description of infaunal communities to evaluate contaminated sediments, has received increasing acceptance in both the scientific and regulatory communities. The bottom approach to link toxicity testing and analysis of benthic structures was described by Reynoldson and Zarull (1989). However, keeping in mind the idea to create the same biological assessment framework for soil as well as for sediments, the evaluation of communities in soil and sediments is not pragmatic because of the different biocenosis structures. The question that must be answered is, How can we offset the weaknesses of toxicity testing?

Another attempt to measure directly the biological effects of contaminants *in situ* is the so-called biomarker approach, where early-warning molecular and physiological responses of organisms to pollutant exposure are determined (Fig. 17.1). New techniques allow one to detect the effects of complex mixtures of contaminants, and many are diagnostic of causes, provide information on the bioavailability of contaminants, and allow more accurate assessments to be made of potential ecological damage. Cellular and molecular indicators provide the greatest potential for identifying individuals and populations for which conditions have exceeded compensatory mechanisms and which are experiencing chronic stress, which, if unmitigated, may progress to severe effects at the ecosystem level.

Biomarkers selected for environmental monitoring should be (1) generic in the sense that they measure fundamental cellular, biochemical, and physiological processes common to most organisms occupying a diverse range of ecosystems and (2) pragmatic, inexpensive, and easy to use. Two examples of biomarkers as indicators of effects and another two biomarkers as indicators of exposure to a human-made stressor will illustrate the contribution to ecotoxicological assessments.

1. *Glutathione metabolism.* The family of glutatione-*S*-transferases often plays an important role in conjugating different xenobiotics to facilitate excretion processes. Glutathione also has the very important role of keeping the cell environment in an oxi-

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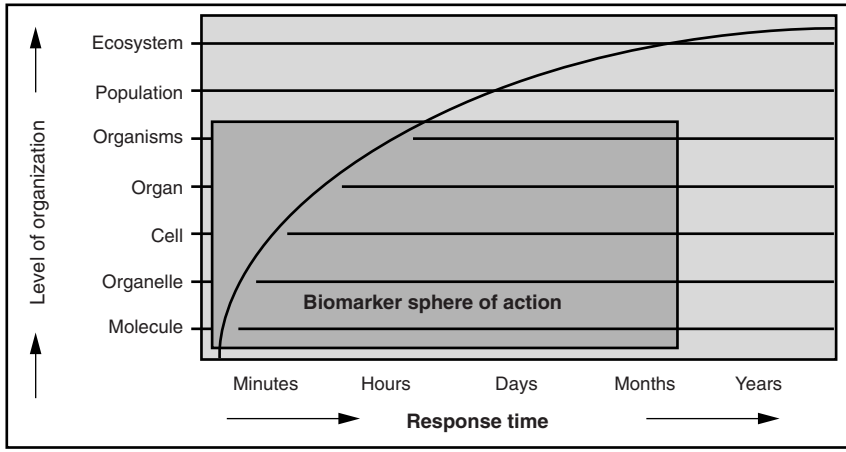

FIGURE 17.1 Relationship between grade of biologic organization and response time. (Redrawn from Brauenbeak (1998)

dized state. Therefore, in situations where the cell is exposed to oxidants of environmental pollutant origin, an increase in glutatione-reductase could be analyzed. The purpose of this induction is to protect the cell from different kinds of oxidative damage. Glutathione reductase activity can be measured, according to Carlberg and Mannervik (1975).

2. *Comet assay.* The comet assay is based on the differential electrophoretic migration of DNA fragments resulting from strand breaks induced by chemical interaction with DNA (Fairbairn et al., 1995). The greater the damage to DNA, the greater is the amount of DNA that migrates into the so-called comet during electrophoresis. The comet assay can be applied to both cells isolated from exposed test organisms and cell cultures exposed to chemicals in vitro. That it is sensitive, rapid, and inexpensive makes it particularly suitable for routine testing of chemical genotoxicity.

3. *EROD activity.* The cytochrome P450–dependent monooxygenase isoenzyme CYP1A plays an important role in biotransformation of carcinogenic aromatic compounds. The induction of CYP1A monooxygenase is one of the best characterized biomarkers of exposure to PAHs and halogenated aromatic compounds. CYP1A activity is measured most conveniently as 7-etoxyresorufin-*O*-deethylase (EROD) activity (e.g., Engwall et al., 1996; Hollert et al, 2002).

4. *Endocrine disruption.* Endocrine disrupters are chemicals that affect human or animal health by interfering with normal hormonal processes. They are mediated by hormone receptors and so could produce toxic effects at very low doses. To identify chemicals that affect normal estrogen regulation, assays with recombinant MCF7 live cells or yeast cells are standard procedures. (Hilschesova et al, 2000; Solo etal, 1995). The detection of an estrogen receptor in two nematode species challenges the development of an assay with soil and sediment organisms (Hood et al., 2000).

Biomarker results indicate classes of pollutants that have affected organisms. Toxicity identification evaluations (TIEs) are used to diagnose the source of toxicity in complex contaminant mixtures that occur commonly in polluted soil and sediments. TIE procedures use experimental manipulations to selectively alter the concentration and/or bioavailability of contaminants in complex mixtures and quantify resulting changes in toxicity using standardized bioassays.

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TIEs characterize and ultimately identify substances responsible for toxicity in an environmental sample. The relative responses of the laboratory organisms to variously treated aliquots of sample describe the characteristics of the toxicant, thereby providing direct, irrefutable evidence of the toxicant's identity. Where definitive toxicant identification necessitates further isolation of the toxicant from other sample constituents, toxicity tests are used to identify the fraction in which the toxicant is contained (bioassay-directed analysis). If the toxic effect to the test organisms is caused by combined pollutants, it may be difficult to identify the origin of the sediment toxicity because of the different solution behaviors of the toxicants.

TIE methods for investigating aqueous samples, including sediment porewaters, rely on manipulations such as affinity chromatography (nonpolar organics), cation exchange (metals), and pH adjustment (ammonia) and are not easily applicable to studies with whole sediments. The success of the TIEs relies on a number of factors such as the relative sensitivity of different species to toxicants, technical proficiency in manipulating the sample and maintaining appropriate exposure conditions, and the skill of the researcher in interpreting the data.

Recent efforts to develop TIE methods for freshwater sediments have focused on the use of specific sorbents or reagents to selectively reduce the bioavailability of sediment contaminants.

It is well known that bioremediation can seriously reduce the bioavailability and consequently ecotoxicity demonstrated by bioassays. There is now an obvious way to combine detoxification of sediments and the development of a scheme for whole soil and sediment TIEs. The first phase is to treat contaminated sediments with resins to reduce the contaminants to nontoxic levels (Kosian et al., 1999). The resins then could be analyzed chemically to identify the pollutants affecting the organisms. If the mixture of contaminants is too large, a second phase of toxicity characterization is to selectively remove from the sediment typical classes of contaminants (Lebo et al., 1999). The advantage of using resins is that then, through toxicity testing of the whole treated sediment, a direct or indirect determination can be made as to which contaminant class is causing the toxicity. The goal of the development is to leave the presence and bioavailabilities of contaminants not within the extracted class largely unaffected. The interpretation could be confirmed if critical body burdens (CBRs) associated with acute toxicity were determined in the test organisms. The CBR approach avoids confounding factors such as variations in bioavailability and uptake kinetics and also could be employed to assess the relative contribution of specific contaminants or contaminant classes in mixtures to the effects observed in toxicity tests (Fay et al., 2000).

A Minimum Suite of Bioassays for the Assessment of Soils and Sediments

Characterizing environmentally acceptable end points for soils and sediments requires an understanding of the impact of chemicals on the compartments and the subsequent effects on the ecosystem. Protecting biodiversity and maintaining a robust ecosystem over time also will require attention to subtle degrees of impact that fall within the limits of the natural variability observed in inherent communities. As Fenchel (1992) pointed out for studies in ecology, it holds true even in ecotoxicology that complex ecosystems can be scaled down if one is looking at microorganisms. We know that chronic exposure to contaminants can alter soil microbial communities dramatically (Fuller and Manning, 1998). Bacteria can serve as indicators of environmental pollution, where the indicators are based on measurements of microbial populations and their activity. However, it is often difficult to distinguish between natural fluctuations in microbial populations and activity and those due to toxicant input. Thus we link effects on indigenous microorganisms with effects measured in bioassays. It is important to note that the responses of test organisms vary in their sensitivity to single compounds. Thus a battery of bioassays typically is used for the detection of potential adverse effects of complex mixtures of contaminants (Keddy et al., 1995). In

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addition, we have to consider the specific properties of the pollutant in question. Is it mobile, in a geochemical sense, because of aqueous solubility or volatility, or is it associated with solid phases? These different exposure routes require a selection of suitable test organisms. Based on further considerations related to bioassay application, it is obvious that rapid, inexpensive methods are needed. We have developed assays that, with consideration of biological test methods using plants and animals, meet many of these requirements and favor microbial test organisms (Rönnpagel et al., 1995; Traunspurger et al., 1997).

Ecotoxicological testing should be conducted on an appropriate, limited battery of species, end points, and exposure routes. If this is done carefully and the results are interpreted as an integrative assessment, there is a clear opportunity to prioritize areas of most concern. In a conceptual soil toxicity exposure model, organisms from different trophic levels can be exposed to toxicants in either of two ways: directly from solid-bound contaminants or via the soil interstitial water. Elutriates often are used as a surrogate for soil interstitial water to assess groundwater hazard. The elutriate test was developed as a leaching procedure primarily to determine the mobility of contaminants subject to release when solid waste was in contact with water. The use of elutriates as toxicant solutions has facilitated the testing of standard bioassay organisms, such as *Scenedesmus subtilis* and *Vibrio fisheri.* In some cases, the extent and severity of environmental contamination were determined adequately with elutriate tests at hazardous waste sites (Miller et al., 1985). However, elutriates (water extracts) enable detection of a part of multiple contamination due to the different solubilities of each contaminant in water. Water elutriation could underestimate the types and concentrations of bioavailable organic contaminants present (Liss and Ahlf, 1997).

An additional approach is to use organisms that have contact with the contaminated solids. It is recommended that within a set of screening tests, soil-living organisms should be preferred (Keddy et al., 1995). At present, toxicological testing is conducted routinely at the individual organism level. Three organism-level measurements are required to provide information on the stability of populations and higher levels of organization: survival, growth, and reproduction (Chapman, 1991). If an organism can fulfill all these integrative functions, then it is not being adversely affected. Many experiments have been conducted to evaluate the toxicity of chemicals to earthworms and to identify the pollutants that may adversely affect the growth and reproduction of this valuable species in the soil ecosystem. The 14-day earthworm survival test is used commonly as an end point. The earthworm reproduction test using *Eisenia foetida* proved to be an appropriate replacement for the earthworm survival test. The test duration must be extended to 3 to 5 weeks. These test procedures are time-consuming and expensive and therefore not well suited for screening contaminated sites. Consequently, short-term tests are needed to measure biological end points characteristic of chronic effects associated with soil contamination. Nematodes are the most abundant and species-rich organisms of the metazoa in soil. Traunspurger et al. (1997) presented a life-cycle-test using soil medium; it needs to run for only 72 hours. The nematode *Caenorhabditis elegans* has been used in tests for contaminants in the liquid phase and in whole-soil samples. The development of first-stage larval worms to the reproductive stage, the number of eggs per adult, and the number of offsprings per worm are useful parameters for the ecotoxicological interpretation of test data.

Ideally, soil toxicity to bacteria should be examined using a representative soil bacterium and conducted in the soil. A contact bioassay using *Bacillus subtilis* or *Arthrobacter globiformis* has been developed using the inhibition of dehydrogenase enzyme activity as an end point (Rönnpagel et al., 1995). An advantage is the exposure time of 2 hours in comparison with the short generation times of the bacteria, which allows toxic effects to be expressed on growing cells for approximately two generations.

In situ alterations occur in the resident microbial community in relation to different

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kinds of stress. Methods of microbial ecology designed to detect changes in soil communities should be incorporated in a comprehensive survey. Methods such as fatty acid analysis, carbon substrate utilization and genomic analysis show considerable promise to improve the speed and precision of soil microbial toxicity tests. At present, a combination of bioassays and a description of the microflora using enzyme activities should be worthwhile for interpretation of the measured effects.

The applied biotest battery includes up to five bioassays:

1. Algae growth inhibition test with *Pseudokirchneriella subcapitata* according to DIN 38412 (part 33) with elutriates
2. Luminescence inhibition test with *Vibrio fisheri* (DIN 38412, part 34) with elutriate
3. Luminescence inhibition test with *Vibrio fisheri* (DIN 38412, part 34) with methanol extract (Kwan and Dutka, 1990)
4. Sediment contact test with *Bacillus cereus* (DIN 38412, part 48; Rönnpagel et al., 1995)
5. Sediment contact assay with the nematode *Caenorhabditis elegans* (Traunspurger et al., 1997) (DIN, Deutsche Industrie Norm = German Industry Standard)

This biotest combination consists of low structured organisms in order to measure toxic effects directly without the obstruction of a complex system. Bioassays examine the reaction of test organisms or biochemical systems after exposure to contaminants. A toxic effect on basic physiological functions such as photosynthesis, respiration, and reproduction most certainly would indicate adverse effects on other organisms in the natural environment. Because bioavailability depends on the sediment type, direct contact tests are an important part of the biotest combination. The results of the two elutriate tests (algae and bacteria) indicate water-soluble contaminants, and bacterial testing of methanol extracts points mainly to lipophilic, strongly adsorbed substances from particles. This is sometimes referred to as *potential toxicity,* because low inhibition in the methanol extract usually indicates low sediment contamination.

Autochthonous bacterial activity in the respective samples also can be measured directly and thus complements the information gained by bioassays with data about effects of long-term impacts of pollutants and a possibly sustained inhibition. In addition, a simple investigation of microbial activity completed the suite of biological assays:

1. Respiration, measured as CO_2
2. Fluorescein diacetate (FDA) breakdown as a measurement of hydrolase activity (Liss and Ahlf, 1997)
3. Dimethylsulfoxide (DMSO) reduction, which is the only method we used in sediments to characterize microbial activity

Because redox conditions in sediments are often very low, measurement of DMSO reduction was chosen as indicator of bacterial activity. DMSO is reduced by enzymes of the electron transport chain under oxic as well under anoxic conditions to dimethylsulfide, although anaerobical reduction rates are higher (Ahlf and Gratzer, 1999). Thus only sediments of a similar redox potential can be compared. However, due to its experimental duration and high sensitivity, this method is easily included in the sediment testing procedure and provides unique information about effects on the biocenosis.

Application of the Bioassay Set to a Contaminated Soil. The bioassays were applied to a soil sample from a 30-year-old petroleum-contaminated site, where 2.7 percent (w/w) mineral oil was detected. Figure 17.2 shows only a part of the ecotoxicological responses

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investigated (Neumann-Hensel et al., 1999). The solid-phase bioassay demonstrates that the sample from a contaminated site is more toxic than new lubricant in soil, where the concentrations are comparable (Ahlf et al., 2001). The result of the algal growth inhibition test suggested that by-products of the degradation or other unknown chemicals increase the toxicity of the water-soluble fraction. Enzyme activity of the microflora was measurable but on a low level. Thus the toxicity data must be seen as supplementary to enzyme activity, indicating in this case a depressed biological degradation.

A tiered examination with the described tests is recommended for evaluation of contaminated sites (Neuman-Hensel et al., 1999). The approach begins with a set of bioassays that help to identify what is important to protect and the impact on the important groundwater pathway. If these tests indicate no meaningful interpretation, investigations of the second or third level are required. In this case, several biological assessment tools are recommended to test soil toxicity on soil microflora, soil animals, and plants. Furthermore, the method describes how information can be interpreted for a hazard assessment or for a bioremedial decision.

Application of the Bioassay Set to Contaminated Sediments. In the years 1995, 1996, and 1997, three surveys were performed. Fifty-one sediment samples were collected from the River Elbe and 14 sediment samples from the River Rhine, respectively. The assessment strategy relied on application of the minimum set of bioassays, completed by assessments of benthic communities, chemical contamination, and geochemical characteristics such as grain size distribution (Ahlf and Gratzer, 1999). The areas chosen for sampling were a transect of 400 km of the River Elbe (about 60 percent from the mouth to the source) and a transect of 150 km within the middle part of the River Rhine, where the river is geochemically similar to the River Elbe. Here we summarize the bioassay results for a comparison of both rivers (Fig. 17.3).

The whiskers around the box demonstrate the range of the sediment toxicity, which is much higher for the samples from the River Elbe due to the larger sampling area and dif-

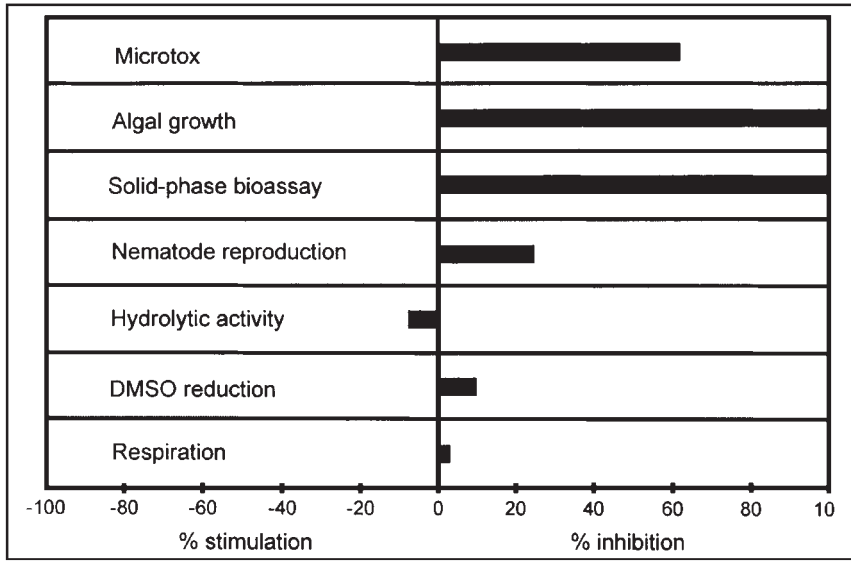

FIGURE 17.2 Effects of a hydrocarbon-contaminated soil in distinct bioassays.

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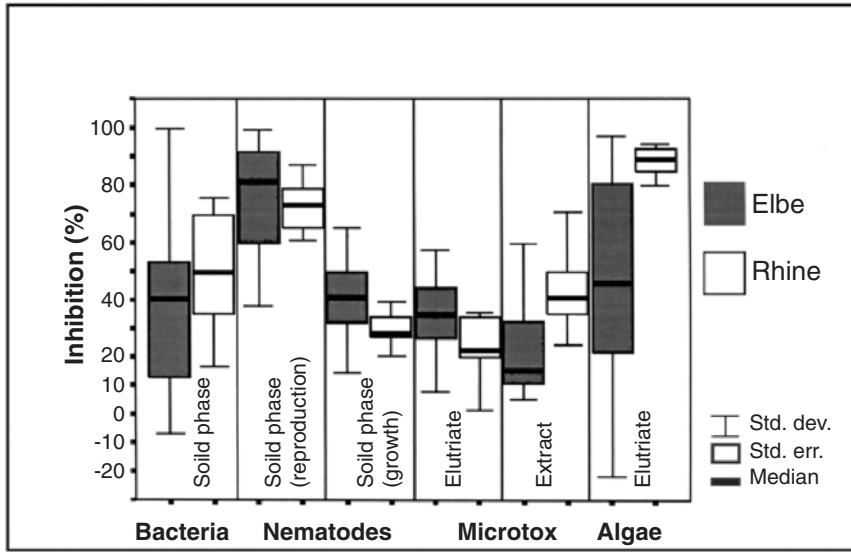

FIGURE 17.3 Box whisker plots of the inhibition measure in five bioassays with direct contact with contaminated sediments or in their elutriates.

ferent seasons. The variability is indicated by the boxes around the central tendency. Only the responses of the microtox test with methanol extract and the algae assay with elutriates show no overlapping between the two rivers. Therefore, it could concluded that both sediment effects are higher in the River Rhine. The most sensitive bioassay was the test with nematodes measuring reproduction. The question arises if we can turn down the less sensitive bioassays for a sediment assessment. The data could assist in the resolution of the issue of whether all bioassays are needed or a minimum set.

Rationale for Evaluation of Biological Data

A growing consensus exists that multiple end points are necessary to assess sediment quality effectively. As mentioned earlier, the use of a suite of toxicity tests is an integral part of sediment quality evaluation studies. Although the essential requirements for the use of such a set of bioassays have been described (Giesy and Hoke, 1989; Giesy et al., 1988), interpretation of the data has found little attention in scientific research. Given the wide range of effect end points and exposure routes, it is hardly surprising that combining toxicity results can be a complicated task. Situations may arise in which both positive and negative responses are measured for the same sediment (see Fig. 17.3). This complexity requires approaches that enhance the information derived from multiple sediment toxicity tests and aid in the decision-making process.

Multivariate analysis differs from the more familiar univariate statistical methods in its ability to analyze complex datasets with multiple responses. A very useful technique is the principle components analysis (PCA) for a dimension reduction to simplify interpretation. PCA is used often where the response of a unit to a gradient can be considered monotonic, such as inhibition due to increasing contamination. Figure 17.4 demonstrats on the basis of three datasets the information content of each bioassay for the interpretation of sediment toxicity.

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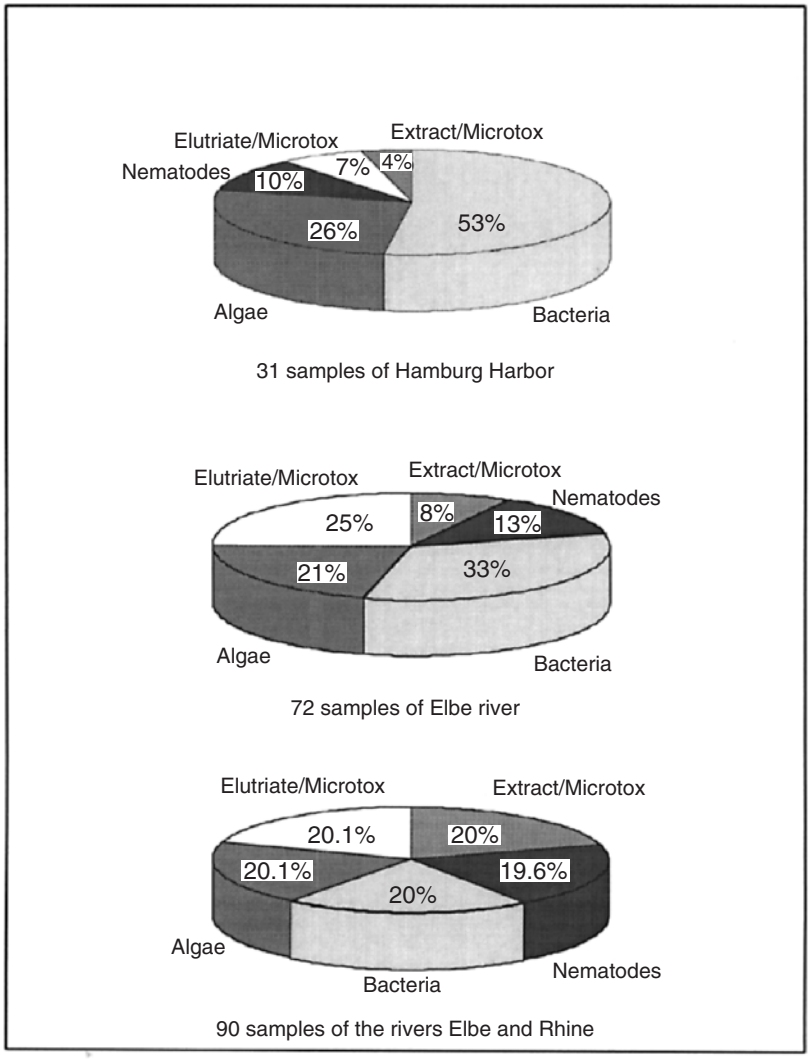

FIGURE 17.4 Principal components analysis of three datasets. Two were obtained from toxicity tests with sediments from the River Elbe; the third was completed with results from River Rhine.

The sediment toxicity of a small area, such as the Hamburg Harbor, could be characterized by only two bioassays without a great loss of information. If we extend the survey in time and space, we need a third bioassay to obtain the same amount of reliability. The combined data, sediments taken along the Rivers Elbe and Rhine, show no measurable redundancy for every one of the five toxicity tests. Thus, each bioassay provided an indispensable part of the overall information for the sediment quality assessment. Moreover, a classification of sediments according to their toxicity needs the five bioassays as a minimum set to be applicable to sediments from different locations of different rivers sampled at different times.

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Biological Quality Criteria for Contaminated Sediments. An integrated assessment that is based on the sediment quality triad (Chapman et al., 1997) in which information is gathered from ecotoxicological, ecological, and chemical methods and processed for decision making is rare. This is due in part to the character of biotests: They are empirical (Förstner, 1990) in the sense that their results have to be revalued with each new test and no absolute scale can be observed easily when a biotest battery is applied. Also, interpretation of results usually demands evaluation by an expert. These problems can be overcome by assessing response patterns rather than absolute toxicities for evaluating toxic effects (Ahlf and Gratzer, 1999). Thus it is possible to identify a general toxicity scale. Five scaled toxicity classes of possible biotest response patterns were identified on the basis of three large-scaled sampling surveys in Germany. This classification was transformed into an expert system using fuzzy logic to account for biotest variability. Actually, this approach has also been applied to develop a site-specific classification system for freshwater sediments (Heise et al., 2000). These classes were described as follows and the description transferred into a fuzzy logic expert scheme:

Class 1. No biotest is above medium toxicity, and the average inhibition is low.

Class 2. Higher extractable toxicity with no or low inhibition in any of the other biotests.

Class 3. High particle-associated toxicity with low or medium toxicity in the elutriate tests.

Class 4. High total inhibition, high elutriate toxicity, and one test shows stimulation.

Class 5. High total inhibition with high toxicity in elutriate testing.

Figure 17.5 shows the application of this classification to exemplary stations in Hamburg Harbor, located in or nearby the main stream, outer region, on the entrance to basins, and in the inner part of the basins. While most sediment cores from 1995 are classified as class 3, the graph shows that the abundance of class 5 in surface sediments strongly increased in 1999. There was only one exception in the western part of the Hamburg Harbor area, where the toxicity decreased.

Integrated Assessment of Contaminated Sediments as a Site-Specific Management Tool. An integrated assessment is based on the sediment quality triad in which information is gathered from ecotoxicological, ecological, and chemical methods (Chapman et al., 1997). Information provided by differential triad responses could be interpreted in a qualitative way and processed for decision making (Chapman et al., 1992). There are management questions where a tiered testing is useful to reduce costs, but the problem of quantitative classifying sediment quality exists also for this approach (Neumann-Hensel et al., 2000). Sediment bioassays are suitable to classify quality with respect to toxic effects in selected test organisms and test systems; however, the tests selected are conducted under laboratory conditions and usually cannot be applied under in situ conditions. Management questions could demand further information. Thus, in order to gain insight into the site-specific state of sediments, integrated approaches are required.

The first step is to broaden the needed information with additional biological investigations. We added two parameters, the sediment toxicity test with *Chironomus riparius* and the demethyl sulfoxide (DMSO) reduction method, to investigate microbial activity of indigenous microflora. Factor analysis has been performed for 14 sediments from the River Rhine in order to test for any improvement in information. Factor analysis is similar to PCA, but can reduce the number of variables and extract factors, which could be interpreted as new variables. The number of factors was determined from the eigenvalues (<1). The four main varimax-rotated factor loadings obtained are represented in Table 17.1, where only relevant loadings over 0.5 are given.

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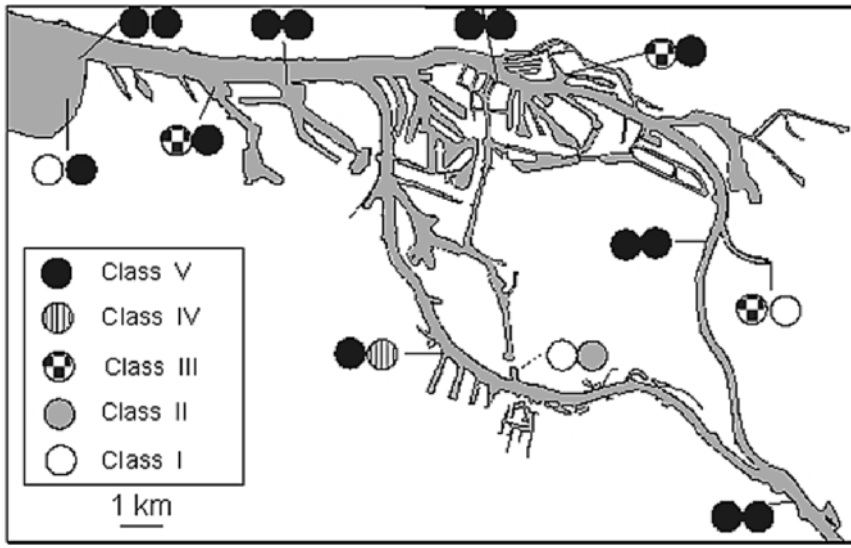

FIGURE 17.5 Toxicity classes in Hamburg Harbor surface sediments, classified according to the site-specific classification scheme, for the years 1997 (*left circles*) and 1999 (*right circles*).

TABLE 17.1 Representation of the Four Main Factor Loadings Resulting from a Factor Analysis (Maximum Likelihood, Varimax Rotation) of Biologic Responses to Rhine Sediments ($n = 14$)

Biotest	Factor 1	Factor 2	Factor 3	Factor 4
Microtox (elutriate)				
Microtox (extract)				0.80
Bacteria (solid phase)	0.97			
Algae			0.93	
Nematodes (growth)		0.75		
Nematodes (reproduction)		0.98		
DMSO reduction				−0.71
Chironomids		−0.64		
Eigenwert	1.27	1.98	1.00	1.19
Information (%)	15.82	24.79	12.44	14.93

In general, the factor analysis confirmed the PCA and demonstrates the consistency of information contribution from the different bioassays, where in this case the microtox test with elutriates is less important. The second factor joins the test end points with invertebrates and indicates that nematode reproduction could replace the toxicological end point chironomide growth. The inhibition of nematode reproduction is inversely correlated with the production of chironomid biomass. Factors 1 and 3 are loaded, with one test demonstrating their importance. Finally, factor 4 brings together the microtox assay and the DMSO reduction, which suggests a relationship that organic pollutants decrease the activity of the indigenous bacteria. We conclude that we got additional information that would

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not necessarily need to be included for a classification because all factors are represented by a part of the minimum set of bioassays.

Integrated Assessment

In order to bridge the gap between ecological, chemical, and biological evaluations, a sediment quality triad (SQT) approach was applied. In small river systems such as the streams of the Neckar River catchment area, there is a marked lack of such studies. Due to the complex hydrological structure and the presence of numerous nonpoint sources, identification and elimination of sources of environmental hazard are most difficult for larger catchment areas. In contrast, in streams shaped by smaller catchment areas, there is usually a higher probability of correct predicting and improving of contamination. Thus, a study was designed to apply an SQT to investigate 12 aquatic sites in streams within the catchment area of the Neckar River with regard to their ecotoxicological burden (see details in Hollert et al., 2001). In contrast with Chapman's original triad approach, not only sediments, but also surface waters were examined. In brief, to obtain a comprehensive insight into the potential ecotoxicological hazard, both acute toxicity and more specific effects such as mutagenic, genotoxic, teratogenic, and dioxin- and estrogen-like responses were recorded. Redox potential and *in situ* pH, absorbable organic halogen (AOW), total organic carbon (TOC), as well as the particle size of the sediments, were determined. Chemical analyses were performed for heavy metals, PAHs, and selected endocrine-disrupting substances. Benthic macroinvertebrate diversity and abundances were assessed using family- and species-based bioindices [e.g., saprobic index and ecotoxicological index according to Carmargo (1990)].

Ranking-Based Classification of SQT Sites. First a survey is presented of the quality classes of a fish-spawning site at Eberbach (two sites) as determined by means of ranking the results (Fig. 17.6). The ranking procedure was carried out according to Canfield et al. (1994). Data for each individual variable of all stations were scaled proportionally between 1 and 100 percent (e.g., the value 1 representing the lowest and 100 the highest effect or concentration measured). Scaling data preserves the relative magnitude of differences between measurements and results in a consistent numerical scaling for all variables. Thereafter, ranked data were classified into five equivalent classes of 20 percent each. In order to aggregate, data for all parameters measured were presented both individually and after calculation of the median. According to Bühl and Zöfel (1995), calculating the median from ordinally scaled data is possible.

This kind of representation allows clear-cut, direct comparison of the distribution of the ecotoxicological burden at the two sites. Site Eb2 is obviously more contaminated than the reference site, Eb1. However, in some cases (e.g., genotoxicity of the porewater in the comet assay and endocrine potential of XAD (tm), resin,water extracts), poor quality had to be diagnosed for the reference site as well.

Overall, results indicate that the ranking method is a suitable tool to gain a comprehensive overview of the pattern of the ecotoxicological damage potential.

Fuzzy Logic–Based Ranking. By means of a classification with both the rank-sum method and cluster analysis, the entire dataset was derived in order to develop an expert system for classifying the results (Hollert et al., 2001). The predicted rules were translated into fuzzy rules applying the commercial software DataEngine (version 3.1, MIT GmbH, Aachen) according to the method of Heise et al. (2000). In contrast to the above-mentioned five classes, in this case a system with four site-specific classes was created. Figure 17.7 gives a survey of the quality classes as determined by means of fuzzy logic expert systems.

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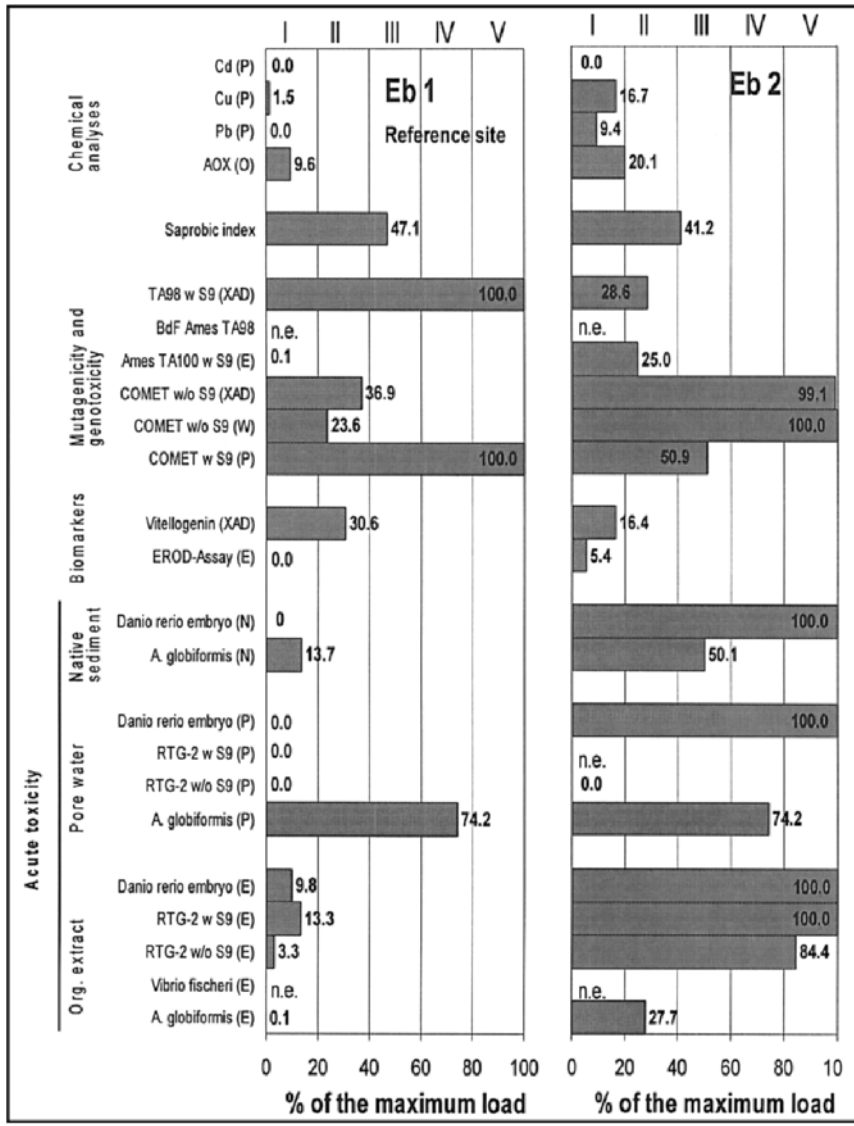

FIGURE 17.6 Results of a comparative evaluation of two sites located in fish-spawning areas connected to the Neckar River. At the location Eb2, the water level is strongly influenced by currents caused by shipping traffic, which lead to both a remobilization of sediments and a temporary desiccation of the habitat, followed by accumulation of easily exchangeable metal species in the sediment and the free water. Eb1 is a reference site of comparable grain size located near the outflow of the fish-spawning area. Data for all parameters at all sites were proportionally scaled between 1 (lowest effect) and 100 percent (highest effect). Thereafter, scaled data were classified according to increasing ecotoxicologic load into five equivalent classes of 20 percent each. (Redrawn from Hallot et al, 2001)

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The reference sites F2, Mb1, and Hil, as well as Eb1, are classified into classes 1 and 2, respectively. For the regeneration site, F4, the system also predicted a minor contamination. All other SQT sites were classified into the quality class 4 (strongly contaminated).

As shown repeatedly by Carr et al. (1996), Chapman (2000), Chapman et al. (1992), DelValls et al. (1998), and Pascoe et al. (1994), the SQT assessment approach allows classification of the study sites into categories prioritized according to the degree of contaminant-induced degradation. Such a classification would not have been possible without all three components of the triad being measured simultaneously. The approach used in the presented study revealed a strong ecotoxicologic burden for some of the streams investigated, all of which are characterized by small catchment areas. In order to identify and eliminate pollution sources, assessment of such streams obviously is an area of major importance.

CONCLUSIONS

Results document advantages and disadvantages of the methods applied for the evaluation and classification of the complex data matrixes. The ranking procedure presented seems to be a suitable tool to gain a comprehensive overview of the pattern of the ecotoxicological load (Canfield et al., 1994). Obviously, this classification method requires expert knowledge to interpret the ranking results with respect to decision making in environmental sciences and policy. In contrast, fuzzy logic both allows the development of site-specific expert systems to assess the ecotoxicological burden and provides insight into the pattern of the contamination. The examples given reveal that the use of different

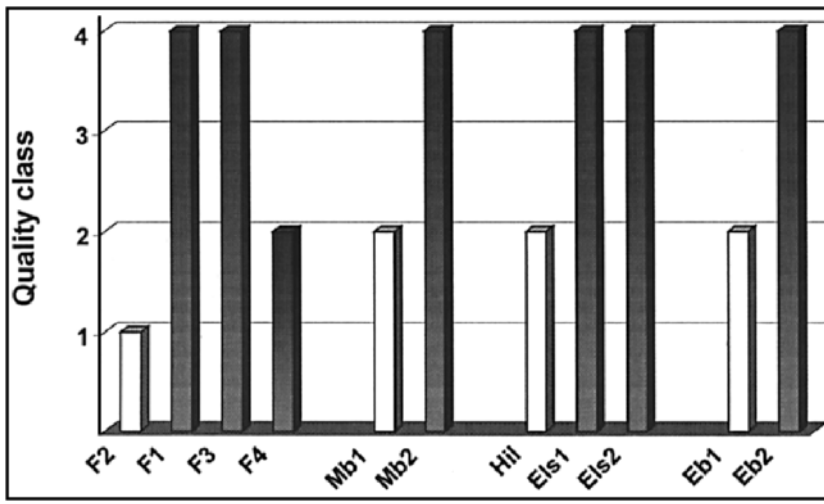

FIGURE 17.7 Classification of the SQT sites by a fuzzy-logic expert system. Calculations were based on the BIO index with 23 bioassay results (Solid phase: *Arthrobacter globiformis*; porewater: *Danio rerio* and RTG-2 cells; extract: *Danio rerio,* RTG-2 cells, *Arthrobacter globiformis,* EROD induction in avian organ liver culture, respectively), the CHE index with 26 chemical parameters, and the saprobic index (SAP). Reference sites are represented by open bars. The reference site F2 was classified into quality class 1; the other reference locations into class 2. In contrast, all other sites, excluding site F4, belong to the higher-loaded quality class 4. (Redrawn from Hallot et al, 2001)

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exposure methods as the data basis for the fuzzy classification allows insight into the character of the ecotoxicological burden. In this study the conclusion may be drawn that fuzzy logic–based expert systems have a large potential for the development of non-site-specific classification systems (Ahlf and Gratzer, 1999). Once created by experts, the programmed fuzzy expert control system can be handled by nonexperts and enables them to interpret their ecotoxicological data (Heise et al., 2000). Until now, the assessment methods have been used primarily for the evaluation of contaminated sediments. However, the same procedure could be applied to soil quality assessment, including a minimum set of bioassays as shown by Ahlf et al, 2002.

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P • A • R • T • 3

ATMOSPHERE

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CHAPTER 18
SURFACE-ATMOSPHERE EXCHANGES OF CHEMICAL COMPOUNDS AND GLOBAL CHANGE

Guy Brasseur, Timothy Bates, and Claire Granier

INTRODUCTION

The chemical composition of the atmosphere is determined by several processes, including mass fluxes between the surface and the planetary boundary layer, ventilation from the boundary layer to the free troposphere, convective exchanges in storms and fronts, troposphere-stratosphere exchanges, advective transport by the general circulation, gas- and aqueous-phase chemical transformations, and wet scavenging of soluble species in precipitation. Exchanges of chemical elements at the earth's surface are associated with natural emissions by vegetation and soils, ocean emissions and uptake, human-induced production and release of pollutants, and surface dry and wet deposition. Fossil fuel consumption and biomass burning are major anthropogenic sources of chemical compounds in the atmosphere.

Prior to the development of intensive agricultural practices and industrial activities, the chemical composition of the earth's atmosphere was determined primarily by biospheric emissions. Occasionally, it has been disturbed by intense volcanic eruptions, but these sporadic effects never lasted more than a few years. In fact, even today, the presence of major gases (N_2 and O_2) in the atmosphere is a direct consequence of microbial activity in soils and of photosynthesis/respiration associated with the presence of living organisms. Biospheric processes are also a source of many minor constituents, including several volatile organic compounds (VOCs), as well as reduced nitrogen and sulfur species. In many cases, however, anthropogenic sources have become large and even dominant. In the case of carbon dioxide, the atmospheric abundance results primarily from exchanges of carbon between the atmosphere and the ocean and between the atmosphere and the continental biosphere. The increasingly large consumption of fossil fuels has perturbed the global carbon cycle substantially with direct consequences on the atmospheric concentration of carbon dioxide.

Table 18.1 provides the globally averaged volume mixing ratios of several well-mixed (long-lived) atmospheric gases for preindustrial (1850) and current (2000) conditions, respectively. These gases are known to interact with terrestrial (infrared) radiation and hence to affect the climate system. The atmospheric concentration of photochemically

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TABLE 18.1 Mixing Ratios of Different Well-Mixed Greenhouse Gases in the Atmosphere

Compound	Preindustrial	Present day
CO_2	280 ppmv	370 ppmv
CH_4	790 ppbv	1600 ppbv
N_2O	288 ppbv	310 ppbv

active (short-lived) compounds also has changed since the preindustrial period, especially in regions most affected by industrialization (Europe, North America, and Southeast Asia) and by biomass burning (Africa, South America, and Asia). In these regions, the level of surface ozone has increased dramatically over the last 150 years as a result of the photooxidation of carbon monoxide and hydrocarbons in the presence of nitrogen oxides.

In this introductory chapter to the part of this handbook dealing with the atmosphere, we present an overview on the exchanges of chemical compounds between the earth's surface and the atmosphere. We focus on the natural emissions over the continents, the exchanges of chemical compounds over the ocean, and the anthropogenic sources of chemical species. The focus is on chemically reactive species rather than on inert gases such as CO_2. We also present a synthetic description of the key processes that determine the photochemical state of the troposphere. We emphasize how human activities have perturbed the chemical composition of the global troposphere and stress the need for more accurate flux measurements at different spatial and temporal scales.

As we will see in the following chapters, much work remains to be done to better quantify the processes that determine the chemical composition of the atmosphere, including the exchange fluxes of chemical elements between the surface and the atmosphere. The field of atmospheric chemistry therefore provides many exciting challenges that will have to be addressed by scientists in different regions of the world [see the IGAC integration/synthesis document by Brasseur et al. (2002)].

CHEMICAL COUPLINGS BETWEEN THE CONTINENTAL BIOSPHERE AND THE ATMOSPHERE

The earth's surface acts both as a source and a sink for trace gases and particles. About two-thirds of the continents are covered by vegetation, and the growth of plants leads to the uptake of carbon dioxide and the release of several types of biogenic compounds. These include primary hydrocarbons, alcohols, carbonyls, acids, sulfur compounds, nitrogen oxides, carbon monoxide, and aerosol particles. Over the years, a large number of field observations have led to the identification of the processes responsible for the emissions and deposition of various chemical species. The extrapolation of local measurements (at the scale of a leaf, a tree, or a small area of soil) to larger areas covering ecosystems under different meteorological conditions remains a major challenge. The current estimates of global emissions therefore remain inaccurate, with uncertainties typically of a factor 2.

We now briefly review in the following subsections the emissions of chemically important compounds by the continental biosphere, primarily under natural conditions. Perturbations associated with land-use changes or industrial activities are discussed later.

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Methane (CH4). Methane is produced as a result of the microbial breakdown of organic matter in oxygen-deficient flooded areas such as lakes, swamps, bogs, boreal marshes, and rice paddies (Fung et al., 1991; IPCC, 1994, 1996). Emissions of this compound in tropical and subtropical areas are regulated by precipitation and flood cycles, whereas at high latitudes they are related to temperature–water table interactions. The characteristics of most major wetlands have been established, but measurements are still scarce, especially in the case of the Siberian wetlands. Approximately 110 Tg of CH_4 are produced annually by wetlands, of which about 60 percent are due to tropical wetlands (between 20°N and 30°S), and 35 percent are due to the northern wetlands (latitude higher than 45° N). The global area and distribution of wetlands are rather well known; significant uncertainties, however, remain regarding the seasonal variation of the wetland areas and the methane production periods. If temperature increases in the future in relation to future climate change, specifically at high latitudes, where precipitation rates are also predicted to increase, higher methane emissions are expected to occur. However, increased evaporation at the surface could lead to reduced fluxes. Termites are also believed to be a significant methane source. In this case, the gas is produced by the activity of bacteria on the organic material consumed by the termites. Methane hydrates are made up of rigid water envelopes surrounding methane molecules. A large amount of methane is trapped in these hydrates, which are found on the continental shelf at all latitudes in deep-cold temperatures. At present, these hydrates are very stable, and the corresponding methane emission therefore is very small. This source could become significant in the future, however, as a result of global warming.

Nonmethane Hydrocarbons (NMHC). Many different hydrocarbons are released into the atmosphere (Singh and Zimmerman, 1992; Guenther et al., 1995). At the global scale, over three-fourths of these compounds are emitted by vegetation. Due to the large number of species emitted, the variety of processes involved, and the complexity of the meteorological and biospheric conditions regulating these emissions, there are still very large uncertainties in the emission estimates. The emissions that have been studied in detail are those of isoprene because they are of large magnitude and have a significant impact on the photochemical production of other species, including carbon monoxide. Isoprene is emitted by many different types of deciduous trees. Monoterpenes are also emitted in large quantities, primarily by conifers and different types of shrubs. Laboratory and field experiments have provided important information regarding the different processes regulating these emissions, including their temperature dependence, the impact of light intensity, and the relation with leaf age, the growth environment, and the plant temperature history. Algorithms have been developed to describe the emissions and their short-term variations (Guenther et al., 1995). These algorithms, together with a compilation of available information on the vegetation types, land cover, emission factors, etc., have been incorporated into models of biogenic emissions. Accurate databases for the variables driving the emissions are still missing for several regions of the world. This leads to significant uncertainties in calculation of the corresponding regional emissions. Furthermore, destruction of the emitted species within the canopy potentially can be significant, and the actual amount of hydrocarbons released into the atmosphere needs to be assessed taking such canopy losses into account. Ketones or aldehydes are also emitted in large quantities by vegetation, but measurements are at present only available for very limited areas, and the global emission has not yet been quantified accurately. Increased temperatures and precipitation changes associated with climate change in the next decades could affect hydrocarbon emissions by vegetation. Changes in land use also could alter emissions of hydrocarbons because deforestated areas often are replaced by more grassy lands with lower emission rates of isoprene and terpenes.

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Nitrogen Oxides (N_2O and $NO_x = NO + NO_2$). Nitrogen oxides [primarily nitrous oxide (N_2O) and nitric oxide (NO)] are produced in soils and released to the atmosphere as a result of microbial nitrification and denitrification processes (see, e.g., Mosier et al., 1998) The first step is the biological fixation of nitrogen into the biomass (plants and microbes), i.e., the enzyme-catalyzed reduction of atmospheric N_2 into NH_3 or NH_4^+. Once fixed, these reduced nitrogen compounds are oxidized in the presence of certain bacteria to form nitrites (NO_2^-) and nitrates (NO_3^-, a process called *nitrification,* with nitrous and nitric oxides released as by-products of these reactions The chemical and biological reduction of nitrates to gaseous forms of nitrogen (mostly N_2, N_2O, and NO) constitutes a denitrification process and occurs in environments with restricted oxygen availability and sufficient quantities of suitable reductants. The N_2O/N_2 ratio in the emission depends on the respective availability of oxidants and reductants in soils. The magnitude of the emissions has changed due to the use of nitrogen fertilizers in conjunction with intensive agricultural practices. The rate of natural NO emission from soils (Yienger and Levy, 1995; Li et al., 1996) remains uncertain by a factor of 2 to 3; in addition, the adsorption of nitrogen oxides onto plants within the canopy probably reduces significantly the actual emissions to the atmosphere. Process-oriented models have been developed to simulate nitrogen emissions and their fate in the canopy (Ganzeveld, 2001). An important additional source of NO_x in the troposphere is associated with lightning in thunderstorm systems (Price et al., 1997; Pickering et al., 1998). The photochemical lifetime of NO_x in the free and upper troposphere is relatively long (compared with its lifetime at the surface), so the impact of this relatively small source plays a significant role for the chemistry of the troposphere, specifically in the tropics and at midlatitudes during the summertime, when thunderstorms are frequent.

Ammonia (NH_3). Ammonia is primarily a product of biological activity (Bouwman et al., 1997). It is released through mineralization of organic material in soils, in animals, and in the ocean (see below). As indicated later, the emissions of ammonia have increased substantially as a result of agricultural activities (Asman and Janssen, 1987). Ammonia is the dominant alkaline gas in the atmosphere and thus is an important neutralizer of anthropogenic acidity. It converts sulfuric acid, for example, into ammonium-containing aerosols (i.e, ammonium sulfate).

Deposition of Chemical Compounds to the Land Surface. The earth's surface does not act only as a source of trace gases or aerosols; it also can act as a sink. The deposition flux F_D can be expressed by the product of the gas or aerosol concentration n by a deposition velocity w_D:

$$F_D = n \times w_D$$

Deposition often is described in terms of a resistance to deposition (defined as the inverse of the deposition velocity). By analogy to the Ohm's law in electricity, the total resistance can be represented by a number of subresistances connected either in series or in parallel and accounting for aerodynamic processes (turbulence) and molecular diffusion in the layer adjacent to the surface. A species-dependent resistance, determined from field measurements, is introduced to represent the role of the canopy in the deposition of the different chemical compounds. For more details, see Weseley (1989).

CHEMICAL COUPLINGS BETWEEN THE OCEAN AND ATMOSPHERE

The ocean is both a source and a sink for atmospheric trace gases and particles. During the past decade, numerous studies have used measured seawater and atmospheric trace gas

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concentrations to calculate the ocean-atmosphere exchange. Aerosol concentrations in the atmospheric marine boundary layer have been used to infer a similar exchange. The following paragraphs summarize some of the recent highlights from studies of chemical couplings between the ocean and the atmosphere.

Air-sea exchange. The ocean-atmosphere flux F of a sparingly soluble gas X can be expressed as

$$F = K_l \times L \times \Delta_p X$$

where K_l is the gas transfer velocity expressed in units of length/time, L is the gas solubility at the ambient surface seawater temperature expressed in units of concentration/pressure, and $\Delta_p X$ is the difference in the gas partial pressure in surface seawater and the overlying atmosphere. K_l is parameterized using wind speed and Schmidt number, which is the ratio of kinematic viscosity of seawater and the molecular diffusivity of the gas (Liss and Merlivat, 1986; Wanninkhof, 1992).

Although the calculations are straightforward, there are still large uncertainties in the resulting values of K_l. While the Liss and Merlivat (1986) wind speed–transfer velocity relationship has been supported by dual tracer techniques (Watson et al., 1991), other studies suggest that this relationship underestimates the flux by as much as a factor of 2 (Smethie et al., 1985; Erickson, 1989; Tans et al., 1990; Wanninkhof, 1992). Resent experiments in the North Atlantic (Wanninkhof and McGillis, 1999) and North Sea (Nightingale et al., 2000) suggest wind speed–transfer velocity relationships that fall between the earlier-published studies at wind speeds of less than 12 m/s. At higher wind speeds, the relationships diverge as the relationships range from linear to quadratic to cubic functions of wind speed.

Since many of the wind speed–transfer velocity relationships are nonlinear, transfer velocities calculated with long-term average winds generally will be lower than those obtained using short-term variable winds (Wanninkhof, 1992). The choice of wind fields depends on the data available and the scientific objective. Studies aimed at obtaining a large-scale (ocean basin or global) average gas flux by necessity use long-term average winds (Bates et al., 1987; Tans et al., 1990; Murphy et al., 1991). The uncertainty in calculating wind speed–transfer velocity relationships, especially at high wind speeds, remains a major challenge to understanding the chemical coupling between the ocean and the atmosphere. The major uncertainty in the air-sea exchange of the gases discussed later is due to the range of potential transfer velocities. New, faster response sensors will provide additional techniques for measuring air-sea gas exchange but must be deployed in a wide range of wind speeds.

Dimethylsulfide (DMS) The ocean is the major natural source of sulfur to the atmosphere. Numerous studies during the past decade have helped to define regional and seasonal variations in surface seawater dimethylsulfide (DMS) concentrations. A global database of sea surface DMS measurements has been compiled recently by Kettle et al. (1999). The database includes over 15,000 point measurements from 23 different institutions. While this effort provides an excellent gridded data set for calculating ocean-atmosphere DMS fluxes in chemical transport models, we still lack the ability to predict how the concentrations of seawater DMS might change with a changing climate. The air-sea exchange of DMS is only a small sink in the seawater sulfur cycle, and thus minor changes in surface ocean biology, chemistry, or physics could have a major effect on the surface seawater DMS concentration and flux (Simo, 2001). Future work is needed to define the processes controlling surface seawater DMS concentrations.

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Carbonyl sulfide (COS) and carbon disulfide (CS2). COS is produced photochemically in the surface ocean (Zepp and Andreae, 1994; von Hobe et al., 1999). Early measurements, which generally were taken in the summer season and during the daytime, suggested that the open ocean was a significant source of COS to the atmosphere. However, recent measurements have shown wide regions of the open ocean, especially in the subtropical gyres and wintertime subpolar waters, to be undersaturated with respect to the overlying atmosphere (Weiss et al., 1995). The revised flux calculations, taking into account the diel and seasonal variability, suggest that the open ocean is on average in equilibrium with the atmosphere (Ulshofer et al., 1995; Weiss et al., 1995). The coastal ocean remains a significant source of COS to the atmosphere. CS^2 is also present in surface seawater from anaerobic bacterial activities and ultraviolet (UV)–induced photochemical transformations of dissolved organic matter (Xie and Moore, 1999). The calculated flux to the atmosphere is about 1 percent of the oceanic DMS flux to the atmosphere (Xie and Moore, 1999).

Methylhalides. Methylhalides are produced and consumed biologically (CH_3Br: Moore and Webb, 1996; Baker et al., 1999; CH_3I: Moore and Groszko, 1999) and photochemically (CH_3I: Happell and Wallace, 1996; CH_3Cl: Moore et al., 1996) in surface ocean waters. Recent measurements have shown that the flux of CH_3Cl (Moore et al., 1996) is significantly less than early estimates and that the open ocean is a net sink rather than a source for CH_3Br (Lobert et al., 1997; Groszko and Moore, 1998; King et al., 2000). Coastal (Nightingale et al., 1995; Itoh and Shinya, 1994) and high-latitude (Sturges et al., 1992, 1993) production of halocarbons is a significant source of bromine to the atmosphere. In the high latitudes, the resulting atmospheric bromine plays an important role in ozone loss.

Carbon monoxide (CO). The ocean is ubiquitously supersaturated with CO with respect to the atmosphere, resulting in a net flux to the atmosphere ranging seasonally and regionally from 0.25 to 13 mol/m^2 per day. However, the total annual emission to the atmosphere is small compared with current estimates from both terrestrial natural and anthropogenic sources. Even in the southern hemisphere, which accounts for two-thirds of the oceanic emissions, the ocean source is relatively small (<1 percent), since both methane oxidation and biomass burning are large sources of CO in the southern hemisphere (Bates et al., 1995).

Methane (CH4). The ocean is a small source of CH_4 to the atmosphere. Open Pacific Ocean saturation ratios (ratio of seawater CH_4 partial pressure to the overlying atmospheric CH_4 partial pressure) range from 0.95 to 1.17. Large areas of the Pacific Ocean are undersaturated with respect to atmospheric CH_4 partial pressures during the fall and winter. On a seasonal time scale, the driving force controlling the saturation ratios outside the tropics appears to be the change in sea surface temperature. Saturation ratios in the equatorial region were always positive and appear to be driven by the strength of the equatorial upwelling. Extrapolating the Pacific data globally, the calculated average flux of CH_4 to the atmosphere is an order of magnitude less than previous estimates (Bates et al., 1996), which lacked fall and winter data. Thus the open ocean is a very minor source of methane to the atmosphere (<0.1 percent) compared with other sources (IPCC, 1994). However, the coastal ocean and marginal seas appear to be a much larger source (Owens et al., 1991; Kvenvolden et al., 1993; Bange et al., 1994; Lammers et al., 1995) due to CH_4 emissions from bottom sediments and definitely warrant further investigation.

Nommethane hydrocarbons (NMHCs). NMHCs are produced in surface seawater possibly by photochemical mechanisms, phytoplankton activity, and/or the microbial breakdown of organic matter (Plass-Dulmer et al., 1995; Ratte et al., 1995; Broadgate et al., 1997). Oceanic concentrations show a strong seasonal cycle (Broadgate et al., 1997). The ocean-atmosphere flux is dominated by alkenes and is small compared with terrestrial emission estimates (<1 percent). However, the emissions may be significant on

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local scales considering the short lifetimes of the unsaturated species (Donahue and Prinn, 1993; Broadgate et al., 1997; Pszenny et al., 1999). Additional seasonal measurements of isoprene, ethene, and propene are needed in different ocean regions.

Ammonia and methlyamines. Ammonia and methlyamines, like other reduced biogenic gases (e.g., methane and DMS), are produced by the microbial breakdown of labile organic matter. The remote oceans are thus a small source of these compounds to the atmosphere (Quinn et al., 1988, 1990, 1996; Zhuang and Huebert, 1996; Gibb et al., 1999). The exchange of ammonia across the air-sea interface is a small sink in the seawater ammonium cycle (Gibb et al., 1999), and thus, like DMS, changes in ocean biology, chemistry, or physics could have a major effect on the flux of ammonia to the atmosphere. Although the current ocean-atmosphere flux of ammonia is small, it plays an important role in atmospheric chemistry. As stated earlier, ammonia is the dominant gas-phase basic species in the remote marine atmosphere and thus can influence the formation, growth, and pH of atmospheric aerosol particles. Additional measurements of ammonia are needed in surface seawater and the overlying atmosphere.

Sea-salt aerosols. Sea-salt particles are ejected into the atmosphere from the breaking of waves and can dominate the mass of both submicron and supermicron marine boundary layer (MBL) aerosol particles in the remote marine environment (Quinn et al., 1998; Huebert et al., 1998). Single-particle analysis during ACE-1 revealed that over 90 percent of the aerosol particles with diameters of more than 130 nm (Murphy et al., 1998) and up to 70 percent of the particles with diameters of more than 80 nm (Kreidenweis et al., 1998) contained sea salt. The dominance of sea-salt aerosol over the remote oceans clearly shows the need to include sea salt in climate models. In moderate- to high-wind-speed conditions, sea salt controls the magnitude of aerosol light scattering (Quinn et al., 1998; Carrico et al., 1998; Murphy et al., 1998) and the number of cloud condensation nuclei (Covert et al., 1998; O'Dowd et al., 1997). Sea-salt particles also provide reactive surfaces for the oxidation of gas-phase species (e.g., SO_2, nitric acid) and thus act as a shunt in the sulfur cycle, limiting new sulfur aerosol formation (Sievering et al., 1999). The liberation of halogen species from sea salt contributes to the tropospheric budget of reactive chlorine (Graedel and Keene, 1995) and may affect the oxidizing power of the marine boundary layer (Sander and Crutzen, 1996).

Deposition of aerosols to the ocean surface. The deposition of aerosol species to the surface ocean can provide nutrients to enhance biological productivity. Anthropogenic nitrogen in the form of ammonium and nitrogen oxides and iron and phosphorous associated with mineral dust all act as nutrients to plankton living in the surface ocean (Prospero et al., 1996). Model results suggest that the present-day deposition rates of NO_y and NH_x over the North Atlantic Ocean are about 5 and 10 times greater than in preindustrial times (Prospero et al., 1996). Coale et al., (1996) demonstrated in the equatorial Pacific Ocean that iron fertilization can induce a phytoplankton bloom that, in turn, will affect the seawater concentration of DMS (Turner et al., 1996) and CO_2 (Cooper et al., 1996). Similar experiments need to be conducted using atmospheric aerosol particles in regions downwind of mineral aerosol and anthropogenic aerosol sources.

ANTHROPOGENIC EMISSIONS

Chemical compounds are released to the atmosphere as a result of industrial activities and agricultural practices. In the following subsections we review the emissions of key chemical species associated specifically with fossil fuel combustion, biomass burning, and agricultural activities.

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Industrial Activities and Transportation

Methane (CH_4). Methane is the major component of coal gas and natural gas (Fung et al., 1991; IPCC, 1994, 1996; Olivier et al., 1999). Coal mining and production and the transmission and distribution of natural gas lead therefore to methane emissions to the atmosphere. Leaks in transmission lines and distribution systems of natural gas are not well quantified and could be significant in certain parts of the world. Venting and flaring at oil wells provide an additional anthropogenic source. Landfills also result in significant CH_4 emissions due to the decomposition of biodegradable organic material dumped there. There are significant uncertainties on this emission because it depends directly on the nature and composition of the wastes and on the management of the landfills.

Carbon Monoxide (CO). CO is released at the surface by incomplete combustion of fossil fuels (Khalil and Rasmussen, 1990, Olivier et al., 1999). A large amount of carbon monoxide results from road transport, with the largest contributions originating in Northern America, Europe, the former Soviet Union, the Middle East, and Asia. Globally, anthropogenic CO emissions did not change significantly during the 1990s. Emissions in the former Soviet Union and eastern Europe, however, have decreased by about 75 percent from 1990 to 1995, and emissions in China, India, and Southeast Asia probably have increased by 12 percent during the same period.

Nitrogen Oxides (NO_x). The major source of nitrogen oxides (mostly emitted as NO) is fossil fuel combustion (Hameed and Dignon, 1988; Benkovitz et al., 1996; Lee et al., 1997; Olivier et al., 1998). About 40 percent of these emissions result from road transportation, with North America and Europe both contributing 25 percent of these emissions. Nitrogen oxide emissions decreased by about 30 percent in Europe between 1990 and 1995 (Olivier, personal communication) as a result of general use of catalytic converters to reduce automobile exhausts. Car emissions of nitrogen oxides increased by about 67 percent in Asia, (53 percent in India and China) between 1990 and 1995. Ships contribute substantially to anthropogenic NO_x sources, especially over the oceans, where other sources are extremely small. The release of NO by aircraft engines provides a small source of active nitrogen. However, this plays a substantial role because it occurs mostly in the upper troposphere and lower stratosphere, where the lifetime of NO_x is long. This source is likely to increase in the future.

Nonmethane Hydrocarbons (NMHCs). A very large number of nonmethane hydrocarbons are released in the atmosphere as a result of fuel production, distribution, and combustion associated with road transportation and various industrial activities.

Sulfur dioxide (SO_2). The largest current atmospheric source of sulfur dioxide is provided by the combustion of fossil fuels, specifically of coal., This source has increased dramatically since the preindustrial era, even though the emissions have decreased significantly during the last decades in the industrialized regions of Europe and North America. In these regions, coal has been replaced in large part by oil and gas as primary sources of energy. The oxidation of SO_2 leads to the formation of sulfate aerosol particles and acidic precipitation.

Biomass Burning

Very large areas of land are burnt each year, mostly as a result of human-led deforestation associated with land clearing, shifting cultivation, savanna clearing (for conversion into

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pastures or agricultural fields), fuelwood use, burning of agricultural residues, forest management, etc. (see, e.g., Crutzen and Andreae, 1990; Hao and Ward, 1993; Hao et al., 1996a, 1996b). Some of the fires are also initiated by lightning strikes, specifically in the remote areas of the high latitudes in the northern hemisphere. Many different gases and aerosols are released into the atmosphere as a result of these fires, which can affect the composition of the atmosphere, as well as regional and global climate. The amount of biomass burnt each year probably has increased by 30 to 50 percent during the past century, mostly as a result of deforestation in the tropics and a large increase in the use of biofuels associated with population growth in the developing countries.

The area of savanna burnt each year is estimated to be between 750 and 1500×10^6 ha (Hao et al., 1990; Goldhammer, 1993). At the same time, large areas of the tropical forest are burnt each year. Boreal fires are also frequent during the summer months. They contribute to perturbations in the chemical composition of the polar troposphere. About 70 percent of these fires are located in Russia, where, on average, 650,000 ha are burnt annually (Stocks et al., 2000). This area may reach 10^7 ha during very dry years. It is estimated that in Canada, 0.8 to 7×10^6 ha are destroyed by fire each year. Although fires in the boreal areas are mostly of natural origin, they are increasingly initiated as a result of human behavior. The average amount of biomass burnt each year is given in Table 18.2, on the basis of the estimated amount of biomass available in each ecosystem.

Burning of biomass associated with cooking and heating provides another atmospheric source of several chemical compounds such as CO and black carbon particles. The amount of biofuel use varies greatly with living habits and is large in several developing countries.

The amount and type of compounds emitted by the fires depend on many factors, including the temperature of the fire, the amount of biomass available and its water content, soil moisture, the wind velocity, and the topography of the area. Over the past two decades, several international measurements campaigns have led to a better understanding of the characteristics of the fires and the relationships between the burning process and the types and amount of compounds emitted. Emissions of the different compounds by the fires are measured either in the laboratory or during field campaigns. The variable used to quantify the emissions of the different gases from different types of fires is the emission factor (Table 18.3), which represents the mass of a compound released per mass of fuel consumed. An accurate estimate of the distribution of trace gases emitted by biomass burning requires knowledge of the emission factor together with the distribution of the amount of the fuel burnt. A climatological average of the amount of biomass burnt for each month of the year is provided by Hao and Liu (1994). Recently, remote sensing has proven to be a

TABLE 18.2 Estimates of the Amount of Dry Biomass Burnt Each Year

Ecosystem	Amount burnt, in Tg dry matter
Tropical forest	1260–1820
Extra tropical forest	640–1150
Savanna + grassland	2670–3690
Fuelwood use	620–1960
Agriculture residues burning	280–1190

Sources: Based on Andreae (1993), Hao and Liu (1994), Liousse et al. (1996a, 1996b), and Lobert et al. (1999), quoted in Brasseur et al. (2002).

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TABLE 18.3 Emission Factors for Selected Gases and Aerosols for Different Forms of Biomass Burning (in grams of species per kilogram of dry fuel burned)

Type of fire species	Savanna	Tropical forest	Extra-tropical forest	Fuelwood	Charcoal	Agriculture waste burning
CO_2	1613 ± 95	1580 ± 90	1569 ± 131	1550 ± 95	2611 ± 241	1515 ± 177
CO	65 ± 20	104 ± 20	107 ± 37	78 ± 31	200 ± 38	92 ± 84
CH_4	2.3 ± 0.9	6.8 ± 2	4.7 ± 1.9	6.1 ± 2.2	6.2 ± 3.3	2.7
C_2H_6	0.32 ± 0.16	0.5–1.9	0.6 ± 0.15	1.2 ± 0.6	0.53 ± 0.48	
C_3H_8	0.09 ± 0.03	0.15	0.25 ± 0.11	0.2–0.8	0.07–0.3	
C_2H_4	0.79 ± 0.56	1–2.9	1.12 ± 0.55	1.8 ± 0.6	0.46 ± 0.33	
C_3H_6	0.26 ± 0.14	0.55	0.59 ± 0.16	0.5–1.9	0.13–0.56	
C_2H_2	0.29 ± 0.27	0.21–0.59	0.27 ± 0.09	0.51–0.9	0.05–0.13	
CH_2O	0.26–0.44		2.2 ± 0.5	0.13 ± 0.05		
Acetone	0.25–0.62		0.52–0.59	0.01–0.04		
NO_2 (as NO)	3.9 ± 2.4	1.6 ± 0.7	3 ± 1.4	1.1 ± 0.6	3.9	2.5 ± 1
N_2O	0.21 ± 0.1		0.26 ± 0.07	0.06		0.07
Org. C	3.4 ± 1.4	5.2 ± 1.5	8.6–9.7	4 ± 1.2	4.8	3.3
Black C	0.48 ± 0.18	0.66 ± 0.31	0.56±0.19	0.59 ± 0.37	1.5	0.69 ± 0.13

Source: From Andreae and Merlet (2002).

useful tool to estimate the seasonal and geographic distribution of biomass burning emissions. It should be used increasingly to calculate these emissions at high temporal and spatial resolutions. The exact determination of the surface area burnt still requires major improvements.

Future changes in surface emissions related to biomass burning are difficult to predict. The clearing of tropical evergreen forests leads to an impoverishment of forest ecosystems, which will reduce the amount of biomass available for burning. Furthermore, the impact on trace gas emissions of changes in cattle grazing, domestic fuel use, and biomass quantity (resulting from desertification) is difficult to quantify.

Agriculture

Intensive agriculture developed over the last centuries in many parts of the world has introduced dramatic perturbations in the emissions of different chemical compounds. The major causes for these changes are perturbations in ecosystems and soil properties, the use of fertilizers, and the larger presence of cattle. Several studies have been conducted to determine how to adjust agricultural practices to reduce surface emissions.

Nitrogen oxides (N_2O and NO_x). With the intensification of agricultural practices, the global nitrogen cycle has been perturbed substantially (Vitousek, 1994). The emissions of nitrogen oxides from soils are enhanced by the use of nitrogen fertilizers (Matthews, 1994). The consumption of these fertilizers has increased dramatically over the past 50 years, mostly in the tropics and subtropics and more particularly in Asia. Additional nitrogen emissions are related to animal production, i.e., animal manure and mineralization of soil matter.

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SURFACE-ATMOSPHERE EXCHANGES OF CHEMICAL COMPOUNDS AND GLOBAL CHANGE

Ammonia (NH_3). The largest source of ammonia is provided by domestic animals (Bouwman et al., 1997). Inorganic fertilizers and animal excreta increase the ammonia and ammonium content of the soil and tend therefore to enhance the soil emissions, especially in regions where livestock are concentrated.

Methane (CH_4). Emissions of methane resulting from rice paddies are an important source of atmospheric methane (Fung et al., 1991; Neue and Sass, 1998; Sass et al., 1999). Temperature, soil characteristics, water management, the abundance of organic matter in soils, and fertilizer use influence these surface emissions. They may have increased substantially over the past decades because rice production has risen by about 30 percent since the 1970s through the combined effect of an increase in the cultivated land area and higher production efficiency. Methane is also released into the atmosphere as a result of anaerobic microbial activity in the stomach of cattle (mostly ruminants). These emissions of methane depend on the quantity and quality of the animal feed, the body weight of the animals, their age, and their activity. It is estimated that the global emission of CH_4 from cattle is about 85 Tg CH_4 per year, with about 75 percent of the emissions being due to dairy cows and nondairy cattle, the rest of the emissions being due to water buffaloes, sheep, goats, pigs, camels, horses, and wild animals. Half the emissions originate in India, China, the former Soviet Union, the United States, and Brazil. The uncertainty on this source is relatively small because the worldwide statistics on the animal population can be considered to be reasonably reliable. Note that the increase in agricultural methane emissions has been offset in part by a decrease in emissions from natural wetlands.

TROPOSPHERIC PHOTOCHEMISTRY

Chemical compounds released at the earth's surface are often oxidized in the atmosphere and eventually converted into soluble gases (e.g., acids), which are removed from the atmosphere by wet scavenging. Details on photochemical processes occurring in the troposphere are given, for example, in Brasseur et al., (1999). The rate at which elements of biogenic or anthropogenic origin are removed from the atmosphere usually is limited by the rate at which the primary compounds are oxidized rather than the atmospheric wet deposition rate. The more effective oxidant in the atmosphere is not molecular oxygen but the hydroxyl radical (OH). Other powerful oxidants include NO_3 (which is abundant only during nighttime), H_2O_2 (which is a powerful oxidant in the aqueous phase), and ozone (O_3).

The hydroxyl radical is produced during the daytime through the oxidation of water vapor by the electronically excited oxygen atom $O(^1D)$:

$$H_2O + O(^1D) \rightarrow 2OH \tag{18.1}$$

with $O(^1D)$ being produced by photolysis of ozone by solar radiation at wavelengths less than 320 nm:

$$O_3 + h\nu \rightarrow O(^1D) + O_2 \tag{18.2}$$

Thus the oxidizing power (and hence the self-cleansing efficiency) of the atmosphere depends on the concentration of water vapor, the concentration of ozone, and the intensity of the solar UV radiation that penetrates into the atmosphere. Other source mechanisms for the OH production have been reported recently, specifically the photolysis of acetone, organic peroxides, and aldehydes. The abundance of these species is determined by the uplift through convective transport of these biogenic and anthropogenic organic species.

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Once produced, the hydroxyl radical (OH) is rapidly converted to the peroxy radical (HO_2) by reaction with carbon monoxide, that is,

$$OH + CO\ (+O_2) \rightarrow HO_2 + CO_2 \tag{18.3}$$

or ozone, that is,

$$OH + O_3 \rightarrow HO_2 + O_2 \tag{18.4}$$

The oxidation of methane and other hydrocarbons by OH also leads to the formation of peroxy radicals [HO_2 and/or RO_2, where R represents an organic chain (e.g., CH_3, C_2H_5, etc.)] HO_2 is converted back to OH by nitric oxide, that is,

$$HO_2 + NO \rightarrow OH + NO_2 \tag{18.5}$$

or ozone, that is,

$$HO_2 + O_3 \rightarrow OH + 2O_2 \tag{18.6}$$

This rapid cycle leads to an equilibrium between OH and HO_2 during daytime. Losses of HO_x ($OH + HO_2$) occur through reactions of OH with NO_2 (to produce HNO_3), of HO_2 with HO_2 (to produce H_2O_2), and of OH with HO_2 (to produce H_2O). The products of these reactions are removed by wet scavenging.

It is important to note that the conversion between OH and HO_2 affects the photochemical budget of ozone. The reaction of HO_2 with NO (Reaction 18.5) produces NO_2, which is photolyzed during daytime, that is,

$$NO_2 + h\nu \rightarrow NO + O \tag{18.7}$$

The rapid subsequent recombination of atomic oxygen O with O_2 in the presence of a third-body M (N_2 or O_2) leads to the formation of ozone.

Ozone in the troposphere is chemically destroyed by its reaction with OH (Reaction 18.4) and with HO_2 (Reaction 18.6). Another destruction mechanism is provided by its photolysis (wavelength less than 320 nm; see Reaction 18.2), if the resulting $O(^1D)$ atom reacts subsequently with water vapor (Reaction 18.1) rather than being quenched by N_2 or O_2.

From the preceding discussion, it is clear that the photochemical destruction of ozone is related directly to the atmospheric abundance of water vapor. On the other hand, the photochemical production of ozone often is limited by the abundance of nitrogen oxides. When carbon monoxide, methane, and other hydrocarbons (the fuels) are oxidized by the OH radical, ozone can be either produced or destroyed depending on the level of NO_x present in the atmosphere. In remote regions (e.g., in oceanic environments), oxidation of the fuels leads to ozone destruction, whereas in many continental areas affected by fossil fuel consumption, biomass burning, and lightning, where the level NO_x is high, the photochemical production of ozone is larger than its destruction.

Organic sulfur-containing compounds are also oxidized by OH during the daytime. Sulfur dioxide (SO_2), which is produced, is also released directly as a result of fossil fuel combustion (e.g., coal). SO_2 is oxidized into sulfuric acid either by the OH radical in the gas phase of by H_2O_2 or ozone inside cloud droplets. These oxidation mechanisms provide a source of sulfate aerosols, which scatter a fraction of the incoming solar radiation back to space and hence tend to cool the earth's surface.

Determining the global or regional distribution of chemical compounds requires that transport processes be known accurately. Transport occurs at a variety of spatial and temporal scales. Advection by the general circulation generally is resolved by global and regional models, whereas subgrid processes, including boundary-layer mixing, convective exchanges, etc., need to be parameterized. Such formulations of complex physical

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processes are not always very accurate and therefore can introduce significant errors in the calculated distribution of chemical compounds.

HUMAN-INDUCED PERTURBATIONS

The release into the atmosphere of chemical compounds is expected to produce changes not only in the concentration of the species emitted but also in secondary compounds such as ozone or sulfate aerosols that are produced in situ (Isaksen and Hov, 1987; Karlsdottir et al., 2000). Model calculations have estimated the concentration changes of these secondary compounds since the preindustrial period. According these models, the largest changes have occurred in the industrial regions of the northern hemisphere (Europe, North America, and Southeast Asia). Over the last 150 years, the ozone abundance near the surface probably has increased by a factor of 2 (or more) in these regions. Changes have been even larger in the case of sulfate aerosols. Calculations for the future evolution of the chemical composition of the atmosphere also have been performed. The predictions depend directly on the expected changes in the surface emissions and hence on the economic scenario that is adopted in the calculation. Most scenarios lead to compositional changes that are largest in South and Southeast Asia. Substantial changes are also to be expected in Central and South America and even southern Africa. It is expected that in response to rapid population growth and industrialization, pollution events will become more frequent in these parts of the world and that the background levels of pollutants generally will be higher. The chemical composition of the tropical atmosphere is very sensitive to photochemical processes, biogenic and biomass burning emissions, and convective transport and lightning. Changes in the level of oxidants in the tropics will have a substantial effect on the oxidizing power of the atmosphere at the global level.

It is well known that the changes in the atmospheric concentration of radiatively active compounds (gases and aerosols) have a large impact on the earth's climate (IPCC, 1994, 1996, 2001). The anthropogenic emissions of the so-called well-mixed greenhouse gases produce a well-determined climate forcing, which should produce a rise in the globally averaged temperature of the earth and other climate perturbations. Additional (positive or negative) forcing is associated with changes in the abundance of stratospheric and tropospheric ozone as well as the different types of aerosols observed in the atmosphere. Global and regional climate changes represent a major challenge for society because they could affect economies and lifestyles. What is less understood is how climate change could affect the chemical composition of the atmosphere. The increase in atmospheric humidity associated with a warmer earth should lead to a modified OH concentration and hence to a change in the oxidizing power of the atmosphere and in the atmospheric lifetime of many pollutants and other chemical compounds. Climate changes also could affect the frequency and intensity of thunderstorms and hence the production of nitrogen oxides by lightning. In the stratosphere, cooling associated with enhanced levels of carbon dioxide could delay ozone recovery in polar regions in response to the ban on the production of chlorofluorocarbons. Significant thermal and compositional changes are also expected in the mesosphere and perhaps in the thermosphere. Finally, biogenic emissions could be modified substantially in a warmer climate; it is well known, for example, that isoprene emissions by the vegetation and NO or N_2O emissions by microbial emissions in soils are increased when the temperature rises. Future earth system models will have to consider these processes and feedback mechanisms when performing predictions of future changes in the earth system. Efforts are currently underway to develop advanced earth system models in which the physical climate system is coupled with the biogeochemical system. These models will include a detailed representation of the dynamics of the atmosphere and

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of the ocean, represent the hydrological cycle and the dynamics of sea ice, simulate the chemistry of the atmosphere and the biogeochemistry of the ocean, represent major ecological processes on land, account for the exchange of energy, momentum, and mass between the different earth components, and be responsive to external perturbations including anthropogenic influences. These models are being developed by interdisciplinary teams that recognize the systemic nature of the global change problem. They will have to be evaluated on the basis of detailed observations, including measurements of emission and deposition fluxes at the surface.

CONCLUSIONS

The chemical composition of the atmosphere has evolved in the past and will continue to do so in the future in response to changes in surface emissions. Emissions result from natural processes involving the biosphere and from various types of human activities (Table 18.4). Today, in many cases, anthropogenic emissions associated with industrialization and land-use changes have surpassed natural emissions, leading to substantial perturbations in the atmospheric abundance of chemical species. A major challenge is to measure these emissions, to understand the mechanisms that control them, and to extrapolate them at the regional and global scales. Modern atmospheric models cannot simply rely on preestablished emission inventories but must include emission models that account for complex biological and meteorological effects.

TABLE 18.4 Summary of the Emissions of Chemical Compounds to the Atmosphere

	CH_4	CO	NO_x	NMHCs
Natural emissions				
Wetlands	145 (115–175)			
Vegetation		110 (60–160)		400 (230–1150)
Soils			7 (5–12)	
Termites	20 (1–40)			
Hydrates	10 (5–15)			
Lightning			5 (2–20)	
Oceans	10 (5–15)	50 (20–200)		50 (20–150)
Anthropogenic sources				
Energy	110 (65–155)	500 (300–900)	22 (20–24)	70 (60–100)
Aircraft			0.5 (0.2–1)	
Landfills	40 (20–60)			
Waste treatment	25 (20–30)			
Agriculture				
Rice paddies	80 (30–120)			
Ruminants	85 (60–105)			
Animal waste	30 (15–45)			
Biomass burning	40 (10–70)	550 (400–700)	8 (3–13)	40 (30–90)

Source: Based on IPCC (1996).

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SURFACE-ATMOSPHERE EXCHANGES OF CHEMICAL COMPOUNDS AND GLOBAL CHANGE

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CHAPTER 19
AUTOMATED WEATHER OBSERVATIONS FOR ENVIRONMENTAL MONITORING

Janne Rinne

INTRODUCTION

Nearly all biological activity, including that of humans, takes place in the lowest part of the atmosphere, called the *atmospheric surface layer* (ASL). The ASL is also important for controlling energy and mass transfer between the surface and the atmosphere. Since meteorological conditions in the ASL affect the physical, chemical, and biological processes taking place on the surface of the earth, monitoring these conditions is important for environmental research.

The set of meteorological parameters required for a study depends on the nature of the investigation. For example, the minimum background information for an ozone monitoring station includes wind direction, temperature, and solar radiation (preferably for wavelengths associated with trace gas photodisassociation), whereas the background meteorological data for monitoring the water quality of a small lake should include wind speed, temperature, humidity, precipitation, and photosynthetic photon flux density.

The aim of this chapter is to offer practical information on surface weather measurements for nonmeteorologists. In the next section the basic structure of the atmosphere near the surface of the earth is described. The basic weather observation station used by national weather services is then described in the third section. The fourth section describes an automated weather station and discusses the infrastructure needed as well as requirements for special environments. The final section gives more detailed information on the sensors and their placement and requirements.

STRUCTURE OF THE ATMOSPHERE NEAR THE EARTH'S SURFACE

The lowest part of the atmosphere is divided into several layers according to the dynamics of the airflow within them. The *planetary boundary layer* (PBL) is defined as the part of

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the atmosphere which responds to surface forcing in time scales of less than few hours and thus responds to diurnal changes in solar radiation (Stull, 1988). Daytime PBL usually extends 1 to 2 km from the earth's surface. The lowest part of the PBL forms the ASL with a daytime height around 100 m.

The airflow in the ASL typically is turbulent. This means that air particles do not solely follow the mean flow but also go up and down and left and right, creating the gustiness of the wind (Fig. 19.1). Other parameters are also affected by the turbulence. Turbulence is the main vertical transport mechanism of substances in the ASL, being orders of magnitude more effective than molecular diffusion. Since there is random short-term variation in many parameters due to turbulence, time averaging is needed to obtain representative measurements of meteorological parameters.

Due to the response to radiation forcing, many meteorological parameters in the ASL, as well as their vertical profiles, have clear diurnal cycles. Solar radiation warms the ground and air just above during the daytime, creating the temperature profile shown in Fig. 19.2. A surface layer with this kind of temperature profile is *hydrostatically unstable,* and mixing in it is very rapid. During calm, cloudless nights, the ground is cooled by long-wave radiation, and the temperature profile shown in Fig. 19.2 is formed. The surface layer with this kind of temperature profile is *hydrostatically stable,* and vertical mixing is very weak in it. The wind velocity in the ASL increases with height, and the wind velocity profile is a logarithmic function of height in a hydrostatically neutral ASL. Since

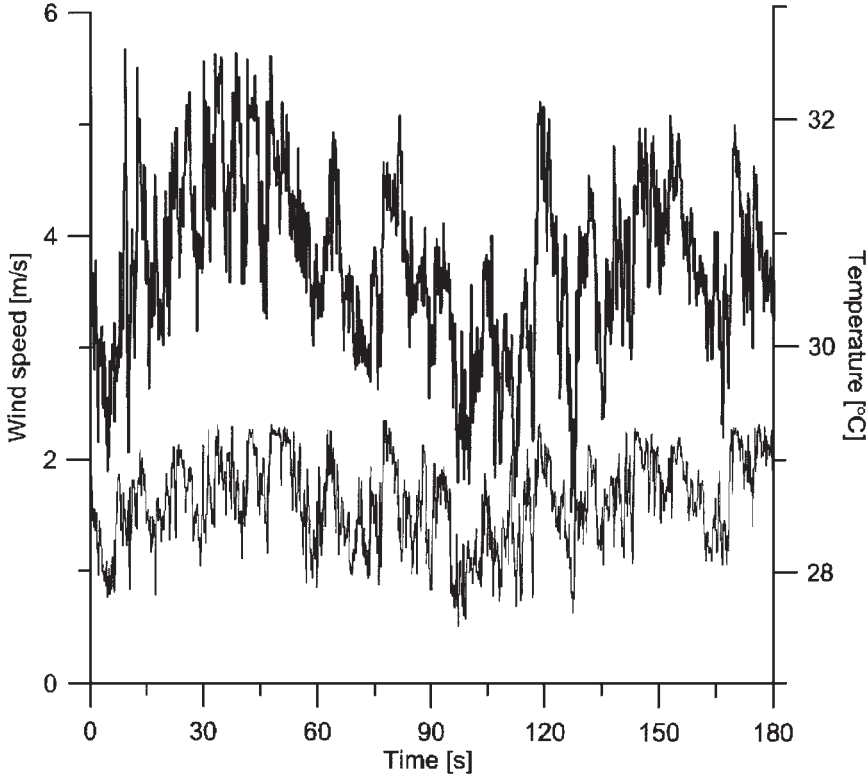

FIGURE 19.1 Wind and temperature in a turbulent flow.

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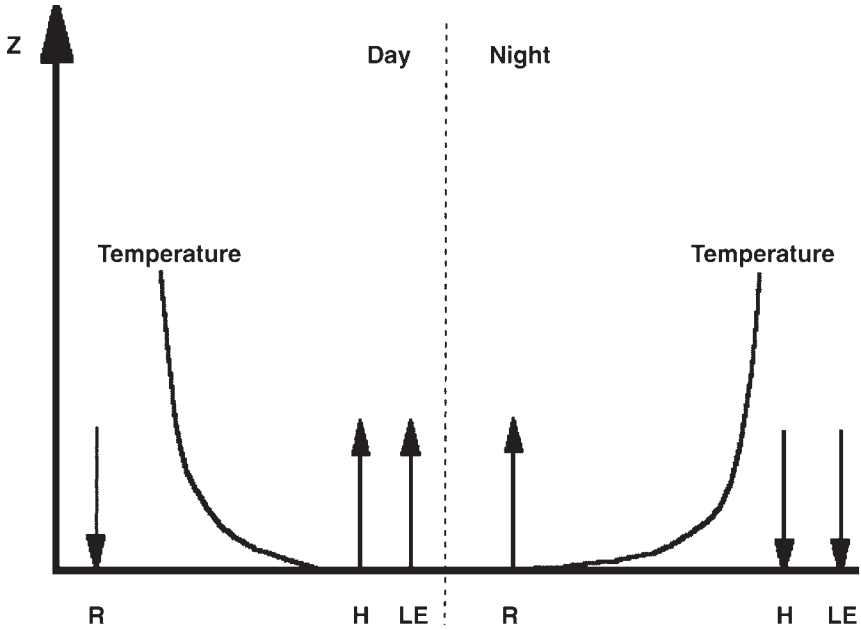

FIGURE 19.2 Temperature profiles and energy fluxes (radiation and sensible and latent heat) in the ASL at day and night.

many parameters vary with height, as discussed earlier, selection of proper measurement height is important.

Solar radiation is the driving force for the diurnal variation in the PBL. The main bulk of energy of the solar radiation is in the visible part the spectrum. The surface of the earth and the atmosphere radiate also, but due to their relatively low temperatures, the bulk of energy is in the long-wave part of the radiation spectrum. The chemical reactions in the ASL are affected by the short-wave part of the solar radiation spectrum, ultraviolet radiation being most important for photochemistry. The photosynthetic photon flux density (PPDF), or photosynthetically active radiation (PAR), is the part of the solar radiation spectrum used for photosynthesis by plants. The wavelength range of the PPFD is 400 to 700 nm, and its contribution to the total radiation depends on solar elevation and cloudiness. Since the activity of vegetation depends on the PPFD, it is an important parameter for many biological applications.

Depending on topography and surface characteristics, many meteorological parameters can vary considerably over small spatial scales. This variation is particularly strong during calm, cloud-free nights. The systematic small-scale variations in meteorological parameters are referred to as *microclimates.* An example of a typical nighttime microclimate is given in Fig. 19.3. Long-wave radiation cools air over hills surrounding a depression. This cold, dense air then flows into the depression, creating pools of colder air. Thus the nighttime temperatures in the depression tend to be lower than at nearby higher elevations. Other typical sites with distinct microclimates are lakesides and within and below vegetation canopies. The placement of a weather station should be such that it offers representative data for the phenomena being studied, and therefore, the influence of microclimates should be taken into account.

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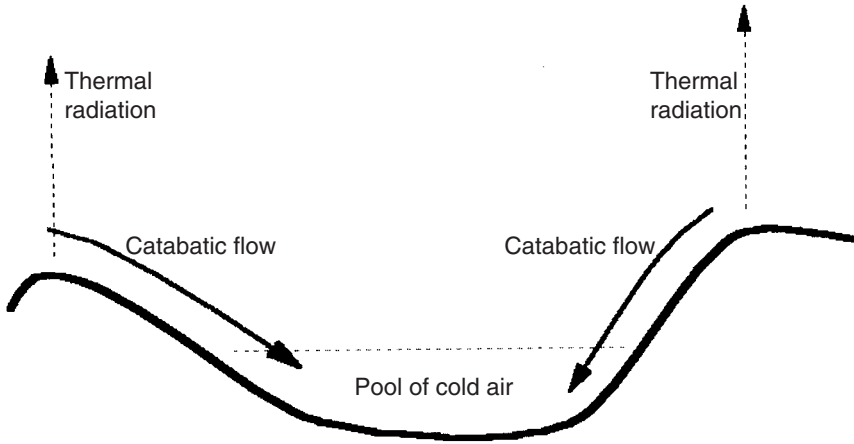

FIGURE 19.3 Example of microclimates (hill and a depression, drainage flow, pool of cold air).

SYNOPTIC WEATHER STATION

One of the cornerstones of modern weather prediction systems is the synoptic weather observation (SYNOP) network (Fig. 19.4). To ensure the representativeness and comparability of the SYNOP data, the observations are standardized. The observations are conducted four times a day at 0000, 0600, 1200, and 1800 Greenwich mean time. The stations measure the same parameters (Table 19.1) with more or less similar methods and instruments. In addition, the environments in which the stations are situated are standardized. Further information on the SYNOP stations can be found in the observation manuals (WMO, 1989, 1996).

For many environmental studies, synoptic weather stations can offer useful data. Even when an automated weather station is set up for the study, nearby SYNOP stations may offer longer time series of the past weather data. The SYNOP weather data also often are processed into climatological databases and published by national weather services. (e.g., FMI, 1991). In industrialized countries, the SYNOP station network usually is relatively dense and offers a large amount of weather data.

For many environmental studies, the major shortcoming of the SYNOP data is the lack of solar radiation observations. The radiation measurement networks tend to be sparser than SYNOP station networks. Furthermore, in many areas, such as undeveloped countries and oceans, the SYNOP station network is sparse, and the time resolution of the SYNOP data may not satisfy all applications.

AUTOMATED WEATHER STATION

An automated weather station (AWS) consists of a set of sensors, a data storage device, and an interface that converts the output of the sensors into a digital format that can be stored. In many cases, the data storage and interface are integrated into a single device called a *data logger*. If data are stored onto a computer disk, then a separate data-logging interface is used.

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TABLE 19.1 Parameters Measured at Typical Synoptic Weather Stations

Parameter	Measurement method	Measurement height
Temperature	Mercury, ethyl alcohol	1.25–2.00 m
Temperature maximum and minimum	Mercury	1.25–2.00 m
Grass minimum temperature	Mercury	25–50 mm
Pressure	Mercury column	
Humidity	Wet-bulb mercury thermometer	1.25–2.00 m
Wind speed and direction	Cup/propeller anemometer and vane	10 m
Precipitation	Manually operated rain gauge	
Visibility	Visual observation	
Weather phenomena	Visual observation	
Cloud cover and type, height of cloud base	Visual observation	
Snow cover, ground status	Visual observation	

Note: For detailed information, see WMO (1989, 1996).

The combination of sensors, as well as the exact placement of the automated weather station, depends on the data requirements of the study. If only basic weather data, such as temperature, humidity, solar radiation, and wind speed and direction, are needed, many standard AWS packages provided by instrument manufacturers (see Appendix 19A) are sufficient.

The second important issue for the design of an AWS is the infrastructure of the measurement site, including availability of AC power, traffic conditions, and a means for electronic communication. If there is no AC power line to the measurement site, then the system must run on batteries, and special attention has to be paid to the power consumption of sensors and data-logging devices. If the site is at a remote location with difficult access, then the system should be as maintenance-free as possible. An electronic communication line may be useful because then the data can be monitored from a central location and any malfunctions can be detected.

A list of parameters, important to many fields of environmental monitoring, that an AWS should measure is given in Table 19.2. The measurement heights given in the table are the same as in SYNOP observations, but they can be altered if there is a reason to do so. The AWS should be situated in an open area with no large objects nearby that shadow the radiation instruments or disturbing wind measurements.

The averaging period of the data depends on the application. Since typical sensors may not have very fast response times, there is no need to use an averaging time of less than 1 minute. Averaging also minimizes the effect of short-term random variation caused by turbulence. A 10 minute averaging time with six measurements per hour offers enough time resolution for most purposes. If there is a problem with the amount of data exceeding the memory size, longer averaging periods can be used, or only part of the data can be stored, e.g., one 10-minute average stored every hour.

Most of the commercially available AWS packages, as well as the one described earlier, are designed to be operated in relatively open areas, such as agricultural fields. They measure temperature and humidity typically at a height of 1.5 to 2.0 m and wind at less than 10 m. If the measurement environment deviates considerably from the open field, these AWSs may not be very practical. Good examples of such environments are tall forests and downtown areas of cities. Forest canopies often are over 10 m high and very dense. The micro-

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TABLE 19.2 Suggestion for Parameters Measured by a Basic AWS for Environmental Monitoring

Parameter	Device	Placement of the sensor
Temperature	PTR	1.2–2 m, inside a radiation shield, also at 0.2 m and/or 5–10 m if possible
Humidity	Polymer film	Close to the temperature sensor
Wind speed and direction	Cup or propeller anemometer, direction vane	3–10 m
Rainfall	Tipping bucket rain gauge	1–1.5 m
Global radiation	Thermopile	Depends on the shadowing objects
Net radiation	Thermopile	3–10 m depending on the homogeneity of the underlying surface and shadowing objects.

climate below a forest canopy can deviate substantially from the climate above. Deep street canyons in cities have their own wind, temperature, and radiation features. In these cases, tailored measurement systems are needed to give representative and meaningful information for whatever purpose the data will be used.

INSTRUMENTATION

Temperature

The suggested height of a temperature sensor is 1.2 to 2 m, which is the World Meteorological Organization (WMO) standard. The closer to the ground the sensor is, the more extreme temperatures it records. Additional measurement heights at higher levels can be useful in revealing strong temperature inversions. If the weather station is not in an open field, more than one measurement height may be needed to give meaningful temperature data. For example, in a forested site, one might use several temperature sensors through the canopy, the highest being just above the canopy. In an open field, a temperature sensor just above the ground can be used to reveal night frosts.

To prevent solar radiation from heating the temperature sensor, it must be mounted inside a radiation shield. These are usually small, white, naturally aspirated shelters made out of plastic or metal (Fig. 19.5). These work well if the weather is not calm. If very accurate temperature readings are needed and the radiation is intense, the radiation shield should be aspirated by a small electric fan.

The most common types of temperature sensors for AWSs are thermistors and platinum resistance thermometers (PTRs). The temperature measurement of these is based on the temperature dependence of the resistance of the sensor. The typical accuracy of these sensors is 0.3 to 0.5°C. A thermocouple is a device in which two wires, made of different metals such as copper and constantan, are connected from both ends, forming a loop. A temperature difference between the junctions creates an electric current in the loop. When the temperature of one of the junctions, called the *reference junction,* is known, the temperature of the other junction can be obtained from the current. In commercial thermocouples, the reference junction is the data logger. Thermocouples can be used where precise measurements are needed because the precision of the measurement can be around 0.01°C. A typical thermocouple application is measurement of the vertical temperature gradient in the surface layer.

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FIGURE 19.4 A synoptic weather station with a hut around temperature measurements and rain gauge.

An infrared radiation (IR) device can be used to measure surface temperature. This device measures the IR emitted by the surface. The radiation depends on the temperature but also on the emissivity. The emissivity of, for example, forest foliages is usually above 0.95 for the wavelengths used by IR thermometers. The IR temperature probes need regular calibration to give accurate data because their calibrations tend to shift. In addition, emissivity of the measured surface can change, e.g., by season. A detailed discussion of IR temperature measurements is given by Fuchs (1990).

Humidity

Most commercial humidity sensors today are based on the capacitance changes caused by water absorption in a polymer film. Since it is important to know the temperature of the sensor, humidity sensors often are mounted together with a temperature sensor. The accuracy of the polymer film sensors is usually 1 to 3 percent relative humidity. The operating range of polymer film humidity sensors is usually in the range of -40 to $+60°C$.

For more accurate humidity measurements, wet-bulb and cooled-mirror sensors can be used. In the former, there is a wet wick around an aspirated temperature sensor. The evaporation of the water from the wick cools the sensor, and the humidity is inferred from the temperature difference between dry- and wet-bulb temperatures. This is a standard method used in SYNOP stations, but its automation can be difficult. The wet-bulb measurements are also unreliable in freezing temperatures.

In the cooled-mirror devices, there is a temperature-controlled mirror that is cooled below the dew point. As the water vapor in the air condenses onto its surface, it is observed by reflection of a light beam from the mirror. The temperature of the mirror at the moment of condensation gives a direct measurement of the dew point. The cooled-mirror devices can

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measure dew points down to −80°C with great precision because the repeatability of the dew-point measurements by a cooled-mirror device can be 0.05°C and the accuracy 0.15°C.

Wind

Since wind velocity increases with height, a standard measurement height should be used to ensure the comparability of the data. The WMO standard for measurement height in an open field is 10 m, but lower heights also are used. The choice of representative measurement height can be difficult in such environments as forests and inner cities. In a forested site, an anemometer could be situated 10 m above the zero-plane displacement height or the canopy height. The effect of any objects shadowing the wind must be minimized. This is ensured by locating the anemometer where there are no shadowing objects closer than 10 times the height of the object.

There are two common types of wind speed and direction sensors: the cup anemometer with vane and the propeller anemometer. These usually offer enough accuracy and durability for most AWS applications. The rotation of the velocity sensor is read by a pulse train created either by contact closure of an optical sensor or by measuring the frequency of ac voltage created by a dynamo attached to the velocity sensor. The position of the direction sensor is read by an optical sensor or potentiometer.

In harsh conditions of high elevations and high latitudes, special attention is needed to keep wind measurement instruments working. Especially in the higher elevations, freezing can stall the instruments, causing interruptions to data. Anemometers with built-in heating are available for these conditions. Anemometers designed for very rough environments may have a higher threshold wind velocity, and they can have less sensitivity to changing wind. In freezing conditions, ice falling from overhead structures also can cause damage to the instruments.

During the past couple of decades, acoustic anemometers have gained popularity in studies of turbulence and related issues in the atmospheric surface layer. These instruments calculate the three-dimensional wind based on the time required for an acoustic signal to travel the same path between a transmitter and a receiver in opposite directions. Acoustic anemometers also provide measurement of air density, which can be used to calculate the virtual temperature. Acoustic anemometers usually measure wind and temperature at 10 to 20 times per second. Using acoustic anemometer data, parameters describing hydrostatic stability and vertical mixing in the surface layer can be calculated.

Acoustic anemometers do not contain any moving parts, which makes them reasonably reliable. They are, however, quite expensive, which restricts their use to special applications. In addition, the amount of data they can create is large: 144,000 values in an hour at a 10-Hz measurement rate. This sets some requirements for the data-acquisition system.

Rainfall

A rainfall sensor should be placed in an open area with no obstructing objects closer than four times the height of the object. Since wind can cause significant underestimation of the measured rainfall rate, the sensor should not be placed higher than 2 m. If the sensor is placed too close to the surface, in-splashing or snow accumulation can cause some overestimation. The rain gauges at SYNOP stations have windshields to reduce the wind error (Fig. 19.4). Most AWS instrument providers do not supply such shields for automated rainfall instruments.

Mechanical tipping-bucket devices are simple and inexpensive rainfall sensors. In these sensors, the rain is collected though an orifice with a diameter of 20 to 30 cm. A funnel leads water into a seesaw with two buckets for water. After a bucket fills up, the seesaw rocks, sending a signal to the data logger. The other bucket moves under the funnel, and the

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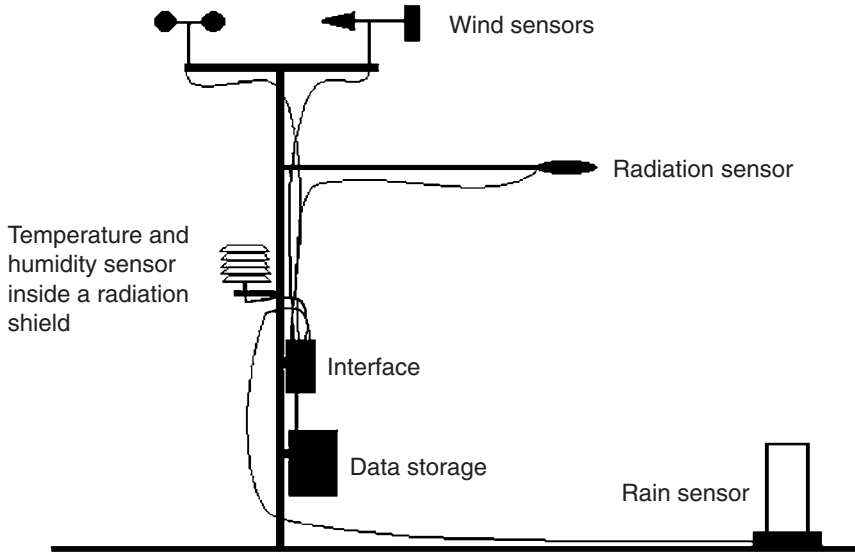

FIGURE 19.5 An AWS.

first one is emptied. The resolution of these devices is typically 0.25 mm. During extremely heavy rainfall, the measured rainfall rate can be affected by the limited capacity of the funnel to drain the collector. For measurement of snow and hail, the funnel can be heated. However, this leads to evaporation losses from the collector.

Another type of mechanical rainfall sensor is based on weighing. In these devices, the highest measurable rainfall rate is not limited by a funnel. These devices also can be used to measure snowfall when the collector is filled with an antifreezing substrate. Rainfall also can be measured using semiconductor devices. These devices measure the wetness of a heated film. These sensors usually give rainfall intensity classes (light, moderate, and heavy) but not the actual rainfall rate.

Radiation

There exists a cornucopia of sensors to measure different parts of the radiation spectrum (Table 19.3). Most of them measure radiation into a flat horizontal surface from the half sphere above or the total vertical radiation flux. Some of them are also designed to measure only direct solar radiation or diffuse radiation. The selection of the radiation sensors should depend on the nature of the monitoring.

Radiation sensors are classified into several quality classes by the WMO according to their properties. Thermopile devices are very accurate, and sensors based on them can be classified as secondary standards. The spectral response of silicon photocells is not uniform enough for them to have a high WMO classification, but they are still accurate enough for many environmental monitoring applications.

Placement of the radiation sensor should ensure an open path to the sky. According to WMO standards, there should be no obstructions more than 10 degrees from the horizon. The sensors should be well leveled. Especially with low solar elevation angles, a large error can be introduced if the sensor is even slightly inclined. Most radiation sensors are

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TABLE 19.3 Radiation Sensors

Sensor type	Parameter	Wavelength region	Wieving angle (steradians)
Pyrheliometer	Direct solar radiation	All	5×10^{-3} to 2.5×10^{-2}
Pyranometer	Global radiation (short-wave radiation)	0.3–3.0 μm	2π
Albedometer	Reflected short-wave (SW) radiation/global radiation	0.3–3.0 μm	4π
Pyrgeometer	Long-wave radiation	3.0–100 μm	2π
Pyrradiometer	Total radiation	0.3–100 μm	2π
Net pyrradiometer	Net total radiation (net radiation)	0.3–100 μm	4π
PAR-meter (PPFD-meter)	PAR: photosynthetically active radiation; PPFD: photosynthetically active photon flux density	400–700 nm	2π
Broadband UV radiometer	Ultraviolet (UV) radiation	UVA: 315–400 nm UVB: 280–315 nm	2π

Source: Based mostly on WMO (1996).

equipped with a bubble-leveling device to adjust the sensor. Otherwise, an external leveling unit should be used. When measuring radiation with downward-looking sensors such as net radiometers or albedometers, special care should be taken to ensure that the ground below the sensor is representative of the site. In addition, the measurement-tower structure can disturb the radiation measurements. To prevent water vapor from condensing inside the sensor heads, some desiccant usually is placed inside the sensor. This desiccant should be checked regularly and replaced when necessary. From time to time the sensor heads should be checked and cleaned of contaminants, such as dust and bird droppings.

Photosynthetic photon flux density under vegetation canopies can be of interest for many applications. The intensity of the radiation can be very nonhomogeneous, varying from shade to full sun. To get a representative value of the radiation under a canopy, one needs to use several conventional sensors or a line quantum sensor. In the latter, the sensor surface is larger than with conventional radiation sensors. The typical dimensions of the measuring surface of such an instrument are around 3×100 cm.

Atmospheric Pressure

Atmospheric pressure itself is usually not very important for environmental monitoring. However, it can give some insight into the weather phenomena on the measurement site. Many of the pressure sensors suitable for AWS use are fairly small semiconductor devices. These can be placed inside any shelter, which protects the sensor from rain and direct sunlight. However, the shelter should not be airtight.

Additional Measurements

This section gives an incomplete list of the instrumentation available for measurement of parameters more or less related to weather. Snow depth can be measured with an acoustic

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distance sensor. This device measures the elapsed time between the emission of an acoustic pulse and the return of a reflected one. This instrument does not disturb the snow surface, which is an advantage over traditional snow sticks. Using albedometer data, a thin snow layer can be distinguished from bare ground. An artificial leaf equipped with a resistance measurement grid can monitor leaf wetness.

Soil water status and evaporation are important in several biological, agricultural, and forestry applications. There exist some instruments suitable for measurements of soil humidity with an AWS. They are not suitable for very dry soil but can be used with more humid soils. The height of the groundwater table can be measured with a pressure-sensing device. This can be inserted into a well, and it measures the pressure caused by water above the sensor head. Soil temperature can be measured using inexpensive sensors. A detailed discussion of soil temperature measurement is given by Berard and Thurtell (1990).

The weather phenomena at the measurement site, including the form of rain, fog, etc., can be detected using a sensor based on forward scattering of radiation from raindrops, snowflakes, fog droplets, etc. Using particle size spectra and some additional information, the system classifies the weather. These instruments are expensive and are most suitable for permanent weather stations.

Data Logging and Storing

The choice of a data-logging device depends on various aspects such as the infrastructure of the site and the amount of data to be stored. At sites with an AC power supply, computer-based systems can be used. The advantages of these are versatility and the large storage capacity provided by the hard disk, which also stores the data during power outages, etc.

At sites with no AC power, the measurement system must run on batteries. These can be charged by solar or wind power or replaced by fresh ones from time to time. The data loggers that can run on batteries have no moving parts, and their memory can be volatile or nonvolatile. Volatile memory can be backed up with separate batteries. The data loggers that are designed to be independent of an external power source often are more rugged than the computer-based systems. This can be advantageous in harsh conditions with high humidity or temperature extremes. The disadvantage of these systems is the limited data storage capacity compared with the computer-based systems.

Many data-logger systems provide a means for remotely retrieving the data from the logger. The communication link can be a telephone line, a cellular phone link, or a satellite link. The first two methods need some infrastructure at of near the site but may be easier and less expensive to deploy than the third.

The data logger must be sheltered from ambient conditions, such as rain, excess heat, and moisture. The type of the enclosure for the logger depends on the logger type and weather conditions. For many rugged stand-alone data loggers, a simple watertight closure is sufficient. A container of some water-absorbing substance may be inserted inside the closure to help keep the electronics dry. For computer-based systems, heating and cooling of the closure often are necessary. Since computers release some excess heat, the temperature inside the closure is usually higher that the ambient temperature. The temperature inside a closure usually can be prevented from overheating by ventilating the closure with an electric fan. In colder climates, heating sometimes may be needed. A thermostat should control heating and cooling devices.

In areas with thunderstorm activity, lightning can induce harmful transient currents into sensor leads as well as ac power lines. Power outages also can cause data interruptions. An uninterruptible power supply (UPS) system can help the AC measurement system over short power outages. A transient current chopper should be placed between power supply and the UPS to prevent lightning-induced currents from damaging the system. Lightning-

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induced currents in sensor leads can damage data loggers because the leads are directly in contact with the electronics of the logger. The proper grounding of the data inputs of the logger can reduce potential damage.

Calibration

All sensors need to be calibrated regularly. The calibration interval and method depend on the sensor type. Some sensors can be calibrated in the field using a suitable standard; e.g., humidity sensors can be calibrated using a humidity generator that generates specified relative humidity into a chamber. Radiation sensors usually are calibrated by comparing them with a standard instrument, thus obtaining new calibration coefficients. By doing this comparison in different light conditions, response factors can be specified.

Some sensors need to be calibrated in a laboratory. Cup and propeller anemometers, for example, are calibrated in a wind tunnel. Since a sensor has to be removed for laboratory calibration for a longer period, continuous data can be obtained by replacing it with another sensor that has been calibrated. Running the newly calibrated sensor for some time side by side with the uncalibrated sensor can reveal drifts in the sensor response. This information can be used to correct the data during postprocessing.

Since calibration methods differ among instruments, readers are advised to refer to information provided by manufacturers for more detailed information.

FURTHER READING

Additional information on surface weather observations is available. This includes general overviews as well as detailed discussions on the measurement techniques of specific meteorological parameters. A description of synoptic weather observations is given by WMO (1989). Tanner (1990) has given a description of AWSs from the viewpoint of biological applications.

Basic meteorological textbooks include Ahrens (1994) and Stull (1995). A detailed description of the surface layer dynamics can be found in Stull (1998) and Kaimal and Finnigan (1994).

More detailed information on specific sensors can be obtained from the manufacturers of specific instruments.

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APPENDIX 19A
SUPPLIERS OF METEOROLOGIC INSTRUMENTS AND SYSTEMS

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815 West 1800 North
Logan, UT 84321-1784
Phone: 435-753-2342
Fax: 435-750-9540
http://www.campbellsci.com/

Davis Instruments
http://www.davisnet.com/

General Eastern Instruments
20 Commerce Way
Woburn, MA 01801
Phone: (781) 938-7070 or (800) 225-3208
Fax: (781) 938-1071
http://www.geinet.com/

Li-Cor
4421 Superior Street
P.O. Box 4425
Lincoln, NE 68504
http://www.licor.com/

Sci-Tec Instruments/Kipp-Zonen
http://www.sci-tec.com/

Vaisala Oyj
P.O. Box 26
FIN-00421 Helsinki, Finland
Phone (int.): (+358 9) 894 91
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CHAPTER 20
TETHERED-BALLOON PROFILING FOR BOUNDARY LAYER ATMOSPHERIC CHEMISTRY

Jim Greenberg and Alex Guenther

INTRODUCTION

The lowest layer of the atmosphere, the boundary layer, is directly affected by the earth's surface. The surface is the source of thermally and mechanically generated turbulence, which quickly mixes gases within the boundary layer. Nearly all important atmospheric trace gases are either deposited to or emitted from the surface. Some gases emitted from the surface are precursors of other trace gases formed in the atmospheric boundary layer.

Trace gas concentrations near the surface may be biased by nearby emission and deposition and therefore may not be representative of the entire boundary layer. A more accurate description of the general chemistry of the well-mixed boundary layer requires measurements aloft from tall towers (>200 m), aircraft, or tethered-balloon sampling platforms. Most towers allow the deployment of instrumentation to 60 m or without highly restrictive weight, size, and power requirements. While useful for characterizing the exchanges between the surface and the surface layer, most towers have a relatively small sampling footprint and may not be representative of the landscape-level phenomena. Aircraft platforms have the advantage that sampling may occur throughout the boundary layer, over an extended area, and with a variety of instruments. Aircraft sampling, however, is expensive, has limited temporal resolution, and is complicated by scheduling, flight hours, and aircraft configuration decisions. Also, it is not possible to sample different levels of an air column simultaneously from one aircraft.

Tethered-balloon sampling is, by contrast, relatively inexpensive, portable, characterizes the boundary layer with a footprint on the order of 10 km, and may be deployed for long periods of time without significantly increased cost. Payload weight, available sensors, and government regulations limit the applications of tethered-balloon sampling. However, the platform has been useful for describing the dynamics of the atmospheric boundary layer and, more recently, for estimating fluxes of trace gases from and to the surface, as well as for characterizing the chemistry of the boundary layer.

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BOUNDARY LAYER METEOROLOGY AND ATMOSPHERIC CHEMISTRY

The daytime atmospheric boundary layer extends from the surface to a capping potential temperature inversion. It is subdivided into the surface layer and the mixed layer. In the surface layer (up to several hundred meters), mechanical turbulence (frictional flow around objects and topography) is the most important transport mechanism and dominates over heights up to tens of meters above ground level. In the mixed layer, which extends from the top of the surface layer to the height of the capping inversion, convective turbulence is most important and extends to heights of hundreds of meters. An entrainment zone where exchanges take place between the atmospheric boundary layer and the free atmosphere above is located at the top of the daytime boundary layer. Since all emission and deposition occur in the boundary layer, its chemistry and composition may differ greatly from that of the free atmosphere above.

The terrestrial atmospheric boundary layer undergoes diurnal variations. During the night, radiative cooling creates a stable layer near the surface (50–200 m in depth). About a half hour after sunrise, the mixed layer begins to grow in thickness as a result of solar surface heating. The mixed layer grows by entraining free tropospheric air and reaches the residual capping inversion by midafternoon. Near sunset, solar surface heating and thermally driven convection stops, and a stable nighttime boundary layer re-forms. The interpretation of tethered-balloon measurements depends on the dynamics of boundary layer height, growth rate, and strength of convection.

The mean mixing-ratio profile of the tracer released from a homogeneous surface source is expected to decrease slowly with altitude in the mixed layer. The concentration will decrease with increasing altitude more rapidly near the surface (close to the source) and at the top of the atmospheric boundary layer (where tracer-free air is entrained). The sampling footprint generally increases with altitude as a consequence of increasingly higher winds aloft. However, the structure of the boundary layer may be more complicated. The presence of clouds, differential surface heating, advection, landscape variability, etc., may result in eddies of different scales that distribute the tracer unpredictably. For integrated sampling (solid adsorbent tubes, Teflon bags, filters, etc.), sampling time should average sufficiently over the scales of convective eddies because individual downdrafts and updrafts may contain substantially different trace gas mixing ratios. With typical vertical wind speeds of about 5 m/s, minimum sample times of 15 to 30 minutes are needed to integrate over a few of the largest convective eddies.

The distribution of chemical species, the incident radiation (frequency and intensity), and the dynamics of mixing determine the chemistry in any region of the atmosphere. Ozone (O_3), central to the chemistry of the atmosphere, is formed chemically in the atmosphere. A large percentage is transported downward from the stratosphere, where it is formed in abundance. It also may be formed in the lower atmosphere through its reactions with nitrogen oxides (NO_x) (which is either emitted from surface sources, largely anthropogenic, or produced by lightning) and volatile organic compounds (VOCs). Atmospheric chemical reactions produce other photochemical oxidants, and together these are responsible for cleansing the atmosphere of most trace gases released from the surface or produced by reactions in the atmosphere. Consequently, in addition to mixing and advection into the boundary layer, trace gases may be removed or created by chemical processes. Chemical losses, boundary layer growth, and advection of trace gases are balanced with surface sources and sinks to determine atmospheric concentrations.

Aerosols (particles) have been shown to affect the radiation balance in the atmosphere. Particles may scatter light and contribute to diffuse radiation, which may add to direct radiation to increase the intensity of some wavelengths involved in photochemistry. Absorbing aerosols, such as soot and black carbon, can attenuate incident solar radiation significantly

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TETHERED-BALLOON PROFILING FOR BOUNDARY LAYER ATMOSPHERIC CHEMISTRY

and affect the production and destruction of other chemicals. Both radiation and aerosol parameters may be observed from the tethered-balloon platform.

INSTRUMENTATION

Meteorological

Several meteorological parameters are important for describing the dynamics and trace gas profiles in the atmospheric boundary layer. The height of the boundary layer may be observed from potential temperature profiles that penetrate into the free atmosphere. Wind speed and direction are important for determining the footprint (area of influence) of measurements at any altitude level; instantaneous wind speed data also are useful in safe balloon operations. Pressure measurements determine the altitude of the sensors. Tethersondes that provide these measurements are available commercially as a whole or in part (Vaisala, Boulder, CO; Campbell Scientific, Logan, UT). A balloon tethersonde also may be constructed from commercial sensors. The data either are transmitted in real time to a ground receiver or may be stored on a data-logging device integrated into the sonde. Examples of vertical profiles of meteorological variables obtained with a tethered-balloon sounding system are given in Fig. 20.1.

Chemical and Aerosol Sensors

Chemical sampling aboard the tethered-balloon platform is constrained by weight, power consumption, physical size, etc. Lightweight chemical sensors for CO_2 (LICOR, Lincoln, NE; Vaisala, Boulder, CO), O_3 (2B Technologies, Boulder, CO; Vaisala, Boulder, CO), and aerosols (Particle Measurement Systems, Boulder, CO) are available commercially and

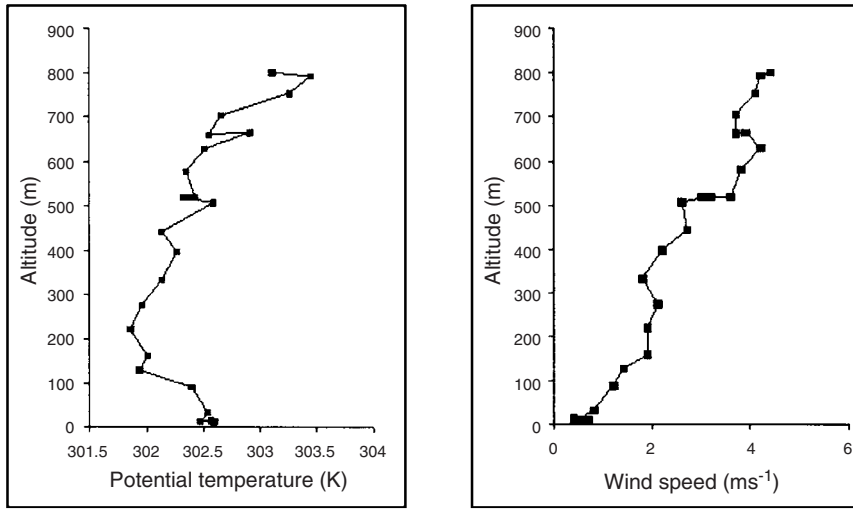

FIGURE 20.1 Vertical profiles of temperature and wind speed observed with sensors attached to tethered balloon.

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are suitable, with minor modifications, for tethered-balloon operations. These sensors have response times of several seconds and are battery powered. Examples of observations made with CO_2 and O_3 sensors are given in Fig. 20.2. Other commercially available sensors may be modified for balloon deployment.

Many of the continuous systems available for the measurement of trace gases have weight or power requirements that prohibit their use on tethered balloons. In other cases, the ability to measure low concentrations of trace gases or a wide variety of compounds requires large, integrated air samples. Tethered-balloon systems for integrated samples are not available commercially. Examples of custom-made systems are given by Greenberg et al. (1999).

Simple (Teflon, Tedlar) bag samplers have been deployed that combine a lightweight electric timer with an air-sampling pump to fill a bag. One or several of these timer, pump, bag systems are deployed at various points along the tether line, turn on and off simultaneously at predetermined times and sampling intervals, and provide altitude profiles of trace gases.

The collection of VOCs onto solid absorbent requires a more complicated design (Fig. 20.3). The volume of air passed through the cartridge must be controlled and integrated accurately. An onboard microcomputer controls sampling sequence and flow on each sampler. A flow sensor is installed downstream of the sample cartridges. The flow is read from the sensor by the computer, which modulates the pump speed to attain the desired flow rate. A pressure sensor records the true sampling altitude [altitude above ground $= Z - Z_0 = \ln(P_0/P)$]. Additional sensors record temperature and humidity continuously, allowing the package to operate as a temperature/humidity sonde.

PRACTICAL FIELD GUIDE

Balloons: Size and Lift

The weight of instrumentation that may be carried on the balloon platform (net lift) increases with volume of the balloon. However, at large sizes, heavier balloon materials are

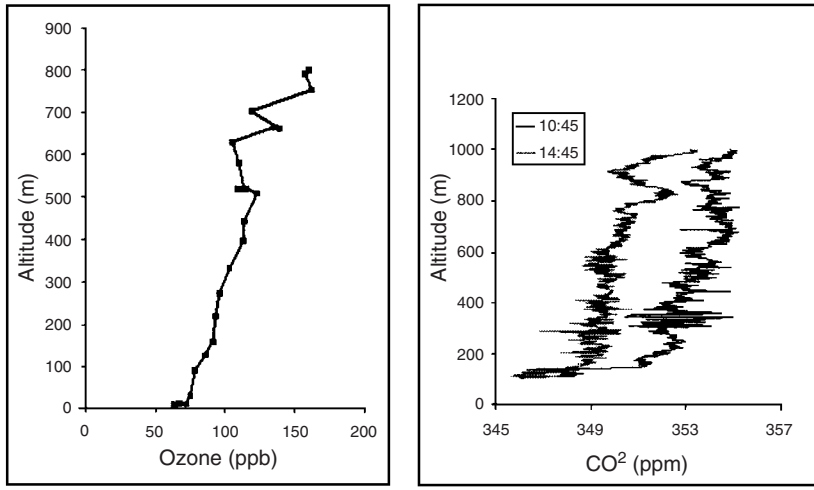

FIGURE 20.2 Vertical profiles of carbon dioxide and ozone observed with sensors attached to tethered balloon.

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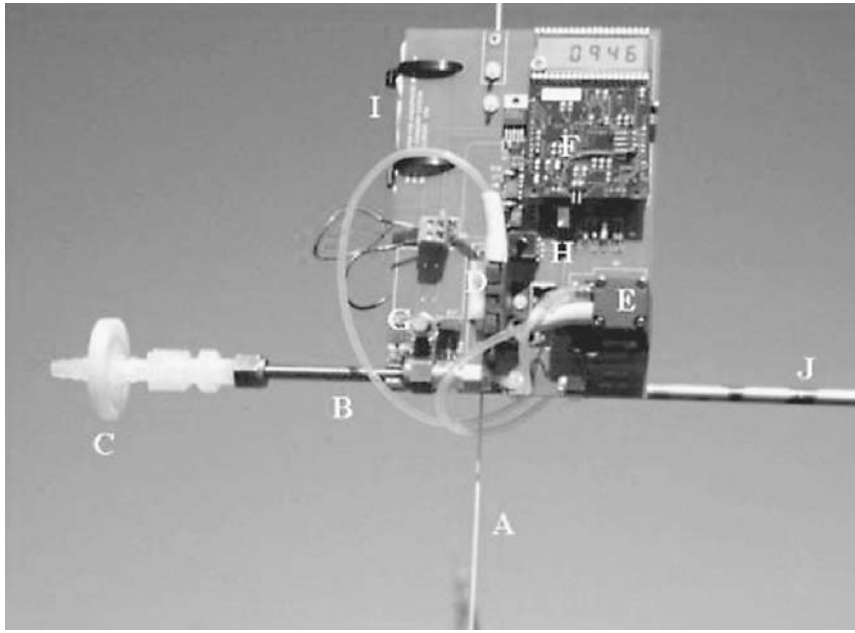
TETHERED-BALLOON PROFILING FOR BOUNDARY LAYER ATMOSPHERIC CHEMISTRY



Schematic of automated air sampling package (weight = 500g) showing the tether line (A), the solid adsorbent cartridge (B), the pre-filter (C) which removes ambient O_3, the flow sensor (D), the pump (E) for which speed is set and maintained by a microcomputer (F) after receiving feedback from flow sensor. Temperature and humidity (G) and pressure (H) sensors are recorded by the microcomputer (F) which also controlled the sampling process (start/stop time, flow rate). A wind vane (J) allows the package to orient into the wind. Power is supplied by a 15 v Lithium battery pack (I).

FIGURE 20.3 Atmospheric trace gas sampling system designed for attachment onto a balloon tether line.

sometimes substituted, which may decrease net lift generally for a specified balloon volume. Some balloons are designed aerodynamically to increase lift but are more difficult to control, especially in stronger winds (>7 m/s). Advertising blimps (Blimpworks, Statesville, NC; Aerostar Industries, Sioux Falls, SD) usually have little aerodynamic lift and are more stable; they will turn into the wind and fly above the tether point under low or moderate wind conditions (<12 m/s). Large spherical advertising balloons are the least expensive and have the most lift for a given volume of helium, but they tend to drift downwind at higher wind speeds. A 3-m^3 aerodynamic balloon, a 15-m^3 blimp, and a 15-m^3 spherical balloon typically lift about 500, 3000, and 6000 g at the surface, respectively.

Tether Lines

Lines for balloons often are high-density polypropylene, with specified breaking strengths (e.g., 240 or 360 lb). Typical tensions during sampling are very much less than the break-

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ing strength, but strong updrafts, wind shears, and sampling package drag add additional tension. Undamaged lines rarely break. Increased breaking strength usually is accompanied by increased line weight and may limit the maximum balloon altitude.

Line Attachments

The tether line is attached to a clasp, which can be connected or disconnected quickly from the balloon bridle. The line should be knotted to this clasp in a manner that minimizes the strain on the line (e.g., anchor bite knot). In many cases, instruments are designed or modified to attach to the balloon bridle or other attachment points on the balloon.

The tether-line attachment system must be designed to prevent damage to the line (cutting, restrictions, friction, etc.) and, in some sampling applications, to orient the sampler into the wind. A simple line attachment scheme is given in Fig. 20.4. Here, the line is wrapped around a polypropylene axle several times, and the ends of the axle are machined so that the line exits the end of the axle within its radius. Endcaps mounted on the sampling packages are spring-loaded onto these axles so that the package is free to rotate about the axle without touching the line. A tail is attached to the package to create enough wind drag to orient the package into the wind.

Winches

Lightweight winches (25 kg) are available for balloons of less than approximately 25 m^3 flown in light winds conditions (Vaisala, Boulder, CO). Winches normally run on ac line power but also may be run from lead-acid batteries with an appropriately sized power inverter. For larger balloons or where higher line tensions are expected, appropriately larger winches are available and may require a portable power generator. Sources of these devices include manufacturers of marine anchor winches (e.g., Sea-Mac Marine Products, Houston, TX). These winches usually have a level-winding mechanism that allows the line to be rewound evenly onto the winch's spool. Heavy-duty drill motors or automobile drive axles can be use to power home-made winches using line wound around a suitable spool, but these need to be guided for proper rewinding.

Storage

Between flights and overnight, it is usually best to moor the balloon at an altitude of 25 to 50 m with a heavy nylon line; the mooring area should be cleared for this distance. In most weather, even with wind gusts, the line tension will keep the balloon from hitting the ground. Hangers or storage buildings usually are unnecessary unless very high winds are expected. After deflation, the balloon must be stored dry and in a dry area or the plastic may deteriorate.

Filling Balloons

1. Balloons should be launched and tethered from a clearing free of trees, power lines, or other tall obstructions within 50 m of the winch or mooring. When the balloon is at lower altitudes, it may move erratically, even in light winds. Balloons also attract attention, so a secured area for deployments is best.

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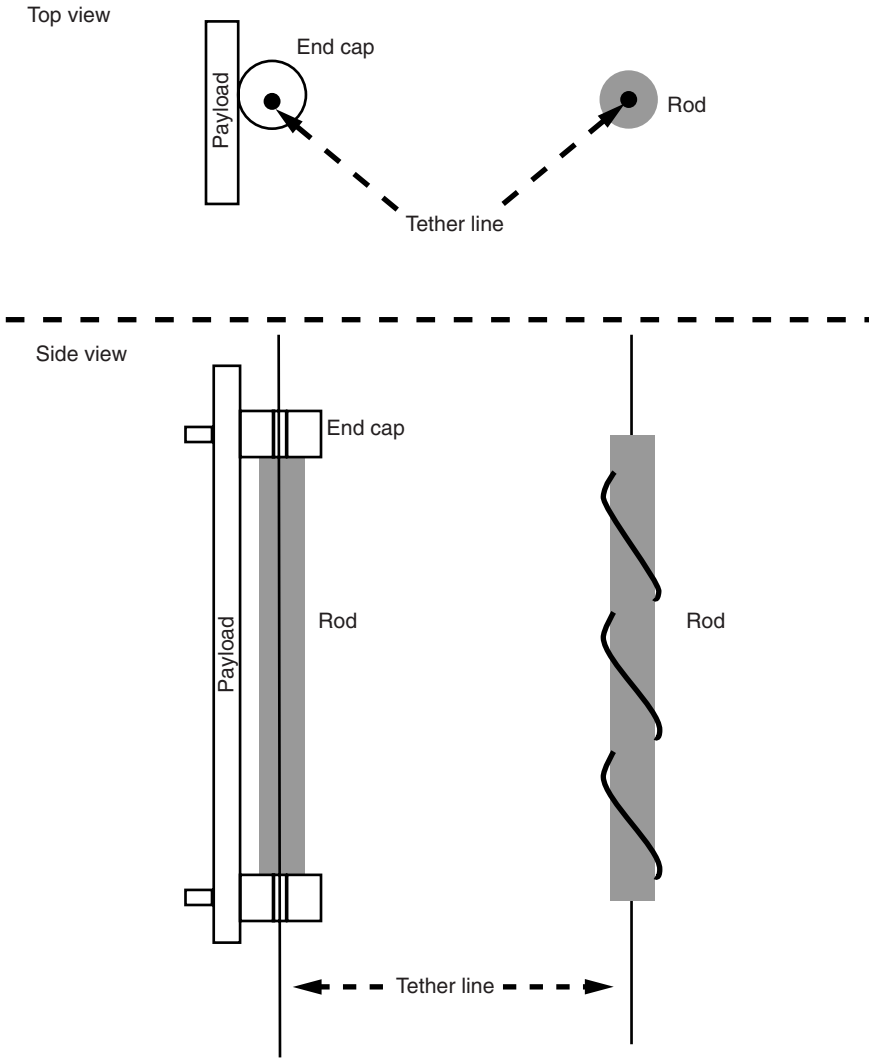

FIGURE 20.4 System for attaching sensors onto a balloon tether line.

2. Balloons may be filled with industrial-grade hydrogen or helium, although helium (approximately 98 percent purity) is used more often for safety reasons. Cylinders contain about 5 to 8 m^3. Extra helium should be purchased because even a balloon with no holes will lose approximately 1 percent of helium volume per day.

3. Spread the balloon out onto a large tarp. Some balloons have inflatable fins; others have rigid fins that must be attached and their support lines configured for proper flying. Prepare the fins before inflation because they may be difficult to reach and manipulate on a fully filled balloon. A 25- to 50-m nylon rope should be anchored

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firmly to the ground before inflation and will serve as a permanent mooring for the balloon between deployments. Wrapping the nylon rope around several helium cylinders and tying the rope onto the caps is usually sufficient, but even these may be moved by strong gusts. The winch is not heavy enough to serve as a mooring anchor. The anchor-line attachment should be smooth or attached to a swivel because movement of the balloon may wear the line against this anchor point. The free end of this rope should have a clasp that can attach to the balloon bridle. This is best done in advance of inflation to avoid runaway balloons during the filling process. Do not proceed with inflation if conditions are breezy because it will be difficult to control a partially inflated balloon.

4. Filling the balloon requires two people: one under the balloon, holding the tether rope and the balloon bridle, and the other holding the inflation nozzle and operating the helium cylinder valve. Balloons may be filled directly from the helium cylinder. The use of a high-pressure regulator is not advisable because filling rates exceed the normal operating range of regulators, and the regulator may be damaged. Some balloon manufactures sell a fill hose. A filling hose (approximately 5 m of a garden hose with the end connectors cut off) may be attached directly to the nipple of the cylinder fitting (for helium, CGA 580) with a hose clamp. The other end of the hose may be fitted directly into the balloon's inflation port. Begin the inflation slowly, increasing the flow in steps and taking care that balloon material does not cover the exit of the inflation nozzle (this may damage the balloon). Let the nose of the balloon up so that it fills first (the inflation point is usually at the tail). Most balloons have an inflation tape fixed to the top of the balloon; when this tape is stretched flat across the balloon surface, the balloon is fully inflated. However, the helium may expand a few percent as it warms inside the inflated balloon, so do not overinflate. When the balloon is fully inflated and the helium is shut off, the inlet must be sealed. In some balloons, there is a formal valve. Some balloons only have a sleeve through which they are filled; in this case, fold the sleeve lengthwise on itself, and then roll it up and secure with a rubber band. When full, raise the balloon up approximately 25 m on the heavy mooring line.

5. The winch must be firmly attached to the ground. Even when flying smaller balloons, gust winds may provide enough lift to topple or drag the winch; secure the winch on all sides to avoid this problem (e.g., chain it to the helium cylinders lying on the ground). The winch also may include a line guide, which must be extended fully when the balloon is attached to the winch. With someone providing tension on the tether line, pull out approximately 5 m of line. Lower the balloon with the rope, attach the tether line to the clip on the balloon bridle, slowly raise the balloon on the rope until the tether line is taut, and then feed out more line through the winch until the balloon is once again supported by the rope. This is a safe, short-time tether strategy to allow you to get ready for the balloon deployment.

6. Most small leaks are repaired easily with the balloon patch kit supplied by the manufacturer (usually just a roll of stretchy plastic tape). Finding the hole is a little more difficult. Most holes are punctures that result from contact of the balloon with a sharp object, so the holes may be small and multiple. Many can be located by visual inspection; others, by feeling with the hands. The holes are simply covered with a piece of the tape. It is easiest to apply the tape when the balloon is fully inflated because this allows the tape to be smoothed against the taut balloon. Long rips in the balloon also may be repaired with tape but may be done more easily with a deflated balloon. Be careful that any exposed tape inside the balloon does not stick to another surface of the balloon; it is sometime necessary to also tape inside the balloon to prevent this problem. Balloons usually can handle a lot of tape, but at some point a new balloon is the only reasonable solution.

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Flying Balloons

1. The electric winch should be connected to line or generator power first. Unroll approximately 5 m of tether line. Lower the balloon on the mooring line, and attach the tether line on the bridle hook.

2. While holding the balloon bridle, detach the mooring line. Before letting go of the bridle, check the tether line connection; this is your last chance. Raise the balloon to 20 m, if not ready for deployment.

3. The tether line may be marked at intervals (50 m) with permanent marking pens of various colors so that the approximate altitude of the balloon may be read from the length of line unrolled. This can be accomplished by measuring 50 m from the winch, walking 50 m with the balloon, and then letting the balloon rise vertically from a pivot point (a smooth metal rod is sufficient). A person at the winch marks the 50-m point on the line with the permanent marking pen and attaches a flag to the line. The winch is then used to unroll line horizontally until the flag reaches the 50-m mark, and the winch person marks the line again and attaches another flag. This is repeated for the length of the line. One coding system uses colored stripes for each 100 m (e.g., one stripe for 100 m, 5 stripes for 500 m), with a single black stripe at the intermediate 50-m marks. The pattern may be repeated for the next 500 m (another color may be used).

4. Balloon flight stability depends on line tension; raise the balloon at a slow rate (0.5–1 m/s) to maintain sufficient tension on the line. More tension will be experienced while pulling in the balloon; lowering at approximately the same rate is advisable. Lowering too quickly may cause the winch motor to overheat and trip a circuit breaker. Balloons do not always remain directly overhead, and the tether line is not usually straight and vertical. The altitude of sampling may vary with wind speed, turbulence, dynamic and static lift of the tethered balloon system, and aerodynamics and weight of the sampling platform.

GOVERNMENT REGULATIONS

Governments usually regulate the deployment of tethered balloons. Rules vary with locality and country. In the United States, the rules may be found in the *Code of Federal Regulations.* These are summarized below as an example of the types of regulations facing most balloon operators. Although the regulations are restrictive, waivers of specific regulations may be granted in many cases. The most restricted locations for deployment are in areas of commercial aircraft routes. Also, local air traffic control towers, in practice, have different tolerances for tethered-balloon deployments. Authorization must be granted at a higher level, but local control will determine flexibility of deployments. Military bases generally control their own airspace and are often very cooperative.

Summary of U.S. Code of Federal Regulation, Title 14 (Space and Aeronautics), Part 101, Sections 101.1–101.25: Moored Balloons, Kites, Unmanned Rockets and Unmanned Free Balloons

Subpart A: General

§101.1. Applicability. For operation in the United States. (1) Any balloon that is moored to the surface of the earth or an object thereon and that has a diameter of more than 6 ft (1.8 m) or a gas capacity of more than 115 ft^3 (3 m^3).

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§101.3. Waivers. No person may conduct operations that require deviations from this part except under a certificate of waiver issued by the administrator.

§101.5. Operations in prohibited or restricted areas. No person may operate a moored balloon in a prohibited or restricted areas unless he or she has permission from the using or controlling agency, as appropriate.

§101.7. Hazardous operation. (a) No person may operate a moored balloon in a manner that creates a hazard to other persons or their property; (b) No person operating any moored balloon may allow an object to be dropped therefrom, if such action creates a hazard to other persons or their property.

Subpart B: Moored Balloons and Kites

§101.13. Operating limitations. (a) except as provided in paragraph (b) of this section, no person may operate a moored balloon or kite (1) less than 500 ft from the base of any cloud; (2) more than 500 ft above the surface of the earth; (3) from an area where the ground visibility is less than 3 miles; or (4) within 5 miles of the boundary of any airport. (b) Paragraph (a) of this section does not apply to the operation of a balloon below the top of any structure and within 250 ft of it, if that shielded operation does not obscure any lighting on the structure.

§101.15. Notice requirements. No person may operate an unshielded moored balloon more than 150 ft above the surface of the earth unless, at least 24 hours before beginning the operation, he or she gives the following information to the Federal Aviation Authority (FAA) air traffic control (ATC) facility that is nearest to the place of intended operation: (1) the names and addresses of the owners and operators; (2) the size of the balloon; (3) the location of the operation; (4) the height above the surface of the earth at which the balloon is to be operated; and (5) the date, time, and duration of the operation.

§101.17. Lighting and marking requirements. (a) No person may operate a moored balloon between sunset and sunrise unless the balloon and its mooring lines are lighted so as to give a visual warning equal to that required for obstructions to air navigation in the FAA publication, "Obstruction Marking and Lighting." (b) No person may operate a moored balloon between sunrise and sunset unless its mooring lines have colored pennants or streamers attached at not more than 50-ft intervals beginning at 150 ft above the surface of the earth and visible for at least one mile (e.g., a 0.5-m length of surveyor's day-glow plastic tape to the line with a paper clip).

§101.19. Rapid deflation devices. No person may operate a moored balloon unless it has a device that will automatically and rapidly deflate the balloon if it escapes from its moorings. If the device does not function properly, the operators shall immediately notify the nearest ATC facility of the location and time of the escape and the estimated flight path of the balloon.

APPLICATIONS OF TETHERED-BALLOON CHEMICAL SAMPLING

Average Mixed Layer Trace Gas Concentrations

Emissions and emission rates have been measured at the leaf level for numerous species of vegetation (Guenther et al., 1995). However, it is very difficult to extrapolate atmospheric

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concentrations from leaf-level emission measurements. Landscapes vary in their species composition, distribution, and biomass density. The emission of biogenic volatile organic compounds (BVOCs) is species-dependent and also depends on light and temperature conditions. In addition, the diurnal cycle of boundary layer development and chemistry also influences the concentrations. The chemistry of the boundary layer is strongly affected by these emissions.

Representative landscape-level boundary layer concentrations may be measured from tethered-balloon platforms, where air may be sampled throughout the boundary layer and then related to regional average emissions. This method averages the contributions from individual leaves, temperatures, canopy leaf position, light conditions, etc. Observations at ground or canopy level are biased toward conditions near the surface and generally do not reflect average boundary layer concentrations observed from a tethered-balloon platform. Figure 20.5 illustrates this contrast. The concentrations of isoprene (a light-dependent emission from local vegetation) increases throughout the day at the top of the canopy as light and temperature increase, but the highest concentrations are late in the day when light levels are already much reduced from the midday period. The maximum concentration at canopy level late in the day is a consequence of continued, light-stimulated emissions into a shallow re-forming nocturnal boundary layer. In contrast the concentration of isoprene in the mixed layer is relatively constant during much of the daytime period, representing a balance between emission modulated by varying light and temperature, boundary layer growth and dilution with free tropospheric (isoprene-depleted) air, and chemical loss of isoprene in the atmosphere. The concentration of isoprene above the surface layer (not shown) often decreases dramatically in the late afternoon and after sunset because of atmospheric chemical reactions (likely with NO_3 radical). This reaction is much less important at canopy level in the late afternoon, while isoprene is still being emitted.

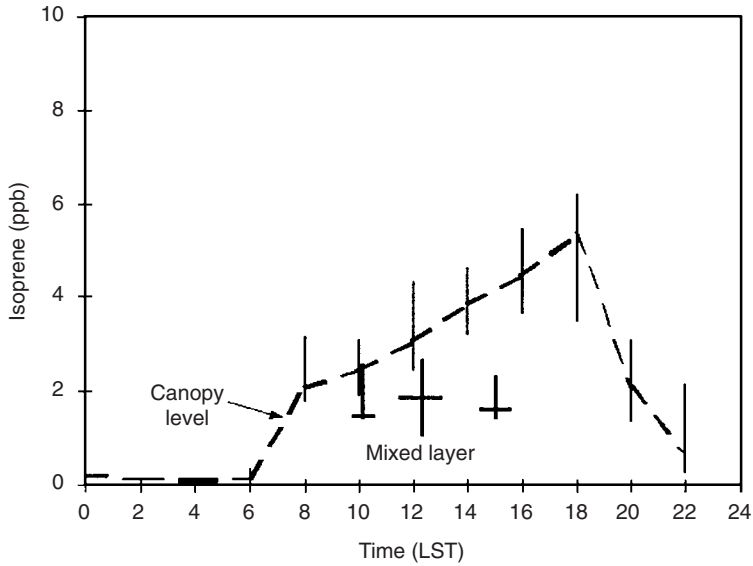

FIGURE 20.5 Vertical profile of average mixed layer concentrations. Mixed layer concentrations are constrained to a much narrower range than canopy-level concentrations.

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Estimating Sources and Sinks of Trace Gases

Tropical rainforests have several hundred woody plant species per hectare, with varying in percentages across landscapes. In temperate forests, woodlands, or grasslands, species diversity is lower, but many species have high BVOC emissions. While emission rates have been calculated for various landscapes from leaf-level or canopy-level models (Guenther et al., 1996a, 1996b), it is difficult to estimate atmospheric concentrations from the emissions because of insufficient information on species variability, average environmental conditions, seasonal vegetation cycles of individual species, etc. In addition, the direct measurement of emission fluxes from towers only reflects emissions from the footprint of the tower, whose species distribution and biomass densities may differ widely from the landscape average.

Tethered-balloon measurements of BVOCs have been used to estimate landscape-level emission fluxes by way of mass balance (MB) and mixed layer gradient (MLG) calculation techniques (Fig. 20.6). The MB approach is based on mass conservation; with several assumptions, the surface flux is equated with the chemical loss of the BVOCs in the atmospheric boundary layer. Average concentrations are calculated from measurements of BVOCs in the tethered-balloon profile, as well as mixed layer height, along with measurements or estimates of other chemical variables (i.e., ozone, NO_x, radiation, etc.). In the MLG approach, an emission flux is adjusted to reproduce the observed BVOC concentrations in the tethered-balloon profile from meteorological observations (Guenther et al., 1996a).

Observation of Cloud Processes

Aerosols (particles) in the atmosphere have received renewed attention in atmospheric chemistry, meteorology, and climate-change studies. Aerosols in the atmosphere may scatter or absorb incoming solar or outgoing terrestrial radiation, affecting the radiation avail-

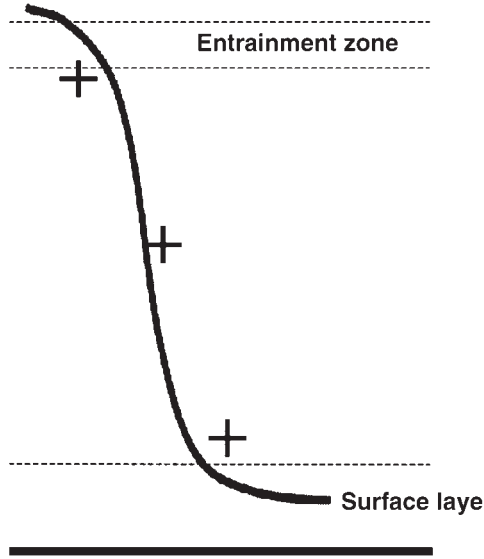

FIGURE 20.6 Mass balance model and mixed-layer gradient models for estimating surface fluxes using concentration profiles measured from a tethered-balloon platform.

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able for atmospheric chemical reactions and the radiation balance of the earth system. Aerosols also may serve as cloud condensation nuclei and therefore are responsible for cloud formation. Aerosol number density and size distributions vary considerably inside and outside clouds. These differences rarely can be observed at ground level, where clouds are encountered only rarely.

Figure 20.7 illustrates a tethered-balloon profile of the number density of aerosol particles in several size ranges in and out of clouds. A commercial particle counter (Abacus, Particle Measurement Systems, Inc., Boulder, CO), weighing approximately 1 kg, was flown from the surface to 1000 m in the Brazilian Amazon primary forest (Floresta Nacionale Tapajos) near Santarem, Brazil. The profile represents the balloon descent on February 12, 2000 (14:57–15:20 LDT). Near the surface, mostly smaller-sized particles are measured. At approximately 700 m, the base of a cloud is clearly illustrated by the changes in the number densities. Small particles (<300 nm) grow into larger particles (condensation), and the number of larger particles (1000–5000-nm cloud droplets) increases simultaneously.

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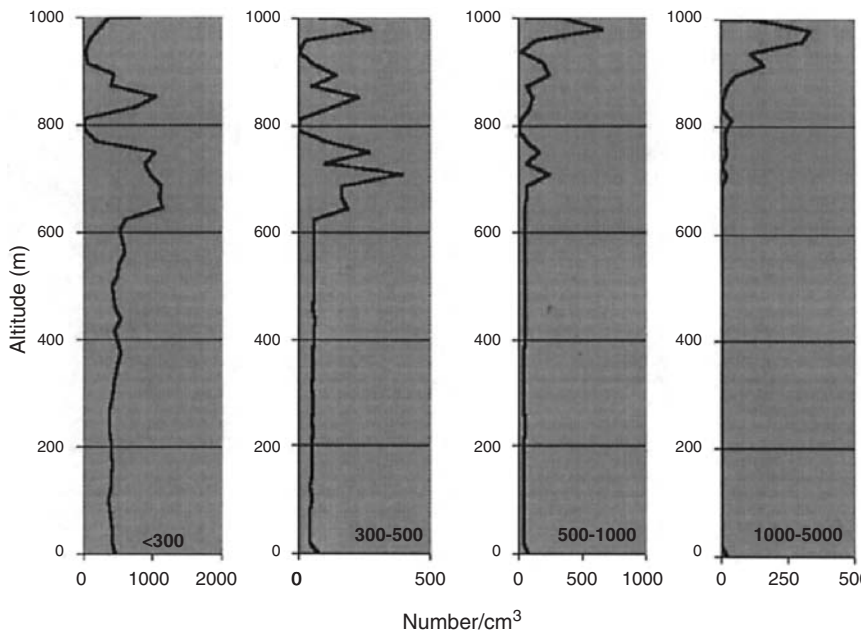

FIGURE 20.7 Boundary profile of aerosol number densities above the Amazon tropical forest.

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CHAPTER 21

SAMPLING OF ATMOSPHERIC VOLATILE ORGANIC COMPOUNDS (VOCS) WITH SORBENT TUBES AND THEIR ANALYSIS BY GC-MS

Paolo Ciccioli, Enzo Brancaleoni, Massimiliano Frattoni, and Christophe Maris

INTRODUCTION

Experimental evidence collected over the last three decades has shown unambiguously that the accumulation in air of volatile organic compounds (i.e., all organic compounds with a vapor pressure greater than 0.13 kPa) might represent an important source of risk for human health (Speijers, 1993; Caldwell et al., 1998) and the environment (Finlayson-Pitts and Pitts, 1986; Rowland and Molina, 1994; Graedel and Crutzen, 1995; Calvert, 1997).

National directives have been promulgated in the United States and the European Union (EU) to force local and national authorities to control VOC emissions through the best available techniques. More important, international protocols (UNEP, 1987; UN-ECE, 1991) have been signed to control the emission of VOCs and their transboundary fluxes. Since different abatement strategies need to be followed as a function of the spatial and temporal scales in which potential adverse effects of VOCs and their degradation products can be observed, it is useful to classify organic pollutants according to the scheme reported in Table 21.1 (Ciccioli, 1993a, 1993b). Table 21.1 is of general use regardless of the criteria adopted by the national legislatures to reduce the impact of VOC emissions on human health and the environment. It also summarizes the main reasons why VOC monitoring is required and the typical spatial and temporal domains where it can be accomplished.

The proposed scheme suggests that the most rational approach to provide reliable answers to decision makers is to select the monitoring strategies and hence the analytical methodologies to be adopted for data collection as a function of the specific effect to investigate. This choice is dictated by the fact that no one of the analytical methods available today is capable of meeting the different requirements necessary to investigate all the effects of VOCs in space and time. While detection limits of few parts per trillion by volume (pptv) are needed, for instance, for the monitoring of VOC-STRAT and VOC-CLIM in remote sites, sensitivities of the order of parts per billion by volume (ppbv) and, in some instances,

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TABLE 21.1 Classification of Volatile Organic Compounds (VOCs) According to Their Possible Effects on Human Health and the Environment

1. Classification

VOC-TOX	VOC for which evidence of toxicity to human, animals, and plants at trace levels has been collected through epidemiological studies
	VOC for which acute and chronic episodes have been documented through in vivo or in vitro laboratory tests carried out with well-recognized and standardized procedures
VOC-OX	VOC characterized by high photochemical ozone and PAN creating potentials (or equivalent indices)
	VOC involved in photochemical and acidification processes occurring in the atmosphere
VOC-STRAT	VOC characterized by high depletion potentials of stratospheric ozone
VOC-CLIM	VOC responsible for the thermal trapping of infrared radiation (greenhouse gases) or for the changing of the optical properties of clouds

2. Reasons for which monitoring of VOCs in air is required

a. To alert the population in the case of accidental release of air toxics in the atmosphere	VOC-TOX
b. To assess short- and long-term exposure of humans, animals, and plants to criteria pollutants	VOC-TOX, VOC-OX
c. To validate prediction models	VOC-TOX, VOC-OX, VOC-STRAT, VOC-CLIM
d. To assess the efficacy of control strategies	VOC-TOX, VOC-OX, VOC-STRAT, VOC-CLIM
e. To investigate the role played by VOCs in affecting short- or long-term equilibria of the earth	VOC-OX, VOC-STRAT, VOC-CL IM

3. Spatial domains of VOC monitoring, areas of the monitoring network, typical grid sizes and frequencies of data acquisition

Class	Type of scale	Area of the monitoring network (km^2)	Typical grid size (km^2)	Time between sample aquisition
VOC-TOX	Local	<2000	4–25	Seconds to a few hours
VOC-OX	Local	<2,000	4–25	Seconds to a few hours
	Synoptic	4,000,000	400–2500	4–24 hours
	Global	Entire hemisphere	10^4–10^6	Days to weeks
VOC-STRAT	Global	Entire hemisphere	10^4–10^6	Days to weeks
VOC-CLIM	Global	Entire hemisphere	10^4–10^6	Days to weeks

Note: Main reasons for which ambient monitoring is required and typical spatial domains in which monitoring should be performed.

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even parts per million by volume (ppmv) are sufficient for tracking the plume generated by the accidental release of VOC-TOX from industrial deposits. Although the adoption of a specific monitoring strategy greatly simplifies the analytical aspects of VOC monitoring, it is not always possible to cover the entire number of components responsible for a given effect. For this reason, many countries have prepared lists of components to be monitored with high priority for each one of the classes of VOCs listed in Table 21.1.

The need of priority lists is also dictated by the fact that the environmental effects of VOCs might differ by several orders of magnitude, and some components present at trace levels in the atmosphere can be more effective than the most abundant ones. The case of 1,3-butadiene and benzene, which are both classified as important VOC-OX and VOC-TOX, serves well to illustrate this point. It has been shown that the potentials for photochemical ozone production displayed by these components are so different that 40 pptv of 1,3-butadiene can generate 8 times the quantity of ozone produced by 240 pptv of benzene in the polluted air masses formed over the British Islands (Derwent, 1999). Analogous predictions can be made for the potential toxicity because it has been estimated (Caldwell et al., 1998) that the exposure to 0.0036 $\mu g/m^3$ of 1,3-butadiene generates the same cancer risk as exposure to 0.12 $\mu g/m^3$ of benzene.

The recent development of accurate indices for quantifying the potential impact of individual components on human health, tropospheric ozone production, earth warming, and stratospheric ozone depletion explain why the practical utility of total nonmethane hydrocarbons has been questioned and analytical methods capable of providing detailed information on specific components have been developed and tested. They are listed in Table 21.2 together with the advantages and disadvantages associated with their use.

Although unsuitable for alerting the population in the case of accidental release of organic pollutants and for checking the compliance of VOC emissions from stationary sources with national legislation (Ciccioli, 1993a, 1993b), gas chromatograph (GC) monitors have never been replaced by other systems in monitoring networks for VOCs. The reason for this success, which can be dated back to the early 1970s, is linked to the fact that although slow in response (the faster GC analyzers have response times of 2–3 minutes), they are the only system that provides a comprehensive view of VOCs present in the atmosphere at the sensitivities requested by the various monitoring strategies listed in Table 21.1.

Another desirable feature of GC systems is that any apparatus that has been produced in the last 20 years can be adapted easily to the monitoring of VOCs without losing any of its original capabilities. A wide selection of injection systems is, in fact, available on the market for the online monitoring of VOCs as well as for the analysis of samples collected over the domain where the impact of VOCs is expected to occur. This is possible because out-of-line sampling of VOCs can be performed on passivated canisters (U.S. EPA, 1999) or traps filled with solid sorbents (U.S. EPA, 1997), and they can be analyzed later in the laboratory. The design of online and out-of-line injectors for the monitoring of VOCs by GC is so simple that the construction of homemade systems is quite common and, as we will see later, advantageous in practice. Commercial and homemade injection systems can be attached to the GC through a small hole in the thermostatic chamber using commercially available connectors.

The identification of VOCs by this type of monitor is ensured by the selectivity of the GC column and by the specificity of the detectors to which it is connected. For some classes of VOCs listed in Table 21.1, a judicious selection of the column is sufficient for the quantification of priority components with nonselective detectors (such as flame ionization detection, or FID). In other cases, the use of selective detectors is required to avoid the interference of coeluted compounds. Some detectors, such as the electron capture detector (ECD), the photoionization detector (PID), and the flame photometric detector (FPD), are used widely because they combine an excellent sensitivity with very high selectivity toward specific components (Ciccioli, 1993b; Cao and Hewitt, 1999). It is possible to detect, for instance, some halogen-containing compounds present at pptv levels in a given

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TABLE 21.2 Methods for Monitoring VOCs in the Atmosphere

Method C	Advantages	Disadvantages
Optical methods Differential optical absorption (DOAS) Fourier transform infrared (FTIR)	Short response time (seconds) Unattended operation Remote sensing capabilities Monitoring over large areas	Limited number of compounds that can be monitored (DOAS) Insufficient sensitivity for the monitoring of background concentrations (FTIR) Difficult calibration
Mass spectrometric methods Proton transfer mass spectrometry (PT-MS) Chemical ionization mass spectrometry (CI-MS)	Short response time (from seconds to minutes) High sensitivity (pptv) Simultanous monitoring of VOCs in a wide range of molecular weights	Impossibility to distinguish isomeric and isobaric components High cost for the instrumentation Single-point monitoring Skilled personnel required
Spectroscopic methods Tunable diode laser (TDLAS) Induced fluorescence (IF) Chemiluminescence	Short response time (seconds) High sensitivity (pptv)	Limited number of compounds that can be monitored High cost for the instrumentation Single-point monitoring Skilled personnel required
Chromatographic methods Gas chromatography (GC) High-performance liquid chromatography (HPLC)	Simultaneous monitoring of a wide number of VOCs High sensitivity Possibility to identify and quantify isomeric and isobaric components General use instrumentation	Long response time (minutes to hours) Long time for data processing Skilled personnel required
Colorimetric methods	No skilled personnel required Selectivity	Insufficient sensitivity for ambient concentrations

*For more details on these techniques, see Ciccioli and Cecinato (1992) and Ciccioli (1993b).

air mixture with an ECD without any interference from hydrocarbons that are present in the same mixture at ppbv levels.

In complex airsheds, such as those carrying pollutants from some urban and industrial areas, the combined use of selective detection and GC retention may not be sufficient for positive identification of certain components. The number of VOCs in the sample can be so great (more than 150 compounds) that frequent overlap occurs between eluted compounds. Because of these limitations, mass spectrometry (MS) has become the preferred method for the monitoring of VOCs with GC systems. With this technique, positive identification is achieved through analysis of the mass spectra or use of specific fragments. It is sufficient that coeluted compounds generate different sets of ions in the fragmentation pattern of the mass spectrum to make their identification possible. The selectivity of the column remains, however, a key factor for the quantification of isomeric VOCs because they often display similar fragmentation patterns in addition to having the same molecular ion.

Although the advantages of GC-MS in the analysis of VOCs was demonstrated more than 25 years ago (Ciccioli et al., 1975), the apparatuses available at that time were too expensive to be used on a routine basis. Moreover, the use of packed columns limited the

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number of VOCs that could be identified to 40 to 50 components due to the low efficiency of packed column and the limited transmission of sample into the ion source. A great improvement in VOC monitoring capabilities has resulted from the development of benchtop mass spectrometers, powerful personal computers, and fused-silica capillary columns, which are more resistant to thermal and mechanical stress than glass columns. In particular, the weight and energy demands of the GC-MS systems have been reduced to such a point that instruments can be installed in the field (Yokouchi et al., 1993; Daughtrey et al., 1998) or in remote sites where they can run unattended for long periods (Helmig and Greenberg, 1994).

In the out-of-line sampling mode, there are no limits to the type of samples that can be analyzed by GC-MS as long as the quality of the sample can be preserved. Since both passivated canisters and traps can be installed on aircraft and tethered balloons, GC-MS methods also have been used to study the vertical distribution of VOCs in the troposphere (Guenther et al., 1996) and their emission and deposition processes by micrometeorological techniques, such as relaxed eddy accumulation (REA) (Valentini et al., 1997). It is not surprising, therefore, that MS detection is one of the methods recommended by the U.S. Environmental Protection Agency (EPA) for the analysis of VOCs (U.S. EPA, 1997, 1999).

As commonly happens with methods dealing with trace level determinations, the accuracy of the final results depends not only on the selection of the instrumentation and the quality of the material used but also on the way each individual step is executed. For instance, the preparation, cleaning, and storage of traps are quite critical for the achievement of satisfactory results, whereas the number of components that can be detected by GC-MS depends on the experience of the operator in the identification of organic components. Some of these procedures are described in great detail in the compendium of methods for the determination of toxic organic compounds in ambient air issued by the U.S. EPA; others are left to the experience of the user.

The purpose of this chapter is to cover those theoretical and practical aspects of the GC-MS analysis of VOCs that, although crucial for the accuracy of the final result, are seldom discussed in the technical literature. We will restrict our attention to methods using adsorption traps for the collection of VOCs because practical aspects are more critical for a successful analysis, and they are not well covered by other references. It is also an area where a higher degree of standardization is needed and future developments are possible.

COLLECTION OF VOCs WITH SORBENT TUBES

Solid Adsorbents for VOC Collection

General Features. A careful choice of the adsorbing material is a fundamental prerequisite for the successful identification and quantification of VOCs by GC-MS because the trap must be able to quantitatively retain the compounds of interest at ambient temperature and to release them by thermal desorption without any degradation of the sample. The materials that better satisfy these requirements are the ones that mainly interact with organic molecules through van der Waals forces because they provide a linear isotherm of adsorption for many organic compounds of interest in atmospheric chemistry, radiative forcing, tropospheric ozone depletion, and epidemiological studies. This means that the ratio between the concentrations of a compound in the adsorbed phase (C_s) and in the gas phase (C_m) is constant at a given temperature T, and plots of C_s versus C_m are described by a straight line passing from the origin. The slope of this curve is called the *adsorption coefficient* K_a. Materials characterized by a linear isotherm of adsorption in a wide range of concentrations produce gaussian peaks when used as solid support in gas chromatography.

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Unfortunately, there are no adsorbents in nature that are able to provide a linear isotherm of adsorption for all VOCs present in air. Even the most homogeneous materials contain some sites in which interactions with the adsorbed molecules occur through hydrogen bonds and/or strong dipole-dipole forces. Compounds able to interact with these sites (called *active sites*) are characterized by a nonlinearity of the adsorption isotherm and produce nongaussian peaks in gas chromatography. Figure 21.1 shows the different shapes of the gas chromatographic peaks that are generated by the nonlinearity of the adsorption isotherm. If the adsorption isotherm shows negative deviations from the linearity, the gas chromatographic peak has a front that is sharper than the tail (tailed peak). In the opposite case, the tail is sharper than the front (overloaded peak).

Several methods have been developed to reduce or eliminate the nonlinearity of the adsorption isotherm, but the most successful one cannot be applied to trapping materials for VOC collection. Since deactivation is obtained by depositing over the sorbent surface small amounts of a high-molecular-weight compound containing polar groups in the molecule (Bruner et al., 1973; Di Corcia and Liberti, 1976), even small losses of the liquid modifier during the thermal desorption step can cause severe artifacts in the analysis of VOCs. Thermal treatments at 1000°C using a flow of hydrogen (Bruner et al., 1976), although highly effective in reducing the number of active sites present on graphitic materials, cannot completely remove them from the surface.

It is evident from the preceding discussion that the adsorbents used for VOC collection exhibit a variable degree of nonspecificity as a function of the chemical nature of the material used, the impurities present in it, and the surface treatments that have been done to

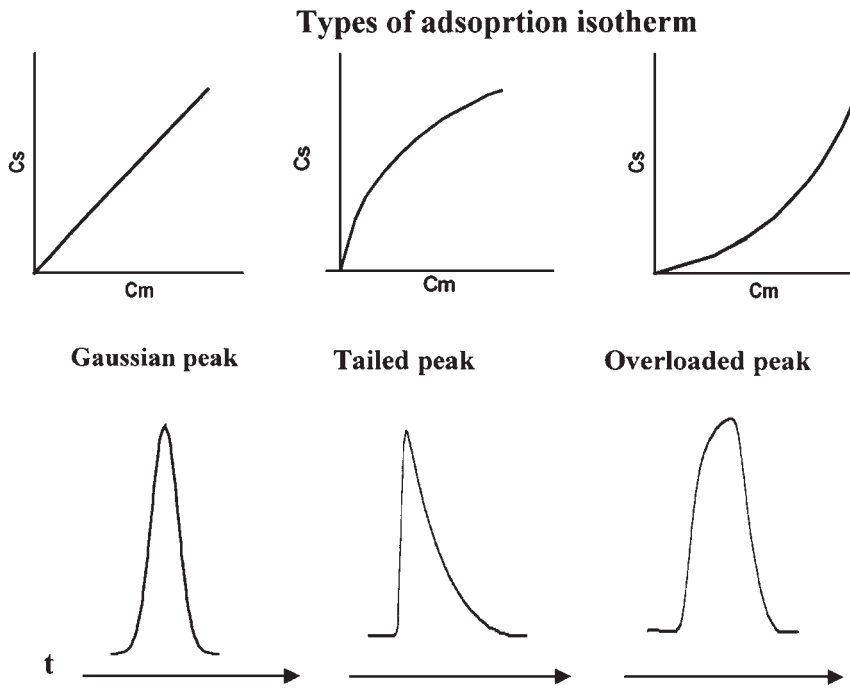

FIGURE 21.1 Shape of the gas chromatographic peak as a function of the adsorption isotherm displayed by a compound over a solid sorbent.

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remove them. According to the approach proposed by Kiselev (Kiselev and Yashin, 1969; Avgul et al., 1975; Gregg and Sing, 1982; Matisova and Skrabatova, 1995), it is possible to define the degree of nonspecificity of an adsorbent by looking at the interactions it has with four different groups of chemical compounds. Examples of the classes of VOCs that can be used to test the degree of nonspecificity of solid sorbents are

Group A:	*n*-Alkanes
	Spherical symmetrical shells
	σ bonds
Group B:	Aromatic, halogenated hydrocarbons and ketones
	Electron density concentrated on bonds/links
	π bonds
Group C:	Organometallics
	Positive charges (+) on peripherical links
Group D:	Primary alcohols, amines, and carboxylic acids
	Concentrated electron densities
	Positive charges (+) on adjacent links

Based on the analysis of the adsorption isotherm they give with these groups of organic chemicals, adsorbents have been classified into three classes (called classes I, II, and III). However, this classification is too broad for the type of adsorbents used for VOC collection because they mainly belong to classes I and III. Table 21.3 lists some of the most common adsorbents used for the collection of VOCs in air and emission samples together with their most important features. As a practical rule, the highest degree of nonspecificity is displayed by the adsorbents showing the lowest affinity for water (hydrophobic materials) and very polar compounds belonging to group D, with a lack of micropores and specific surface areas smaller than approximately 500 m^2/g.

Adsorption and Retention Mechanisms on Solid Surfaces: Definitions, Theory, and Useful Concepts for VOC Collection. The capability of a material to quantitatively retain a compound *n* is measured by its adsorption capacity C_n, which is defined as the maximum amount of *n* that can be collected by a fixed weight of adsorbent (Namiesnik, 1988). It is usually expressed in nanograms of VOC per gram of adsorbent. From knowledge of C_n it is possible to calculate the volume of air necessary to meet the sensitivity of the GC-MS system. Factors affecting C_n are

1. The vapor pressure, molecular weight, and polarity of the compound to be enriched
2. The chemical nature and specific surface area of the adsorbent (in m^2/g)
3. The temperature and flow rate at which sampling is performed
4. The concentration and composition of the air sample

To analyze the effect that each one of these factors has on C_n, it is useful to consider the trap as a gas chromatographic column working in frontal chromatography, where the compounds to be separated are added continuously to the carrier gas (in our case, air). In this type of chromatography, the elution of a component *n* is detected by an increase in the baseline of the detection system that is proportional to the concentration of *n* present in the mobile phase (Fig. 21.2*b*) (Namiesnik, 1988). For a compound *n* characterized by a linear isotherm of adsorption, the retention time tr_n corresponds to the inflection point of the half-gaussian curve describing the stepwise increase in the concentration of *n* measured at the column outlet (Raymond and Guiochon, 1975).

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TABLE 21.3 The Most Commonly Used Adsorbents for the Collection of VOCs in Air Showing Enough Stability for Thermal Desorption at 250°C

Commercial name	MDT[a] (°C)	SA[b] m^2/g_1	Porosity [c]	Type [d]	Hydrophobicity [e]	Class [f]
Carboxen 1000	400	1200	MIP	CMS	L	III
Carbosieve S III	400	840	MIP	CMS	L	III
Chromosorb 106	250	750	P	SP	H	III
Porapak Q	250	550	P	EVD-DVB-CP	H	III
Carbograph 5	>400	520	MAP	GCB	H	I
Carboxen 569	400	390	MIP	CMS	M	III
Chromosorb 102	250	350	P	S-DVB-CP	H	III
Porapak S	300	350	P	PVP	H	III
Carbotrap X	>400	260	MAP	GCB	H	I
Carbotrap	>400	100	MAP	GCB	H	I
Carbopack B	>400	100	MAP	GCB	H	I
Tenax TA	350	35	P	PDPPO	H	III
Tenax GR	350	35	P	PDPPO+ GCB	H	I
Carbotrap C	>400	12	MAP	GCB	H	I
Carbopack C	>400	12	MAP	GCB	H	I
Carbopack F	>400	5	NONP	GCB	H	I
Glass Beads	400	<1	NONP	Silicate	H	II

[a]MDT = maximum desorption temperature.
[e]SA = specific surface area.
[c]MIP = microporous (mean pore diameter 1–10 nm); P = porous (mean pore diameter 20–100 nm); MAP = mesoporous (or macroporous) (mean pore diameter 100–300 nm); NONP = nonporous (mean pore diameter > 300 nm).
[d]CMS = carbon molecular sieve; EVB-DVB-CP = ethylvinylbenzene-divinylbenzene copolymer; GCB = graphitized carbon black; PDPPO = poly(2,6-diphenyl-*p*-phenylene oxide); PVP = polyvinylpiridine; S-DVB-CP = styrene-divinylbenzene copolymer; SP = polystyrene polymer.
[e]H = high; M = medium; L = low.
[f]Classification according to Kiselev (see text).

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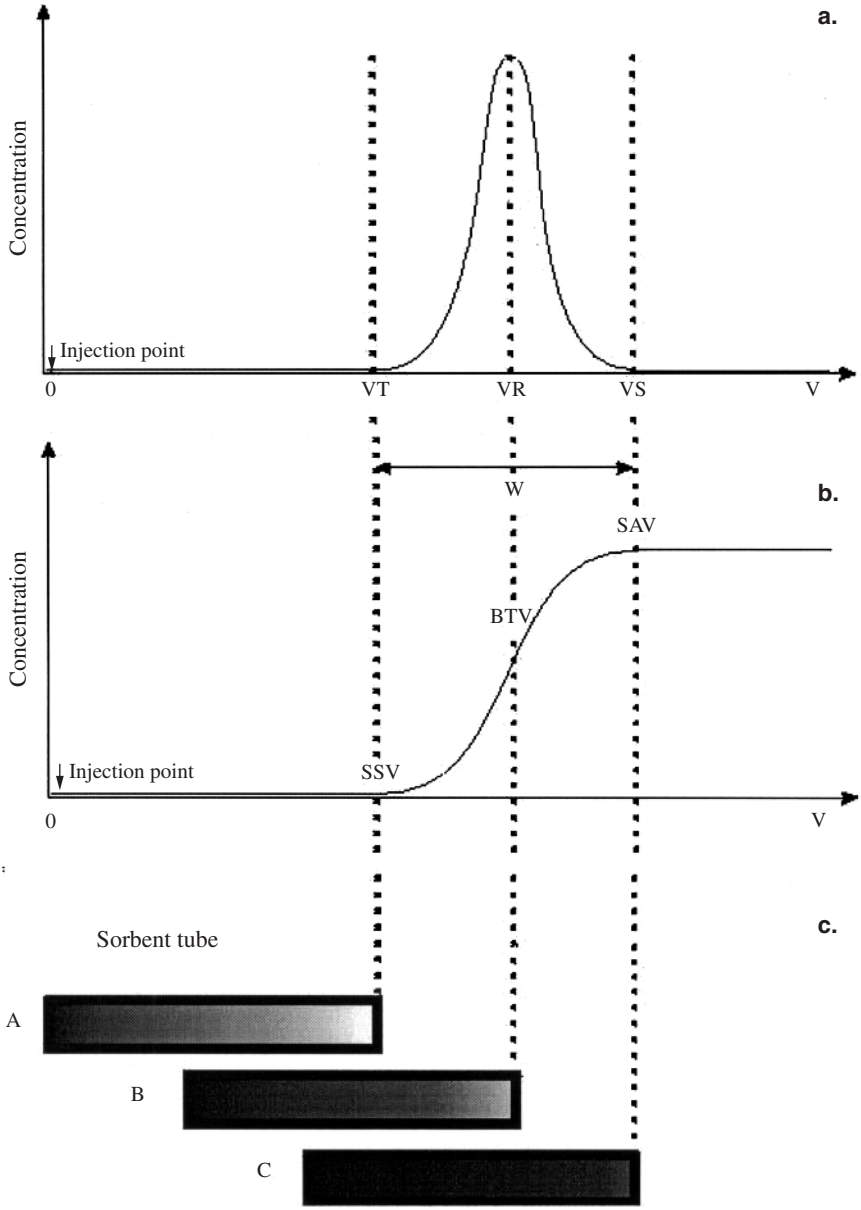

FIGURE 21.2 Chromatographic profiles observed in pulsed (*a*) and frontal (*b*) chromatography and relation existing between the retention parameters characterizing these two types of elution process. (*c*) The migration steps in frontal chromatography used to define BTV, SSV, and SAV in frontal chromatography.

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Strictly related to the retention time are the net retention time $t'r_n$ and the capacity ratios k'_n of the compound n that are defined as

$$t'r_n = tr_n - t_o \tag{21.1}$$

$$k'_n = \frac{tr_n - t_o}{t_o} \tag{21.2}$$

where t_o is the time spent inside the column by a compound not retained by the adsorbent.

With collection tubes, the retention of a compound n is expressed in terms of breakthrough volume (BTV) per gram of adsorbent. By indicating with $t'r_n$ the retention time in minutes of the compound n and with Φ_t the flow rate of the gas mixture through the trap in liters per minute, the BTV can be defined as (Raymond and Guiochon, 1975; Pellizzari et al., 1976; Brown and Purnell, 1979; Bertoni et al., 1981)

$$BTV_n = tr'_n \times \Phi_t \tag{21.3}$$

In addition to the BTV, two other indices can be derived for the same component n. They are the safe-sampling volume (SSV_n) and the saturation volume (SAV_n). Their meaning is well illustrated in Fig. 21.2c.

The SSV_n is defined as the maximum volume of gas for which a complete retention of the compound n is achieved by a gram of adsorbent (Namiesnik, 1988; Riba et al., 1991). It corresponds to the volume in which less than 1 percent of the molecules of n entering the trap are emerging from it. The situation corresponding to the SSV is well depicted by the case A of Fig. 21.2*c*. Knowing the SSV for the compound n, it is possible to calculate the capacity of the adsorbent for this compound through the following equation:

$$C_n = SSV_n \times M_n \tag{21.4}$$

in which M_n is the concentration in nanograms per liter of the compound n in the mobile phase.

The SAV is defined as the minimum volume of eluant in which more than 99 percent of the molecules entering the trap have already emerged from it. It is the volume where the maximum number of molecules of n are accommodated over the sorbent surface. The situation is illustrated by the case C of Fig. 21.2*c*. For collection volumes larger than the SAV_n, a constant recovery of n is obtained with thermal desorption (Riba et al., 1991).

Compounds exhibiting a linear isotherm of adsorption are characterized by a value of the BTV that is the arithmetic means of the SSV and the SAV. For these compounds, it is possible to express the SSV and the SAV as a function of the BTV because a symmetrical spreading of the chromatographic band (w) can be assumed with respect to the BTV (Raymond and Guiochon, 1975). Therefore, we can write that

$$SSV_n = 1 - w/2 \tag{21.5}$$

$$SAV_n = 1 + w/2 \tag{21.6}$$

Since $w/2$ can be related to the BTV and the number of theoretical plates N of the trap through the equation

$$w/2 = \frac{BTV_n}{2 \times N^{1/2}} \tag{21.7}$$

the SSV_n and the SAV_n also can be expressed as

$$SSV_n = BTV_n\,(1 - 2/N^{1/2}) \tag{21.8}$$

$$SAV_n = BTV_n\,(1 + 2/N^{1/2}) \tag{21.9}$$

These equations demonstrate that it is possible to calculate the SSV_n, and consequently C_n, by knowing the BTV_n and the efficiency of the trap. From gas chromatography, it is

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known (Bruner, 1993) that the number of theoretical plates per unit of length of the trap depends on geometric factors (such as the size of the particles and the internal diameter of the tube) as well as on the linear velocity of the carrier gas u passing through it. Data from the literature (Bruner et al., 1973) indicate that columns with internal diameters of 4 mm filled with carbon particles ranging between 40 and 60 mesh can provide 1000 theoretical plates per meter at linear gas velocities of 10 cm/s. This means that a trap 10 cm long is characterized by a value of N of approximately 100. In these conditions, the SSV_n will be equal to 0.8 BTV_n. With larger particles, values ranging from 0.5 to 0.7 of the BTV_n represent a realistic estimate of the SSV_n. The corresponding SAV_n thus will range between 1.3 and 1.5 of the BTV_n.

It is important to note that the larger the size of the particles, the larger the internal diameter of the sampling tube must be to achieve optimal efficiency of the trap. This is the reason why tubes with 6-mm inside diameters (IDs) are better than those of 4 mm for making traps with particle sizes of adsorbent ranging from 20 to 40 mesh. Although not justified in terms of numbers of theoretical plates, the use of large particles is also quite common with smaller trap diameters because flow rates as high as 300 ml/min can be used with limited losses in efficiency. The larger permeability, however, results in lower efficiency, and values of 0.5BTV and 1.5BTV must be assumed for the SSV and the SAV, respectively. Various approaches have been used to measure the BTV of VOCs on solid sorbents, but at the moment, none of them allows an accurate prediction of the SSV for all the components present in air.

The simplest method uses the net retention volume of n (VR_n) as a surrogate of the BTV_n (see Fig. 21.2*a*) (Raymond and Guiochon, 1975; Vidal-Madjar et al., 1978; Brown and Purnell, 1979; Betz and Supina, 1989). This parameter differs from the BTV_n because it represents the volume of pure air necessary to elute a fixed amount of n from the adsorbent. Since n is not added continuously to the mobile phase but is injected into it in small amounts (pulsed injection), a peak will be generated by the chromatographic process. For components exhibiting a linear isotherm of adsorption, the elution of n produces a gaussian peak whose maximum value corresponds to VR_n. From the equivalence between VR_n and the BTV_n, we have that

$$SSV_n = VT_n = 0.5\ VR_n \tag{21.10}$$

$$SAV_n = VS_n = 1.5\ VR_n \tag{21.11}$$

where VT_n and VS_n are the volumes of air corresponding to the beginning and the end of the elution of n, respectively (see Fig. 21.2*a*). These two parameters define the width of the gaussian peak appearing in the chromatogram.

Although widely used because of its simplicity, this method might greatly overestimate the SSV. This happens because the interactions occurring in frontal chromatography are different from those observed when the elution of organic molecules is performed with a pure eluant (Pankow, 1988). Strictly speaking, the equivalence between the BTV and VR can only be assumed if the concentrations of VOCs in air are so low (infinite dilution) that the mutual interactions between the organic molecules deposited on the sorbent surface (the so-called lateral interactions) can be neglected (Pankow, 1988; Bertoni et al., 1981; Gomes at al., 1993). Although this approximation seldom holds in practice, the equivalence between the BTV and VR allows use of the theoretical basis of adsorption gas chromatography (Kiselev and Yashin, 1969; Avgul et al., 1975) to estimate the range of VOCs that can retained by the trap at ambient temperature and the upper temperatures needed for their complete desorption (Vidal-Madjar et al., 1978; Brown and Purnell, 1978; Betz and Supina, 1989).

The key equation used for these calculations is the one relating VR_n to the physicochemical parameters of the adsorption process. It states that (Kiselev and Yashin, 1969; Avgul et al., 1975)

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$$\ln VR_n - lnV_0 = -(\Delta H_n/T) + \frac{(\Delta S_n + R)}{R} \tag{21.12}$$

where ΔH_n and ΔS_n are the enthalpy and entropy, respectively, of the adsorption process of n (in kcal/mol), R is the gas constant in (cal/mol, that is, (1.98), and V_0 is the void volume of the column ($V_0 = \Phi$).

For compounds characterized by a $k' >> 3$ and $V_0 << \mathrm{VR}_n$ and Eq. (21.12) also can be written as

$$\ln VR_n = \ln BTV_n = \frac{a}{T} + b \tag{21.13}$$

where $a = -(\Delta H_n/R)$ and $b = (\Delta S_n + R)/R$.

Since ΔH is negative (the adsorption of a gas over a surface is an exothermic process), an exponential decrease in VR_n will be observed by increasing the temperature of the adsorbent. The linearity of ln VR_n with the temperature allows us to calculate the value of the BTV_n, SSV_n, and C_n at infinite dilution if the heat of adsorption of n ($q_n^{\mathrm{st}} = -\Delta H_n$) is known on a given adsorbent. Lists of the terms a and b to predict the retention features of a large number of VOCs on graphitic carbons have been measured since the middle of the 1970s, and they can be found in the technical literature (Avghul et al., 1975). However, these values are subjected to uncertainties related to the low sophistication of the gas chromatographic techniques available at that time. Indeed, data collected in recent years (Betz and Supina, 1989; Mastrogiacomo, et al., 1995; Matisova et al., 1999) are more accurate, and they can be used to predict the retention features of different sorbents at infinite dilution.

The instrumentation needed for measuring q^{st} is so simple that these types of determinations can be performed in any laboratory equipped with a gas chromatograph connected to a standard detection system (such as the FID). The only thing required is to prepare a column filled with known amounts of the solid sorbent and to accurately measure the VR of the compounds of interest at different temperatures (usually 6 or 7). In doing this, it is essential that the particle size and the packing density of the gas chromatographic column are exactly the same as those of the sorbent tube used for VOC collection. The slope and the intercept of the linear plot of ln VR_n (or better, k'_n) versus $1/T$ directly provide the values of the terms a and b of Eq. (21.13). Data can be normalized to 1 g of adsorbents by dividing VR_n for the number of grams present in the column.

Since this technique allows us to calculate the VR at any temperature and flow conditions, it is possible to estimate the number and types of VOCs that can be completely retained by the trap at infinite dilution and the exact temperature at which they will be desorbed. This last parameter can be determined by looking at the temperature at which the SAV of n is lower than the maximum volume of carrier gas necessary to transfer the VOC from the collection trap to the injection system. This methodology is extremely accurate for the compounds characterized by a linear isotherm of adsorption in a wide range of concentrations; it is less accurate for polar compounds exhibiting a severe tailing or overloading of the chromatographic peak because their retention greatly depends on the amounts of n injected into the column.

Data on the BTV at infinite dilution are the ones reported most by suppliers of sorbent materials because they are better able to highlight differences in retention. Manura (1995) has measured them for a large number of organic compounds and in a wide range of temperatures (0–300°C). These results can be useful for predicting the temperature necessary for their thermal desorption. These data can be obtained directly on the Internet at *http://www.sisweb.com/index/referenc/resin10.htm.*

Another fundamental equation useful for estimating the range of VOCs that can be retained and released by a trap filled with solid sorbents is the one relating the increment of

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q^{st} to the number of functional groups present in the molecule (Kiselev and Yashin, 1969; Avgul et al., 1975; Vidal-Madjar et al., 1975). It states that

$$q_n^{st} = -\Delta H_n = c\,n + d \tag{21.14}$$

where c and d are constants depending on the type of functional group characterizing the homologous series and n is the number of functional groups in the molecule. Under constant temperature conditions, the following equation can be used for predicting the *BTV* of all the members of the homologous series:

$$\ln VR_n = \ln BTV_n = \frac{c\,n + d}{RT} + b \tag{21.15}$$

It has been shown that Eq. (21.14) holds for many homologous series, although the best results are obtained with linear hydrocarbons and aromatic components (Avgul et al., 1975; Raymond and Guiochon, 1975). Use of this rule allows a drastic reduction in the number of experimental measurements needed for calculating the BTV of VOCs at infinite dilution. Its validity is well summarized by Fig. 21.3, where the logarithmic plots of the BTV of *n*-alkanes at infinite dilution measured on different adsorbents are plotted against the number of carbon atoms present in the molecules. The BTV values reported in this figure refer to 1 g of adsorbent. They were measured at a temperature of 25°C.

Although some differences exist in the slope of these curves, a substantial parallelism is observed between them, and their increment is well described by values of b and c corresponding to 1.95 and 3 kcal/mol, respectively. The fact that the same constants allow a fair prediction of the increment in retention of *n*-alkanes on different adsorbents indicates that the contribution of each methylene group to q^{st} is quite independent from the surface area and chemical nature of the material used. This means that the same increment can be reasonably expected on all solid sorbents used for VOC collection. Indeed, values of q^{st} calculated with this method substantially fit with those reported by Mastrogiacomo et al. (1995) and Matisova et al. (1999), who have measured the q^{st} of some *n*-alkanes on different graphitic carbons, Tenax adsorbents, and microporous carbons.

The constancy of the terms c and d of Eq. (21.15) offers the possibility of finding an empirical equation to predict the increase in retention of *n*-alkanes as a function of the specific surface area of the adsorbent used (*SA* in m^2/g). A regression analysis of the data shown in Fig. 21.3 indicates that at 25°C the following equation holds for *n*-alkanes:

$$\frac{\Delta\,(\ln VR_n)}{\Delta\,(\ln SA)} = \approx 2.2 \tag{21.16}$$

This relation tells us that the chemical nature and surface structure of the adsorbent play a fundamental role in affecting the entropy term of Eq. (21.13) and that the use of 1 g of an adsorbent having a surface area 240 m^2/g might not be equivalent to the use of 3 g of an adsorbent with a surface area of 80 m^2/g. This effect can be explained by the fact the increase in the specific surface area of materials listed in Table 21.3 is obtained by increasing the surface porosity of the adsorbent. While materials with surface areas ranging from 1 to 10 m^2/g are essentially nonporous, the ones ranging from 10 to approximately 400 m^2/g are usually porous or mesoporous. Above 400 m^2/g, almost all the adsorbents are microporous.

The presence of pores definitely affects the entropy of the adsorption process because gas and vapors diffusing through them are subjected to much stronger lateral interactions than those deposited over a flat surface. Depending on the size and volume of the pores, adsorbed molecules can be assembled so closely to one to another that a thick film of liquid can be formed inside the cavity. Of coarse, materials characterized by comparable size and distribution of pores exhibit a linear increase in retention of *n*-alkanes with *SA*. Due to the complexity of the physicochemical processes contributing to the nonlinear increase in

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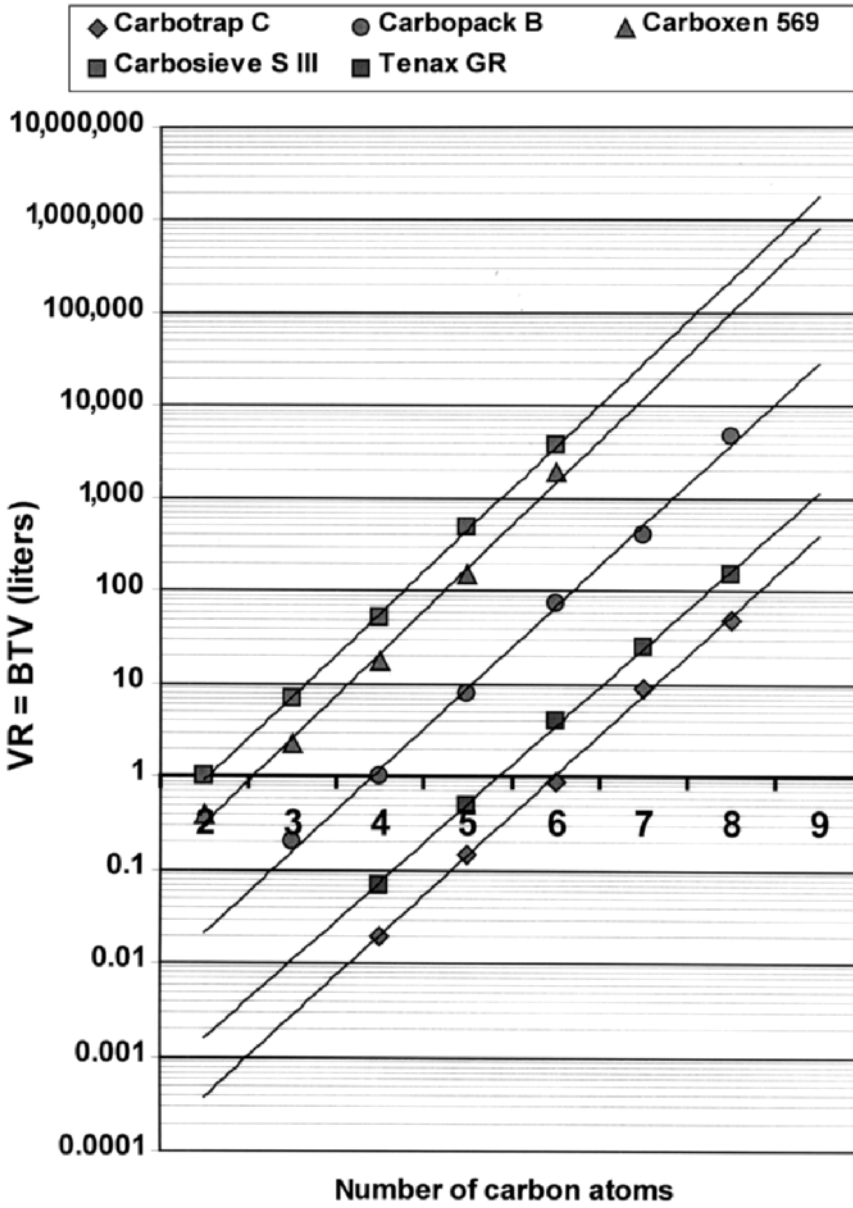

FIGURE 21.3 Plots of the BTV at infinite dilution for a homologous series of *n*-paraffins measured on solid sorbents characterized by different surface area. Data refer to a temperature of 25°C and to 1 g of adsorbent.

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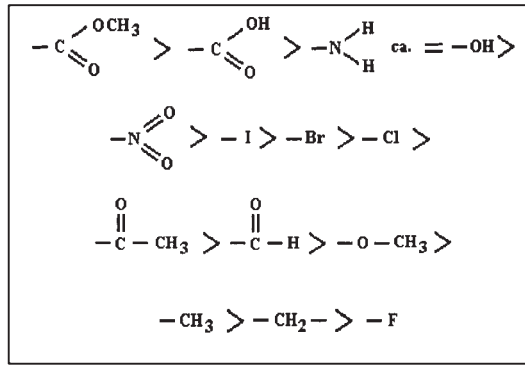
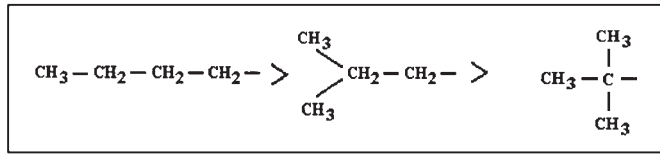
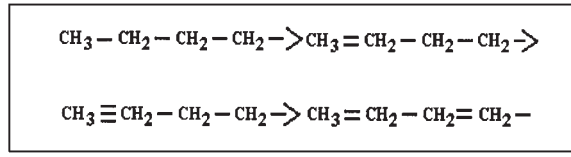
retention of *n*-alkanes with *SA,* Eq. (21.16) should be regarded only as a practical rule to roughly estimate the difference in BTV at infinite dilution existing between adsorbents characterized by large differences in the surface area.

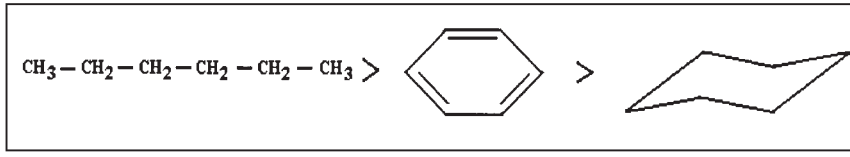
The theory of adsorption chromatography allows us to predict the retention features of organic compounds other than *n*-alkanes (Avgul et al., 1975; Vidal-Madjar et al., 1975). Since the term c is constant for any hydrocarbon chain, the substitution of a methyl group with another functional group will produce a shift in the plots of Fig. 21.3. The extent and direction of this shift will depend on the type of interactions the new functional group has with the sorbent surface. If the contribution of the new functional group to q^{st} is greater than that of the methyl group, a positive shift will be observed in the plots of Fig. 21.3. In the opposite case, a negative shift will be produced. It is clear that the maximum increase in retention will be produced by those polar groups interacting with the sorbent surface through hydrogen bonds. Steric factors and the presence of lone pairs become, instead,

TABLE 21.4 Influence of Different Functional Groups on the Retention of VOCs on Solid Sorbents. Data Refer to Ambient Temperature (25°C)









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important in the case in which the functional group interacts with the sorbent surface through strong dipole-dipole forces.

Table 21.4 summarizes the effect that the most common functional groups have on the BTV measured at infinite dilutions. In practice, large differences can be observed in the *c* terms of Eq. (21.16) as a function of the class of adsorbent used. However, the general trend is known, and a simple but general rule can be provided to roughly estimate the effect exerted by different functional groups on the BTV. The common practice suggests that it is safe to assume that the replacement of a methyl group with a carboxylic group produces an increase in retention that is higher than that produced by the addition of 2 methylene groups to the hydrocarbon chain. The addition of a hydroxyl or amino group to the same molecule produces, instead, an increase in retention larger than that given by approximately 1.5 methylene groups. The effect of a carbonyl group can be estimated to be larger than that produced by the addition of 1 methylene group. This means that any adsorbent that retains *n*-butane also will retain acetic acid, propylamine, propanol, iodopropane, bromopropane, chloropropane, propanal, and acetone. The table also suggests that the presence of double and triple bonds and rings in the hydocarbon chain have a definite effect on the retention. Effects also are produced by branching of the organic molecule. It is not certain, therefore, that the adsorbent retaining *n*-butane also can retain isopropane, cyclobutane, 1-butene, 2-butene, 1,3-butadiene, 1-butyne, and 2-butyne.

A procedure similar to that followed to estimate the retention at ambient temperature can be used to assess how many of them will be recovered by thermal desorption. This requires that plots similar to those reported in Fig. 21.3 be available for the temperature at which this step is performed. Although the thermal stability of some solid sorbents would allow the use of desorption temperatures much higher than 300°C, many polar compounds start to decompose above 250°C. Therefore, temperatures equal or lower than 250°C are most suitable for the thermal desorption of VOCs with available adsorbents. For a safe transfer of VOCs into the cryofocusing unit, it is also required that high flow rates (10–40 ml/min) of an inert gas (usually helium) be passed through the trap before the temperature gradient is applied to it. Another useful step to reduce VOC decomposition is to remove the bulk of oxygen, oxidants, and, when possible, water and CO_2, by passing few hundreds of milliliters of inert gas through the cartridge immediately after the collection of VOCs (McClenny et al., 1995). Sample losses are also minimized if the whole desorption step is performed in approximately 5 minutes and the trap is maintained at the maximum temperature for no more than 2 minutes. In any case, the flow direction used during the desorption step should be opposite to that used during the sampling and precleaning steps.

Concentration Effects on VOC Retention. Although the frontal chromatographic process of VOCs is described by the same equations used for estimating the BTV at infinite dilution, the simultaneous presence of different VOCs over the sorbent surface drastically changes the values of the enthalpic and entropic terms of Eq. (21.11) (Bertoni, 1981; Pankow, 1988).

Data obtained in gas-liquid-solid chromatography (Bruner et al., 1973; Di Corcia and Liberti, 1976) have shown clearly that these changes are quite complex and that they depend strongly on the chemical nature of adsorbed molecules and the degree of coverage (θ) of the sorbent surface. Figure 21.4 reports the general trend followed by VR and q^{st} as a function of θ. As can be seen, the most dramatic variations occur in the transition between zero coverage (equivalent to the infinite dilution situation described earlier) and the case in which a monolayer of organic molecules is formed over the sorbent surface ($\theta = 1$). It has been suggested (Bruner et al., 1973; Di Corcia and Liberti, 1976) that the formation of the monolayer dramatically affects the surface potential of the adsorbent by shielding the interactions with the organic molecules moving in the mobile

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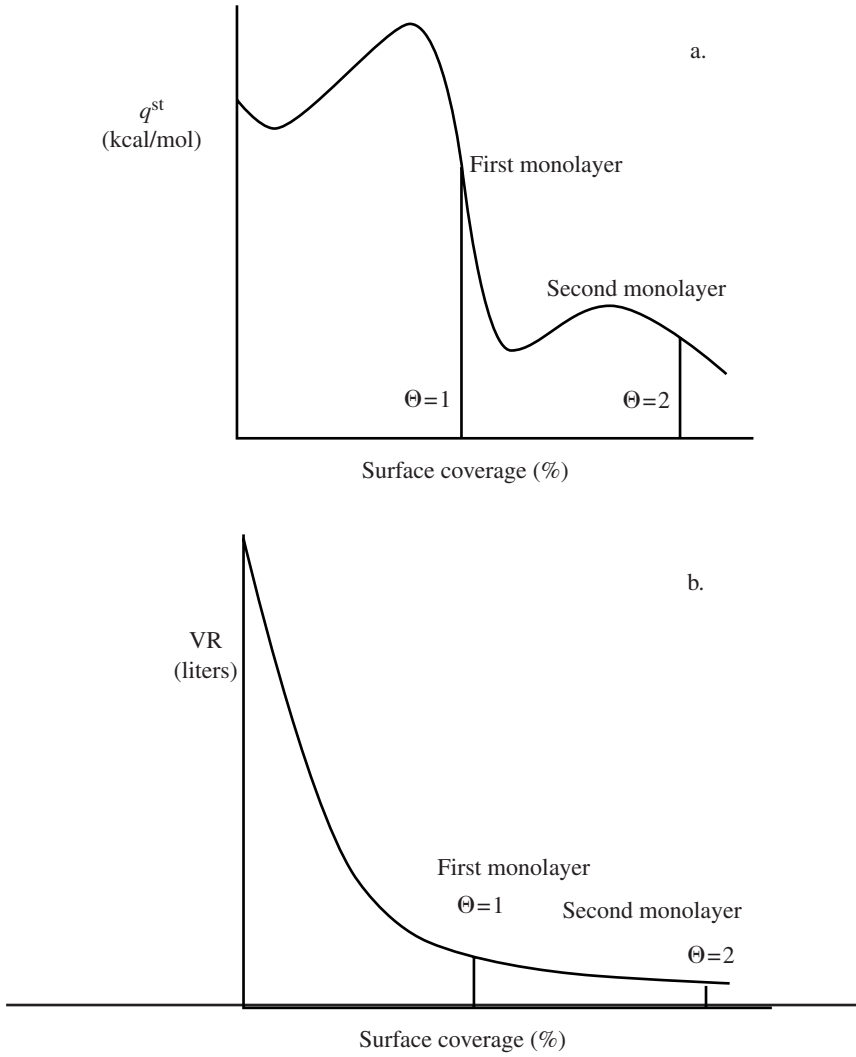

FIGURE 21.4 Typical changes of the isosteric heat of adsorption (*a*) and retention (*b*) of a compound eluted on a solid adsorbent as a function of the surface coverage (Θ). Data refer to experiments carried out in gas-liquid-solid chromatography.

phase. Strong lateral interactions between adsorbed molecules occur, instead, in the region where θ is slightly smaller than a monolayer. Usually, the highest values of q^{st} are reached between 0.5θ and 0.8θ. It should be noted that the changes in q^{st} and VR with θ depend strongly on the chemical nature of adsorbed molecules. The largest variations are observed when the analyte has the same polarity as the liquid modifier deposited on the surface.

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Observations made in gas-liquid-solid chromatography are in full agreement with the dependence of the BTV on the concentration and composition of the gaseous mixtures observed in frontal chromatography (Bertoni et al., 1981; Pankow, 1988; Comes et al., 1993; Peters and Bakkeren, 1994; Simon et al., 1995). In particular, the experimental work carried out with different hydrocarbon mixtures has shown that the dependence of the BTV on the concentration of VOCs present in the mobile phase (C_g) can be described by the following equation (Bertoni et al., 1981):

$$\log \text{BTV} = h + i \log C_g \tag{21.17}$$

where h and i are empirical coefficients depending on the temperature and the nature and composition of VOCs passing through the trap. Equation (21.17) becomes quite similar to the adsorption isotherm originally proposed by Freundlich if the constant h is expressed in a logarithmic form ($h = \log l$). By adding increasing contents of monoterpenes to the mobile phase, Simon et al. (1995) have shown that a 38 percent drop occurred in the BTV of α-pinene on Tenax GC maintained at 17°C when C_g was increased from 10 pptv to 100 ppbv. Much larger drops were reported at 33°C due to the influence of temperature on h and i. Consistent with the data displayed in Fig. 21.4, the decrease in the BTV was mirrored by an increase in the heat of adsorption of α-pinene.

The data reported in Fig. 21.5 illustrate the drastic differences existing between the values of the BTV of selected alkanes measured at infinite dilution (C = 0) and the values obtained when C_g is 1 ppmv (C = 1ppm). Curves refer to two graphitic carbon adsorbents (namely, Carbotrap and Carbotrap C) widely used in VOC collection. The frontal chromatographic experiments were performed at 25°C by passing through the trap an air mixture containing nine alkanes (from methane to heptane), nine alkenes (from ethylene to 1-hexene), and two arenes (benzene and toluene) (Brancaleoni et al., 1999). Each component was present at 50 ppbv levels.

Since mutual interactions of VOCs in the adsorbed phase affect all the energy terms involved in the adsorption process, observations made with artificial mixtures cannot be extrapolated easily to the real atmospheres, and the common procedure of estimating the SSV of VOCs as a fixed fraction (usually 0.75 or 0.5) of the BTV (Brown and Purnell, 1979; HSE, 1992; Harper, 1993) is not justified by any theoretical consideration. This is particularly true when the air mixture is complex (100–200 components) and very polar constituents, such as free acids, are present in large amounts. Since they are strongly retained by the sorbent surface, they can dramatically reduce the BTV of nonpolar and moderately polar components eluted before them. The impact produced by diethyl ether on the BTV of *n*-pentane on Carbopack B, reported by Bertoni et al. (1981), serves well to illustrate this point. From a practical viewpoint, we can say that the SSV can be assumed to be equal to 0.5 BTV (Brown and Purnell, 1979; HSE, 1992) measured at infinite dilutions only when the total concentration of VOCs in air is less than 300 ppbv. Above this value, all factors described might affect the SSV dramatically. When higher concentrations are suspected to be present in air, it is thus advisable to collect air samples using two sampling tubes set in series. This allows one to check if some compounds have exceeded the SSV during sampling.

Among the inorganic components potentially affecting the BTV of VOCs, water is definitely the most important because of its high concentrations in air and its strong ability to interact with the active sites of the adsorbent surface. The few studies performed adding water to the eluant (Bertoni et al., 1981; Ciccioli et al., 1992) have shown that the effect on VOC retention is rather small on highly hydrophobic adsorbents (such as graphitic carbons and porous polymers of the Tenax family). Dramatic effects on the BTV can be observed instead on microporous carbon materials (such as the carbon mol-

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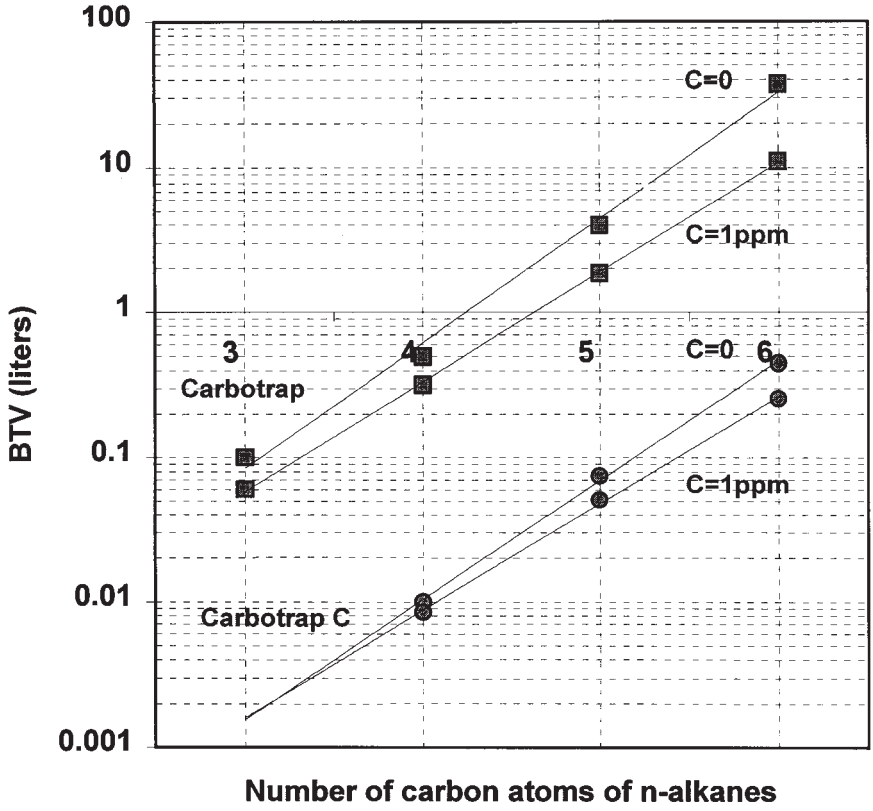

FIGURE 21.5 Effect of the concentration on the BTV of *n*-alkanes on Carbotrap and Carbotrap C adsorbents. Data refer to 25°C and 1 g of material. For the composition of the elution mixture used in frontal chromatography, see text.

ecular sieves belonging to the Carboxen and Carbosieve families) (Ciccioli et al., 1992) because they show large capacities in the collection of water (Helmig and Vierling, 1995). The formation of thick water layers over the surface gives rise to an adsorption-partition process of VOCs, which is difficult to describe with the equations reported earlier. The amount of water retained by these materials at relative humidities larger than 60 percent can be so high as to prevent the analysis of VOCs by capillary chromatography (Ciccioli et al., 1992).

By considering the difficulties in quantifying all effects influencing the BTV of VOCs on solid sorbents, the most reasonable way to compare their performances is to report the interval of *n*-alkanes that they can retain at ambient temperature and recover at 250°C. These data are displayed in Fig. 21.6. They refer to a condition in which 5 liters of air at 60 percent relative humidity containing 1 ppmv of VOCs is passed on 1 g of adsorbent. The composition of VOCs added to the mobile phase was the same as that used in the dotted plots of Fig. 21.5. Using a conservative view of the criteria illustrated in Table 21.3, it is possible to have an idea of the types of components other than *n*-alkanes that can be retained by these materials.

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Multistage Traps for the Collection of VOCs

The data in Fig. 21.6 suggest that a possible way to maximize the range of compounds collected by a trap and to limit the decomposition of VOCs is to use cartridges filled with different solid sorbents set in series. By assembling the various layers according to a sequence that processes and increases the surface area of the trap along the direction of the airflow, compounds can be distributed among the adsorbents that can better release them by thermal desorption. With this arrangement, only compounds below a certain molecular mass and polarity can be transmitted from one layer to another. By retaining the heaviest and more polar components, each layer protects the succeeding layer from compounds that could be irreversibly adsorbed on it or decomposed by thermal desorption. As a result of this selective fractionation process, only a limited number of VOCs entering the trap can reach the last, more tenacious layer. It is worth noting that decomposition processes are pre-

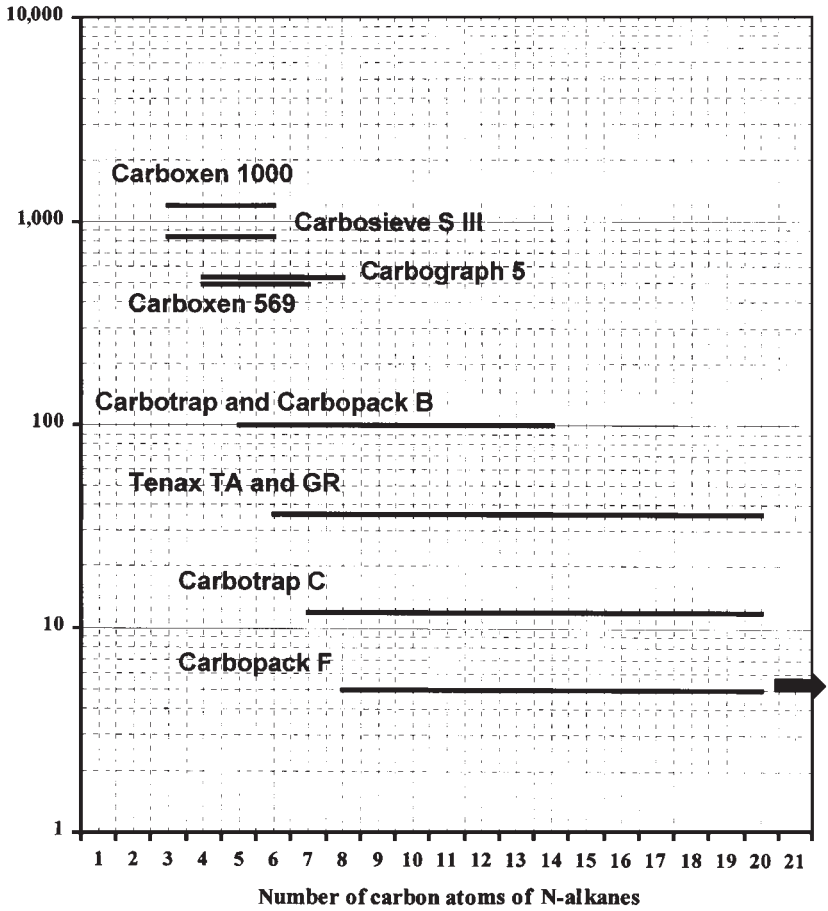

FIGURE 21.6 Range of *n*-alkanes that can be retained and released by thermal desorption at 250°C by different adsorbents. Data refer to conditions in which $T = 25°C$, RH (relative humidity) = 60% and $C_g = 1$ ppmv. For the composition of the mixture, see text. The arrows indicate that the range goes beyond the scale.

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vented and the energy demand required for the volatilization of VOC is minimized only if the flow direction used in the desorption step is opposite to the one used during sampling.

Multistage traps were first used by Rudolph et al. (1981) for the concentration of very volatile VOCs collected in air by grab sampling. Mosesman et al. (1988) later proposed their use for the collection of organic components in water samples using the purge and trap technique. By 1990, a semicontinuous monitor using a trap containing Carbotrap C, Carbotrap, and Carbosieve SIII set in series was available for the GC-FID analysis of alkanes, alkenes, alkynes, and arenes in air (Bloemen et al., 1990). The system was equipped with a complex system of ion-exchange membranes for the selective removal of water from the airstream. The great potential of multistage traps in the collection and GC-MS analysis of VOCs was fully confirmed by the laboratory studies performed by Bishop and Valis (1991), who tested 10 sorbent materials for their collection capacities and thermal desorption potential. The real possibilities were demonstrated, however, 1 year later when the first GC-MS determinations of VOCs in air appeared in the literature (Ciccioli et al., 1992). More than 140 components with carbon atoms ranging from 4 to 14 were identified and quantified in urban and suburban samples using traps filled with different carbon adsorbents set in series. These encouraging results were confirmed by later studies performed in remote areas of the earth (Ciccioli et al., 1993, 1999). Since then, the use of multistage traps has become the preferred method for the analysis of VOCs in air (Cao and Hewitt, 1999).

The range of VOCs that multistage traps can retain and release depends on the combinations of adsorbents used. The widest range can be achieved by selecting adsorbents with surface areas going from less than 1 to 1000 m^2/g. This is possible only if highly nonspecific and hydrophobic sorbents (such as graphitic carbons and polymers of the Tenax family) are combined with carbon molecular sieves and glass beads. While the first are used to cover the range of VOCs from C_3 to C_5, the latter are placed at the tube inlet to retain semivolatile compounds larger than C_{20}. Although various combinations have been proposed, none of them is able to cover the whole range of VOCs present in air.

With method TO-17 (U.S. EPA, 1997), the U.S. EPA suggests three different types of sampling tubes for the collection of VOCs in air. Tube type 1, suitable for VOCs ranging from C_6 to C_{20} at any relative humidity, is packed with a combination of Tenax GR and Carbotrap (or Carbopack B). Tube type 2, packed with Carbotrap (or Carbopack B) and Carbosieve SIII (or Carboxen 1000), is recommended for the collection of VOCs from C_3 to C_{12} in air with relative humidities lower than 65 percent. Finally, tube type 3, consisting of a combination of Carbotrap C, Carbotrap (or Carbopack B), and Carbosieve SIII (or Carboxen 1000), is suggested for the collection of VOCs from C_3 to C_{16} in air with relative humidities lower than 65 percent. In all cases, the recommended volume is 2 liters. Other combinations than those recommended by the U.S.-EPA are available on the market. Some of them are just small modifications of the same basic arrangement proposed in method TO-17; others have been proposed for the solution of specific problems. A detailed list of the types of multistage traps used for VOC collection can be found in the paper of Matisova and Skrabakova (1995).

One of the advantages of this approach is that cartridges can be built as a function of the range of VOCs to investigate. This can be done either by changing the number and type of adsorbents present in each layer or by changing the relative amount of material present in it. In doing this, it is useful to remember that adsorbents do not have the same bulk densities, and it is often useful to consider the net surface area provided by a given volume of adsorbent to estimate the range of VOCs that given layer can retain (Brancaleoni et al., 1999).

The need to selectively collect compounds that the succeeding layer might not release justifies the use of combinations in which differences in surface areas between two contiguous layers are rather small. A case in which the adoption of a such strategy might be successful is that of volatile olefins collected on tube types 2 and 3 recommended by the

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U.S. EPA. It has been shown recently (Dettmer et al., 2000) that slow decomposition of some olefins, particularly important in atmospheric chemistry (such as isoprene and 1,3-butadiene), takes place on microporous carbons (Carboxen 569, Carboxen 1003, and Carbosieve SIII) maintained at ambient temperature. Losses as high as 40 percent were reported when the residence time of volatile olefins on these adsorbents exceeded 30 to 40 minutes. Their poor recovery is consistent with the data obtained in our laboratory using multistage traps in which the most tenacious layer was made with these types of adsorbents (Fig. 21.7). In this case, sample recoveries were measured by frontal chromatography using the same 1 ppmv hydrocarbon mixture previously adopted for testing the BTV of different adsorbents. Data suggest that a poor recovery of very volatile olefins could be achieved with tube types 2 and 3 recommended by the U.S. EPA.

A possible way to solve this problem is to insert between the last two layers an adsorbent that can selectively retain the olefins with carbon numbers ranging from 4 to 5. Figure 21.7 shows that a successful interception of these VOCs can be accomplished by inserting a layer made of Carbograph 5, a graphitic carbon material characterized by a surface area of 500 m^2/g, between those made by Carbotrap and Carbosieve SIII. Brancaleoni et al. (1999) have shown that 175 mg of this material is sufficient to prevent the transmission of these olefins to Carbosieve SIII on 5-liter samples. Data from the literature (Dettmer et al., 2000) also indicate that Carbopack X, a mesoporous carbon with a surface area of 250 m^2/g, can do the same job as well. The introduction of a new layer made by these carbonaceous materials in tube types 2 and 3 can prevent the negative artifacts of olefins and reduce the temperature needed for the thermal desorption of all VOCs.

These examples highlight one important rule that should be taken into consideration in building multistage traps for VOC collection: The larger the number of layers is, the better the results are in terms of collection and recovery of VOCs. This happens because few of the very volatile components reach the more tenacious layer made by microporous adsorbents and lower temperatures can be applied to release VOCs from the trap.

The extensive use of multistage cartridges for the monitoring of VOCs in air during the last decade has shown that sampling artifacts are more frequent than it was thought previously. In particular, the question of whether the existing materials can provide a complete recovery of all polar and nonpolar components in air is still partly unresolved. The limited knowledge of the tropospheric composition of VOCs combined with practical difficulty in generating artificial mixtures simulating the range of compounds that can be released or formed in the atmosphere prevents the possibility of testing the performances of various sorbent combinations used in multistage traps. It is not surprising, therefore, that extensive research has been done to identify the positive and negative artifacts that might arise from the presence of certain materials in multistage traps.

In discussing this aspect, we must start from the fact that certain organic components that are important in atmospheric chemistry will never be recovered by thermal desorption, although they certainly are retained by all available materials. The most relevant case is represented by dicarboxylic acids, which are formed either by biomass burning or by photochemical reactions. Their thermal stability is so low that derivatization is needed to analyze them by gas chromatography. Similar considerations apply to some hydrocarbons containing more than one polar group in the molecule. It is clear that their decomposition can lead to positive artifacts that are impossible to eliminate even with the most inert adsorbent.

In addition to this general type of artifact, others exists that are specific to one of the sorbent present in the multistage trap. If the artifact is negative (decomposition) and is observed on the most tenacious layer, the same approach proposed for reducing the recovery of olefins from tube types 2 and 3 recommended by the U.S. EPA can be followed. If negative artifacts occur in the first layers, the only possibility is to replace the adsorbent with a more inert one.

In the case of positive artifacts, several strategies are possible. If the production of a given component arises from the decomposition of one or more VOC present in air, we

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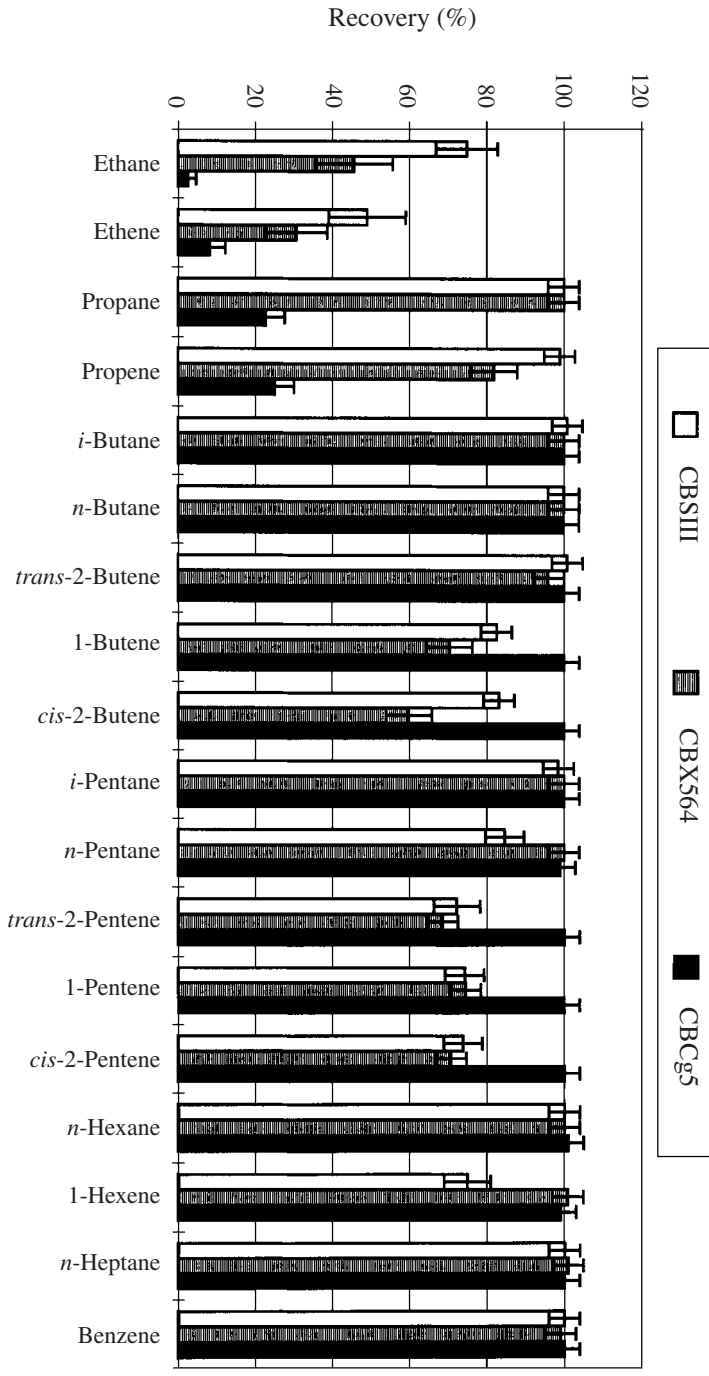

FIGURE 21.7 Recoveries of different VOCs obtained by using multiplayer traps composed by three layers in which the most tenacious ones were made by Carbosieve SIII (CBSIII), Carboxen 564 (CBX564), and Carbograph 5 (CBCg5). Data were obtained in frontal chromatography at 25°C by passing 1 liter of air containing 50 ppbv of each component through the traps. Evident losses of olefins are observed with the combinations using microporous carbons.

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must replace the adsorbent. In the case in which the compound is produced by the adsorbent itself, we can still use the trap, provided that the compound does not interfere in the GC-MS analysis and we are not particularly interested in its quantification. A classic example of this type of artifact is the production of benzaldehyde, acetophenone, and phenol from Tenax GC and TA reported by several authors since 1984 (Pellizzari et al., 1984; Ciccioli et al., 1986; Cao and Hewitt, 1994). Multistage traps containing this material can be used for any purpose except for the quantification of benzaldehyde, acetophenone, and phenol in air and emission samples. If we are interested in quantifying a compound that is known to be formed in a specific layer, we must replace the adsorbent present in it.

Finally, a third type of artifact exists to which all types of adsorbents are subjected. It is the one arising from the reaction of adsorbed VOCs with some air constituents. The most important case is represented by ozone. Although present in smaller concentrations than other trace gases (its maximum concentration seldom exceeds 100 ppbv), this pollutant is particularly efficient in oxidizing some olefinic compounds deposited on sorbent surfaces. Laboratory experiments (Calogirou et al., 1996) have shown that this reaction can be a source of strong artifacts in the determination of some mono- and sesquiterpenes with Tenax. Although these losses can be limited using graphitic carbon materials (Larsen et al., 1997), they cannot be prevented completely, and substantial decomposition of some mono- and sesquiterpenes takes place at ozone levels exceeding 60 ppbv. In such cases, the only possibility is to selectively remove the interfering agent from the airstream. Unfortunately, none of the solutions proposed is fully satisfactory (Helmig, 1997). Although some of them are quite promising (Calogirou et al., 1997), the determination of reactive compounds (such as sesquiterpenes emitted by plants) still can be affected by large uncertainty.

Based on these considerations, complete recovery of all VOCs in air is still an active area of research, even though substantial progress has been made in the last 20 years. While intensive studies have been devoted to improving the combination of adsorbents in multistage traps, research on new sorbent materials is still lacking. Almost all the adsorbents listed in Table 21.3 were developed 30 years ago, and some of them were used extensively as stationary phases in gas chromatography. A decisive advance in this field is needed to improve the accuracy of VOC determination in air by enriching systems. Not only should it address the development of more inert and versatile adsorbent materials, but it also should study materials capable of selectively removing ozone from the airstream without affecting VOCs.

Critical Aspects in the Preparation, Cleaning, and Storage of Multistage Traps Filled with Solid Sorbents

The first practical difficulty encountered by someone who wants to start the monitoring of VOCs with adsorption traps is represented by the fact that no standards have been fixed for the size and material of sampling tubes used. It is possible to find on the market tubes made either of glass or stainless steel with lengths varying from 18 to 7.6 cm and internal diameters going from 13 to 2 mm. The external diameter also can be different, although typical sizes are $^5/_8$, $^1/_4$, and $^1/_2$ in and 6 mm. Only in a few cases are such huge differences justified by the presence of different amounts of packing inside the tube. More often these parameters are defined by the type of heating system developed by the supplier for the thermal desorption process.

This situation has been determined by the fact that companies have developed their own desorption systems before the use of adsorption traps for the collection of VOCs was endorsed by official environmental agencies. The first official document regarding the use of adsorption tubes for the sampling of VOCs in ambient air was released by the U.S. EPA in 1997, although many of adsorbents described in the document were developed, used, and tested much earlier. This delay resulted from the reluctance of many environmental chemists to accept the use of

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these enriching devices for the analysis of VOCs in air. For long time it was believed, especially in the United States, that this sampling system was unreliable and affected by severe artifacts. Others claimed that it was impossible to achieve acceptable blanks with sorbent tubes and that collection on passivated canisters provided much more reliable results.

This general skepticism toward the use of adsorption tubes may have been dictated simply by the disappointing results that were obtained in their practical use. In many instances, the reasons for this failure lay in the incorrect handling of the material. The most frequent error was the static precleaning of the adsorbents in the oven or the use of temperatures higher than those necessary to prevent disruption of the solid matrices. Although these mistakes are today largely prevented by the availability on the market of precleaned tubes, it is important to know what the basic procedures are for the preparation, cleaning, and storage of sorbent tubes. This is fundamental when repetitive sampling is performed with the same trap or when cartridges need to be prepared in the laboratory for research or extensive monitoring. In particular, the ability to compare the results obtained by research teams equipped with the same GC-MS system but different thermal desorption units is linked to the ability to build, clean, and test traps with different geometries.

The first step is to be sure that the tubes, fittings, and inert materials used to keep the adsorbent in place are cleaned adequately before introduction of the adsorbent. This step can be achieved by putting them into a glass container filled with CH_2Cl_2 placed in an ultrasonic bath. The solvent must be replaced every 15 minutes for 3 times to eliminate contaminants (usually oil) added during the manufacturing process. The cleaning process should be performed in areas where the use of chemicals is forbidden and exposure to dust is limited. After this step, all different parts must be stored in sealed glass containers. Before introduction of the sorbents, it is a good practice to heat the empty tubes at 300°C under a flow of helium of 200 ml/min for at least 20 minutes. Cotton gloves should be used to handle the tubes during the filling process because fingers contain hydrocarbons (such as squalene and fatty acids) that can contaminate the tube and the sorbing materials. Once the quartz wool is placed at the bottom of the empty trap, the adsorbent can be introduced inside the tube with a glass funnel connected to the top of the trap by a Teflon tube.

Before inserting the adsorbent, it should be determined that the mesh range of the batch used has maintained the original features declared by the supplier. A partial breaking of the adsorbents might be observed with soft materials, such as graphitic carbons with specific surface areas lower than 12 m^2/g. By putting a few milligrams of the material over a glass specimen, it is possible to see, using a microscope, if particles have a homogeneous size distribution. If a high density of smaller particles is observed, it is advisable to sieve the material again.

If glass tubes are used, it is possible to measure the portion of the tube occupied by the adsorbent. By marking with a pencil the segments of the empty tubes corresponding to the desired amounts, it is possible to prepare a large number of traps in short time. The packing inside the tube should be tight enough to achieve the best efficiency possible, but the adsorbent should never be subjected to mechanical stress because breaking of the particles gives rise to increased resistance of the cartridge to the airflow and to changes in the total surface area available for adsorption. The use of quartz wool prevents these effects. It can be put in place by using a piece of Teflon tubing with an external diameter of 3 to 4 mm and an internal diameter of 0.5 mm.

With metal tubes, more attention should be paid to preventing the breaking of the sorbent material because is not possible to see the volume occupied by the adsorbent. With some practice, it is possible to define the level inside the tube that corresponds to an optimal packing and use calibrated Teflon spacers to prevent excessive pressure on the particles. Before starting the cleaning procedure, it is recommended to check the resistance of the traps to gas flow. This operation can be performed by sending helium through the cartridge at a fixed inlet pressure and by measuring the flow rate passing through it. Flow rates deviating by 50 percent from the standard value provided by a good trap can be indicative

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of potential damage to the adsorbent. It is a good practice to keep records of the flow resistance of each trap and note the day it was prepared and the batch of adsorbent that was used.

Once prepared, sorbent tubes must be cleaned for use. An apparatus such as that shown in Fig. 21.8*a* is suitable for this purpose. The cleaning temperature depends on the types of adsorbents used for VOC collection. As a general rule, a temperature 30 to 50°C higher than that used for thermal desorption of VOCs is suitable for cleaning traps in a short time (10–15 minutes). With traps filled with materials that might be subjected to thermal decomposition, it is preferable, however, to maintain the temperature closer (10–20°C) to that used in the thermal desorption step and purge the traps for longer times (from 30 minutes to several hours) to completely remove VOCs from the adsorbent. The same procedure is recommended for materials characterized by surface areas larger than 400 m^2/g. Helium of high purity grade should be used for a purging gas, and it must follow a flow direction opposite to the one used during the air sampling. With multistage traps filled with different materials, the helium should pass first through the strongest adsorbent. The flow rate of the purging gas should be equal to or higher than the maximum flow rate allowed during sampling. In general, flow rates of 200 to 300 ml/min are adequate for the purging process.

It is advisable to close the traps when they are still hot and to remove the helium line immediately before closing the two ends. Traps must be numbered and marked with a clear identification code for the packing material present in them. With glass tubes, the use of metal labels is preferred to paper labels. In all cases, the use of glow or plastic tape to keep paper labels attached to the trap must be avoided. Fewer problems exists with metal tubes because numbers and codes can be cut on the external surface.

Once closed and labeled, purged traps can be stored in a closed container that limits the exposure of traps to air contaminants. Three-liter glass jars, normally used for food storage, are suitable for preventing contamination of the traps, provided that they are equipped with glass caps and a tight enclosure is ensured by a rubber O-ring. Such containers can store from 20 to 60 cartridges depending on the geometry of the traps used. If glass tubes are used, aluminum foil is necessary to protect cartridges from sunlight and, partly, from mechanical shock. To keep the gas inside the container clean, it is advisable to place passive samplers for organic vapors made of active charcoal at the bottom of the jar, as shown in Fig. 21.8*b*. When long storage times are expected, the container also can be flushed with helium for 1 to 2 minutes before closure. In any case, one trap for each container should be tested to see if cleaning procedures provided a satisfactory blank. Another trap for each container should be used for testing that no contamination occurred during transport. For shipment in cars or on aircraft, the availability of containers, such as those displayed in Fig. 21.8*c,* is highly recommended. Battery operated refrigerators are also needed to keep the temperature of traps below 10°C when long times are expected to occur between sampling in the field and analysis. They are available in many supermarkets. The procedure described here does not differ greatly from that proposed by Helmig (1996), who reported no detectable contamination of sorbent tubes when strict procedures were followed for their cleaning, handling, and storage.

With homemade traps, it is very important to keep records of the batch of the sorbent used because some differences in the adsorbent properties might exist from batch to batch. It is a common practice among suppliers to indicate the batch number of the material directly on the label placed on the container where the adsorbents are stored. In any case, adequate control should be done on the performance of the various batches. Figure 21.9 shows one of the tests that were performed in our laboratory to verify the performance of a new carbon adsorbent (Carbograph 2) suggested by the manufacturer as an alternative to Carbotrap C for VOC collection. A mixture of monoterpenes was injected in traps filled with two different batches of this material, and percentage recoveries were compared with the one afforded by two different adsorbents for which the recovery was known. Monoterpenes were used as test compounds because easy decomposition has been reported for these components on carbon and porous polymeric sorbents (Cao and

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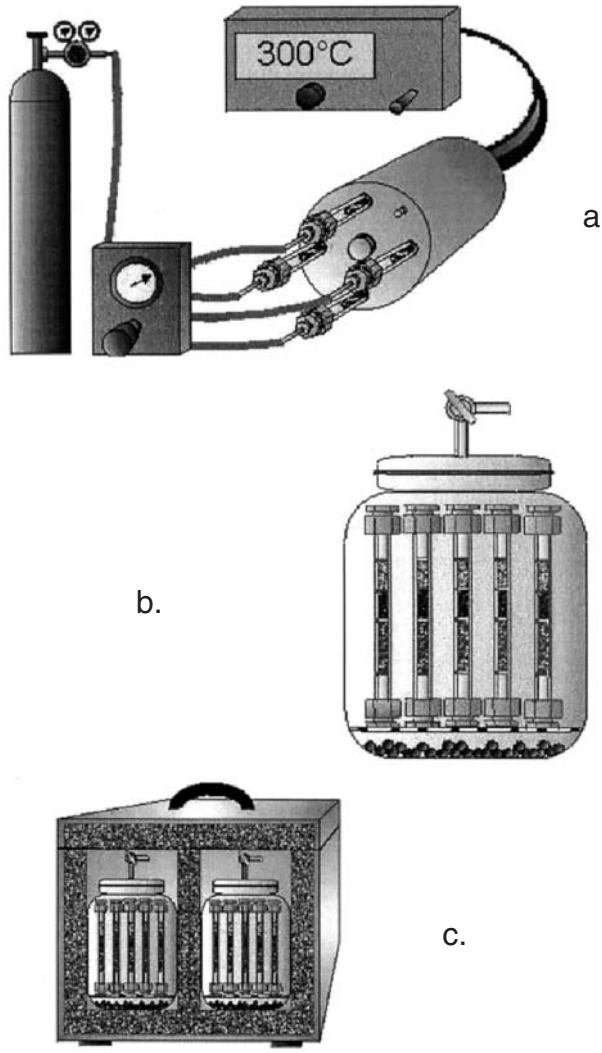

FIGURE 21.8 Typical apparatus for the cleaning (*a*), storage (*b*), and transport (*c*) of sorbent tubes. Note the bed of active charcoal on the bottom of the jar shown (*b*) used to adsorb air vapors.

Hewitt, 1999). The comparison with known materials is essential to exclude decomposition effects that arise from the desorption system used. The figure shows that one batch of Carbograph 2 provided very good performance when compared with Tenax GR and Carbotrap C, whereas the other showed substantial decomposition of sabinene and ß-pinene. With this batch, the poor recovery of these two compounds was mirrored by formation of thujene, camphene, *p*-cymene, myrcene, and α- and γ-terpinene in different amounts. It was found that this batch contained a strong residue of heavy metals catalyzing the conversion of monoterpenes at high temperatures. They were added in the plant during the graphitization process of the raw material.

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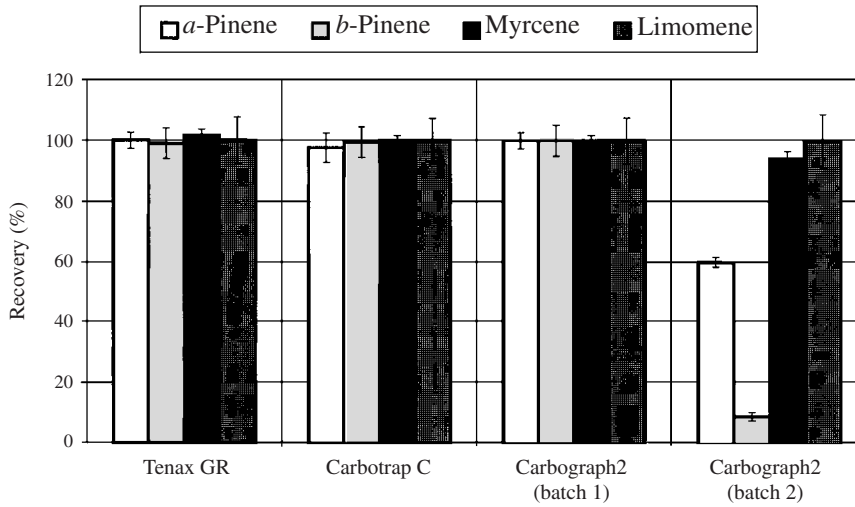

FIGURE 21.9 Percent recoveries of selected monoterpenes from reference adsorbents (Tenax GR and Carbopack C) and two different batches of the same adsorbent (Carbograph 2) graphitized at different times and under different conditions.

Similar tests need to be done to check the losses in performance arising from a repeated exposure of the sorbent surface to atmospheric pollutants. Ozone, SO_2, NO_2, HCl, and HNO_3 can slowly change the surface properties of many adsorbents. In particular, ozone is extremely efficient at oxidizing polymeric materials whose matrix contains double bonds. Slow oxidation of the sorbent surface also can be induced by condensation of water containing strong acids and peroxides into the cartridge.

The main effect of these surface reactions is the gradual transformation of nonspecific sites into active sites. By affecting the linearity of the adsorption isotherm, aging effects produce a stronger retention of polar compounds and severe tailing and/or overloading of the chromatographic peak. Aging effects can be particularly rapid when traps are used for the collection of VOCs in emission samples where huge amounts of acids often are present. Together with incorrect desorption procedures (such as desorption temperatures higher than 250°C), these effects can explain the conflicting results reported in the literature regarding the use of adsorbing materials used for VOC collection. By following the testing procedure described earlier, we have never observed the high decomposition rates of α- and ß-pinene on Carbotrap that has been reported (e.g., Cao and Hewitt, 1999).

SYSTEMS FOR THE THERMAL DESORPTION OF SORBENT TUBES AND FOR THE INJECTION OF VOCs INTO THE GAS CHROMATOGRAPHIC COLUMN

The advent of a fused silica column internally coated with chemically bonded phases has made capillary chromatography the most suitable and used method for the GC-MS analysis of VOCs in air and emission samples. Columns of this type can be connected directly to

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the ion source of the mass spectrometer because they combine high efficiencies and low flow rates with good mechanical resistance and thermal stability of the stationary phase. Since bonded phases are immobilized within the tubing, they can reach higher temperatures than those of liquid phases simply deposited on the wall. With them, a wide range of organic compounds can be analyzed without contaminating the ion source of the mass spectrometer with column bleeding.

Direct coupling with the detector allows one to exploit the whole effluent of the GC column for the ionization process and prevents mass losses associated with the use of separation systems (such as jet or membrane separators) necessary to selectively remove the carrier gas from the eluate. However, it poses an upper limit to the flow rate of carrier gas (normally helium) that can be used in capillary GC. The maximum input of gas that the ion source of commercially available mass spectrometers can receive is usually in the range of 1 to 1.2 ml/min (2 ml/min with MS units equipped with very strong pumping systems). Above this value, the presence of the carrier gas start to affect the ionization efficiency of the source by limiting the collisions of the analyte with high-energy electrons (electron impact) or secondary ions (chemical ionization).

Such small flow rates hinder the direct transfer of VOCs from sorbent tubes to narrow-bore columns because they are too low with respect to those necessary for a rapid, nondegradative desorption of VOCs from the trap (10–40 ml/min). To inject the entire mass of VOCs into the column using flow rates that can be sustained by the MS system, we must concentrate the effluent from the sorbent tube into the smallest volume possible (typically 30–50 μl). This goal can be achieved by passing VOCs released from adsorption traps into a narrow-bore tube (0.32–0.52 mm ID) kept at low temperatures. By recalling that the dependence of lnVR from $1/T$ holds for any type of retention process (i.e., adsorption and partition), a temperature must be reached in which the value of the VR of VOCs in the capillary tube largely exceeds the total volume necessary to release them from the adsorption trap (100–200 ml).

With temperatures approaching those of liquid gases (such as liquid nitrogen, oxygen, and argon), a large portion of VOCs condenses onto the internal walls of an empty tube. Only a few components have enough vapor pressure to move through it. Since these are the ones that are not usually retained by sorbent tubes kept at ambient temperature, a complete recovery of the sample is achieved. At temperatures higher than those of liquid gases, solid sorbents are needed to retain VOCs released from the adsorption trap. The surface of solid sorbent necessary for a complete retention will depend on the minimum temperature provided by the cooling system. Because of the small volumes and temperatures used, it is common to identify this concentration process as the cryofocusing step.

After all VOCs emerging from the adsorption trap are transferred into the cooled tube, the cryofocusing unit is set in series with the capillary column, and VOCs are injected into it by thermal desorption. Due to the small volume of the collection tube, a flow rate of 1 ml/min ensures a rapid transfer of VOCs at the column inlet, provided that fast temperature gradients (15–40°C/s) are applied to capillary tube. In these conditions, the whole injection process can be accomplished in about 5 minutes.

Since VOCs move into the column as soon as they reach their desorption temperature, the GC oven must be maintained at a temperature that substantially limits the migration of VOCs through the column. Although the total volumes necessary to transfer the sample from the tube to the column are much lower than those required to recover VOCs from the sorbent tube, they are sufficiently large (5–6 ml) to reduce the efficiency of the column drastically if compounds move quickly through it. This is the reason why the GC oven is often kept at subambient temperatures during the injection step. The smaller the spreading of the chromatographic band is, the better the partition equilibria driving the separation process can be exploited.

Figure 21.10 shows a schematic diagram of a homemade unit designed for the GC-MS analysis of VOCs sampled in multistage traps. In this unit, which can be built easily

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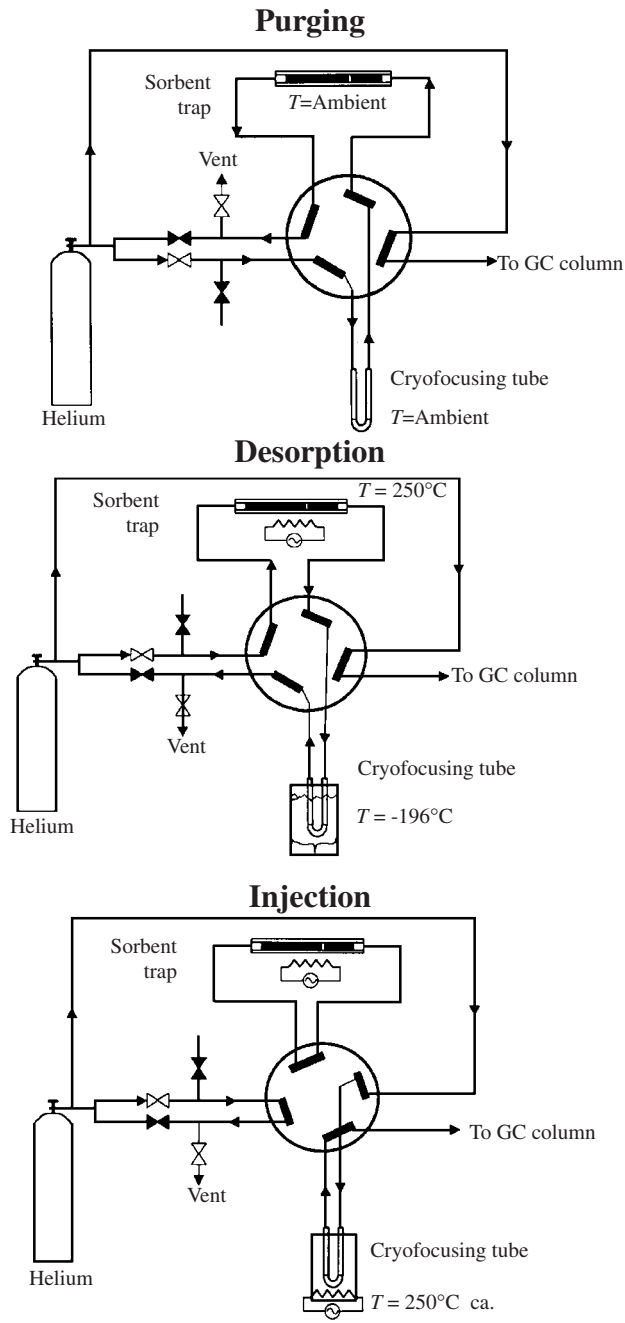

FIGURE 21.10 Schematic diagram of a homemade cryofocusing unit and main phases used for the transfer of VOCs from the sampling tube to the capillary column.

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in any laboratory, the cryofocusing of VOCs is performed in an empty tube, 25 cm long, made by silcosteel having an internal diameter of 0.5 mm. To efficiently condense VOCs into it, a temperature of −196°C is used. It is obtained by immerging the silcosteel tube in a Dewar flask filled with liquid nitrogen. To prevent condensation of oxygen, water, and CO_2 during the concentration step, the trap is washed with pure helium before thermal desorption (McClenny et al., 1995). To limit sample losses, the gas stream follows the same direction used during sampling. The purging step is necessary to eliminate air diffusing into the connecting lines and the trap during installation of the tube in the cryofocusing unit. The desorption of VOCs from the concentration tube is achieved simply by replacing the Dewar flask with an electric furnace constantly kept at 260°C. The temperature gradient is applied 1 minute after the tube outlet is connected in series with the capillary column. We found that this simple system provides performances that are comparable with those of the most sophisticated commercially available units. Noticeable is the limited consumption of liquid nitrogen necessary for the cryofocusing step. We also found that any student could perform all these operations in a very reproducible way after 2 days of training.

The steps shown in Fig. 21.10 do not differ too much from those of commercial units using liquid gases as a cooling system. With respect to homemade units, however, they provide a high degree of automation and an accurate control of all steps necessary to transfer VOCs from the multistage trap to the column. In these units, cryofocusing of VOCs usually is performed on short (10–30 cm) capillary tubes (0.52 mm ID) made by fused silica internally coated with chemically bonded phases. These stationary phases do not show any appreciable bleeding at the desorption temperature reached by the cryofocusing unit because they can be used at up to 320 to 330°C once they are conditioned properly. With small modifications, the number of VOCs that can be collected with these cryofocusing units can be extended beyond the range retained by multistage traps operated at ambient temperature. By filling small portions (1–2 cm) of the fused silica tube with solid sorbents such as Carbopack B (Ciccioli et al., 1997), it is possible to quantitatively retain all VOCs except methane. This capability can be exploited for the analysis of very volatile compounds directly in air or canister samples. In this case, however, only rather small volumes can be collected because of the rapid condensation of water in the cooled tube.

Cryogenic units using liquid gases are quite expensive to buy and to maintain, however. In addition to the sophisticated control devices necessary to drive the purging, cryofocusing, and injection steps, they need large containers for the liquid cooler and special valves for its transfer into the cryofocusing unit. The consumption of liquid gases are on the order of 10 to 15 liters/d, including the normal losses occurring in the refueling process. Although the price of liquid nitrogen is not particularly high, it definitely increases the cost of the analysis. The cost of liquid gases can be reduced by using closed-cycle coolers based on a standard refrigeration cycle with helium as the working gas (McClenny, 1993).

Operational costs can be reduced drastically and cryogenic procedures simplified by using units equipped with electric coolers (Woolfenden and Broadway, 1992; Woolfenden, 1997). The minimum temperatures that Peltier cells can reach is −30°C, however, and such cooling power only applies to small volumes. To achieve an efficient collection of VOCs with such temperatures, solid sorbents are inserted inside the collecting tubes, usually made of quartz. The range of VOCs that can be concentrated with these devices is function of the surface area of the adsorbent used. While solid sorbents having surface areas ranging from 35 to 100 m^2/g (such as Tenax TA, Tenax GC, or Carbotrap) provide an efficient collection or components with volatilities ranging from C_5 to C_{16}, tubes filled with microporous carbons with surface areas ranging between 500 and 1000 m^2/g can be used to retain VOCs with higher volatilities. Although much easier to run, these cryofocusing units suffer the same limitations as adsorption traps. As we stated earlier, they can give rise to both negative and

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positive artifacts. Although the occurrence of artifacts is greatly reduced by the limited exposure of the sorbent to air contaminants, the low temperatures used in the concentration step, and the small residence time of VOCs in the concentration tube, they cannot be eliminated completely. These effects are definitely enhanced in cryofocusing units in which the sample is forced to cross the sorbent bed to reach GC column during the injection step.

The analysis of VOCs collected in sorbent tubes also can be performed by adapting existing instruments. Particularly suitable for this specific purpose are the GC units designed for the determination of VOCs in passivated canisters because they are already equipped with cryofocusing systems.(U.S. EPA, 1999). It is sufficient to insert a thermal desorption unit and an eight-port valve in the line connecting the pressurized canister with the cryofocusing system to achieve performances comparable with those of commercial units.

Figures 21.11 and 21.12 show the modifications made in our laboratory to a commercial VOC analyzer built in Europe. Since the cryofocusing unit was connected in series with a splitless injector, a tee-type of union was used to allow prewashing of the trap and injection of the sample into the GC column. Figure 21.12 shows in detail how these connections were made. In this unit, the range of VOCs analyzed by GC-MS was extended by filling the fused silica tube of the cryofocusing unit with Carbopack B. Excellent performances were obtained.

Whichever the choice is, it is important to remember that dead volumes or cold spots between the concentration tube and the column affect the performances of the whole system dramatically no matter how good the GC-MS apparatus, the thermal desorption system, or the sorbent tubes are. This is really the most critical part of any cryofocusing unit. It must be checked with high priority when homemade or commercially available systems are combined with GC-MS instruments. This can be done by injecting a mixture of *n*-alkanes into the system. For this test, as many components as possible should be used. If tailed and broad peaks are observed in the whole range of carbon atoms, a serious possibility exists that the void volume of the concentration system is not negligible with respect to that of the GC column. This happens when the inner diameter of the cooled tube is too large with respect to that the capillary column or when bad connections are made between them. The occurrence of cold spots results instead in selective losses of higher-molecular-weight components relatively to smaller ones. They must be eliminated by heating the zone or by avoiding contact of the sample with strong adsorbing surfaces.

For an overview on the collection, cryofocusing, and injection methods used for the analysis of VOCs, readers should refer to the extensive and excellent paper by Helmig (1999) recently published in a gas chromatography journal.

SELECTION OF THE CAPILLARY COLUMN FOR THE GC-MS ANALYSIS OF VOCs IN AIR

General Requirements for the GC-MS Analysis of VOCs

Within the flow constraints posed by the mass spectrometer, the column that better meets identification purposes is the one providing the best resolution (R) and capacity (C) in the widest range of carbon atoms as possible.

In gas chromatography, R defines how well two peaks are separated one from another (Freeman, 1981; Reoussac, 1982; Bruner, 1993). Under isothermal conditions, it is measured as follows:

$$R = 2\,\frac{tr'_2 - tr'_1}{w_1 + w_2} \tag{21.18}$$

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SAMPLING OF ATMOSPHERIC VOLATILE ORGANIC COMPOUNDS (VOCS) WITH SORBENT TUBES AND THEIR ANALYSIS BY GC-MS

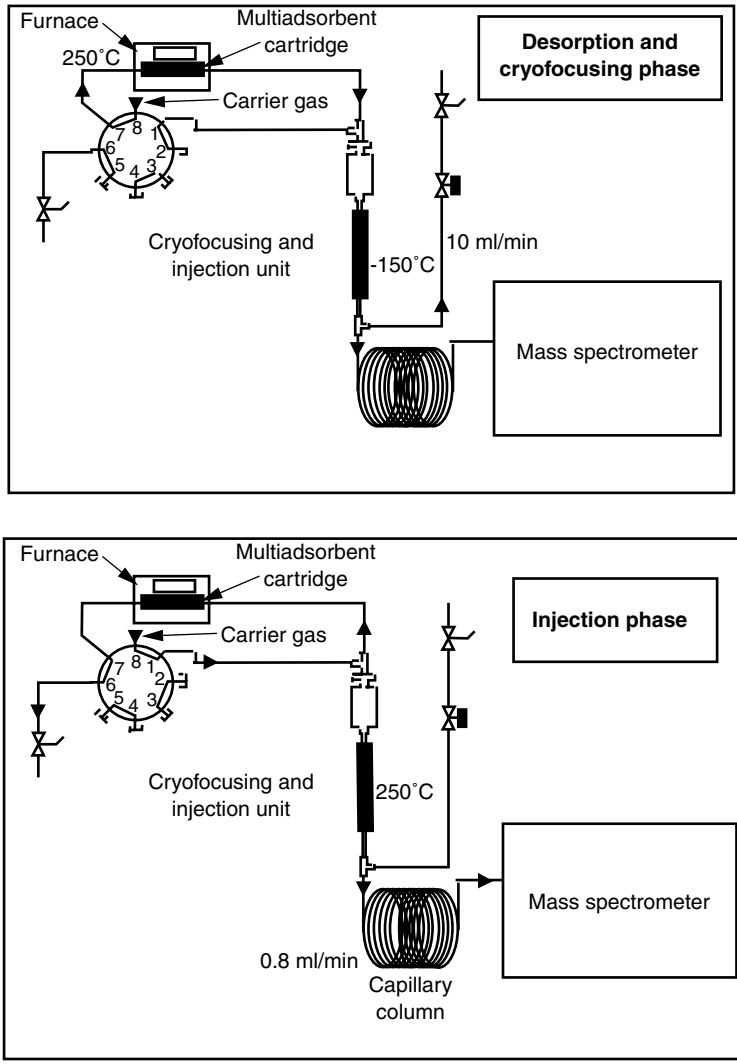

FIGURE 21.11 Modifications made to adapt a commercial VOC analyzer originally developed for the analysis of canister samples to the analysis of sorbent tubes by thermal desorption.

where tr'_2 and tr'_1 are the net retention times of two chromatographic peaks, and w_1 and w_2 are the corresponding peak widths. This equation tells us that two contiguous components are completely separated when R is equal to or larger than 1.5. Compounds showing a 50 percent overlap will be characterized instead by a value of $R = 0.83$.

The capacity C corresponds to the maximum concentrations of solute for which a linear partition isotherm is observed. Above this point, the partition coefficient K_p, which is analogous to the adsorption coefficient defined previously, usually is higher than the one measured in the linear part of the isotherm, and overloaded peaks are generated in the

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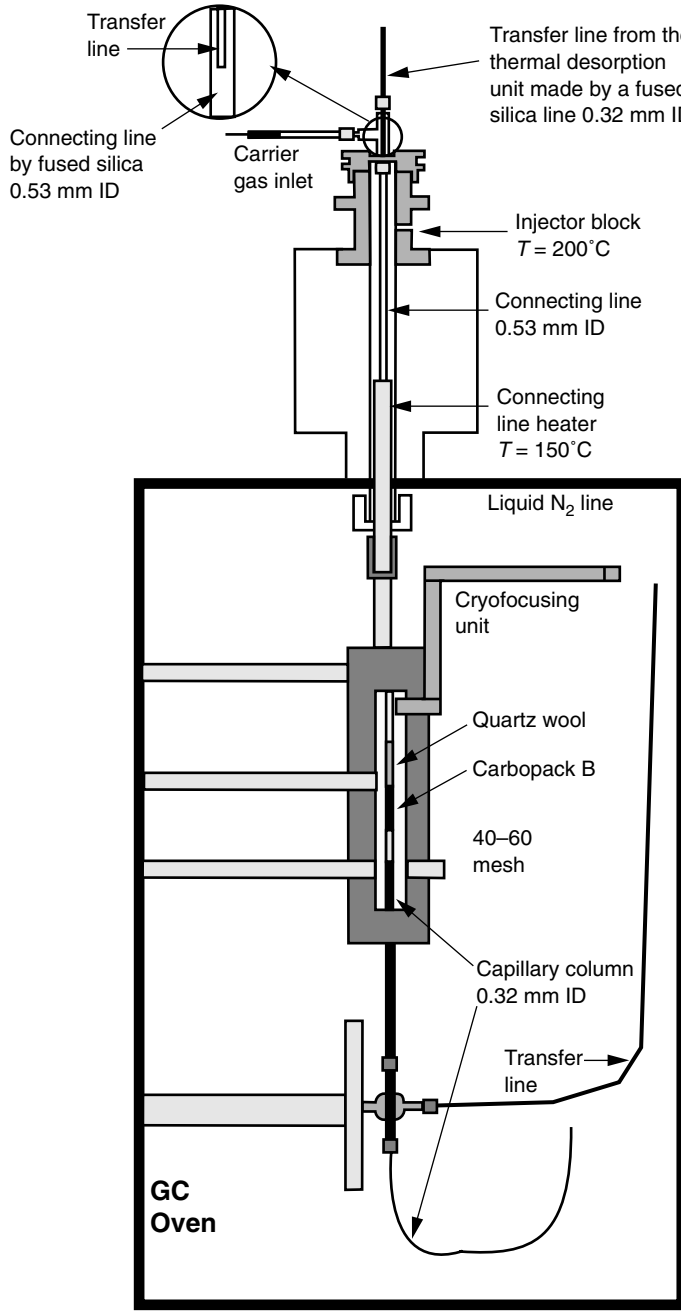

FIGURE 21.12 Details of the modifications made to the apparatus. Shown in Figure 21.11

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chromatogram. As we shall later, this effect reduces the resolving power of the column by affecting the column efficiency.

The optimization of these two parameters is fundamental to maximizing the number of components that can be identified unambiguously by mass spectrometry. The better separated the compounds are, the easier it is to obtain spectra approaching those of pure compounds by GC-MS. It is also clear that larger capacities result in higher masses that can be used for the ionization process. In this way, even the smallest fragments can be used for structural information. Unfortunately, the fundamental properties of a chromatographic column are linked together in such a way that it is not possible to maximize one of them without affecting the others (Freeman, 1981; Rouessac, 1982; Bruner, 1993).

The Relative Retention Index of VOCs and the Polarity Scales of Stationary Phases

Before we discuss the influence of various chromatographic factors on R and C, it is important to provide some basic information on the way GC separations are performed. Since compounds are distributed in a range of carbon atoms going from 2 to 20, their complete elution can be accomplished only by raising the temperature of the column to the maximum value the stationary phase can stand without contaminating the ion source. Although partition of a gas into a liquid is the process used most in capillary GC to separate injected compounds, the equilibria established inside the column are described by the same equations used in adsorption chromatography (Bruner, 1993). By combining Eqs. (21.13) to (21.15), it comes out that all members of a homologous series of *n*-alkanes will show a linear increase in retention when the temperature of the GC column is linearly programmed. This generates an equal difference between the retention of two contiguous members. Since the greatest part of the elution is performed when the proper temperature is reached, all compounds will be characterized by the same peak width. It is thus possible to evaluate the performance of a column by looking at the number of peaks that can be fitted between two contiguous paraffin compounds. This number, called the *separation number* (Freeman, 1981; Bruner, 1993), provides an index of efficiency equivalent to that of the number of theoretical plates (N) measured under constant temperature conditions.

In addition to indications on the range of VOCs that can be analyzed by a column, the elution of *n*-alkanes can be used for identification purposes. This can be done by expressing the retention of a compound x with respect to the *n*-alkanes immediately proceeding and following its elution. This index, called the *relative retention index* (RI_x) or *Kovats index* (Haken, 1976 and references therein), can be determined as follows (Freeman, 1981; Roussac, 1992):

$$RI_x = 100n + 100 \frac{\log tr'_x - \log tr'_n}{\log tr'_{n+1} - \log tr'_n} \tag{21.19}$$

where tr'_x is the net retention time of compound x, and tr'_n and tr'_{n+1} are the net retention times of the *n*-alkanes eluted before (n) and after ($n+1$) the component x. According to Eq. (21.19), a compound with RI = 1150 is eluted exactly in the middle between C_{11} and C_{12}, whereas a solute with RI = 705 will be eluted just after C_7. In the latter case, the increase in retention with respect to *n*-heptane will be 5 percent of the difference existing between C_7 and C_8. Clearly, a compound with an RI = 710 will be eluted after one having an RI = 705. By recalling the exponential dependence of VR_n on T, it is possible to use the elution temperature of x, n, and $(n + 1)$ to derive the RI with Eq. (21.19).

This identification method is quite accurate because it does not require a complete separation of all components in the mixture. It is sufficient that the maximum of the peaks is

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clearly detected and that their retention times (or elution temperatures) are measured accurately. A useful feature of the RI is that its value does not depend so much on the temperature program and the amount of liquid phase present in the column as long as the polarity remains the same. Because of this, data reported in the literature can be used for identification purposes as long as the same stationary phase is used. In GC-MS, knowledge of the retention index is the only way to positively identify compounds (such as many isomeric or enantiomeric components) characterized by similar or equal fragmentation patterns in electron impact and chemical ionization.

The strong dependence of the retention index on the chemical nature of the stationary phase has been exploited (Rohrschneider, 1966) to define polarity scales in gas-liquid chromatography. The polarity of the liquid phase is a fundamental parameter to optimize the resolution of the column, and such scales provide practical criteria for selecting the most suitable coating as a function of the composition of the organic mixture to separate. To define indices that are sufficiently representative of solute-solvent interactions occurring inside the GC column, probe compounds are used. They have been selected according to criteria accounting for the structural features of the molecule and the presence in it of different functional groups. With this method, differences in polarity are measured with respect to a nonpolar column coated with an alkane (squalane) characterized by a number of carbon atoms equal to 30. By measuring the RI of probe components on columns coated with a given phase *f* and with squalane, it is possible to calculate the polarity of *f* using the following equation (Haken, 1976; Rouessac, 1992):

$$Pa = (RI_f^a - RI_{\text{squalane}}^a) \tag{21.20}$$

where P_a is the polarity term given by test compound *a,* and RI_f^a and $\text{RI}_{\text{squalane}}^a$ are the retention indices of *a* measured on the stationary phase *f* and squalane, respectively.

Five probe compounds normally are used to measure the polarity of a column with this method. They are benzene, butanol, pentanone, nitropropane, and pyridine. Their corresponding indices are indicated as x', y', z', u', and s', respectively (Haken, 1976; Rouessac, 1992; Supelco Bulletin 880, 1997). They are called *McReynolds numbers* in honor of the scientist who modified in 1970 the original Rohrschneider scale. The more polar the phase is, the higher are the values of these polarity indices with respect to squalane, whose indices are all zero by definition. To give an idea of the numbers that this type of scale gives, it is sufficient to remember that very low polar phases give values for x', y', z', u', and s' ranging from approximately 3 to approximately 15, whereas high polar phases are characterized by values ranging from approximately 400 to approximately 700. Since all numbers shift to high values going from nonpolar to polar phases, the sum of the individual indices is also used to assess the polarity of a liquid phase.

This type of polarity scale translates into a numerical form the fact that polar components dissolve better into a polar liquid that in a nonpolar one. It is extremely useful for the classification of columns (Supelco Bulletin 880, 1997) but provides only general indications on how the column polarity affects the resolution of different solutes. This happens because the polarity indices are expressed relative to *n*-paraffins. Consequently, the increase in relative retention of probe compounds with the column polarity is due not only to their increased solubility in the liquid phase but also to the decreased solubility of *n*-alkanes in the same phase. To avoid misleading applications of the polarity scale, we must always remember that nonpolar columns retain and resolve VOC mixtures composed of nonpolar compounds better, whereas polar columns, are unsuitable for this purpose. Since analogous considerations hold for the case of polar compounds on polar columns, the composition of the mixture dictates the type of column to be used.

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SAMPLING OF ATMOSPHERIC VOLATILE ORGANIC COMPOUNDS (VOCS) WITH SORBENT TUBES AND THEIR ANALYSIS BY GC-MS

The Polarity of the Stationary Phase

Owing to the wide variety of organic components present in air, two basic approaches can be followed to select the type of liquid phase that provides the best resolution. If we are interested in a specific class of components in air, we must optimize the column polarity as a function of it. To accurately quantify carboxylic acids in air, we need, for instance, a very polar column because it provides the best resolution and a linear isotherm of adsorption in a wide range of concentrations for carboxylic acids. We obviously can quantify other components but not necessarily with the same performance. A problem encountered with very polar phases is that not all of them can be bonded chemically to fused silica tubing, and column bleeding can limit their use in GC-MS. In this case, it is important to see if stabilized phases are available. Although not permanently bonded, they have greater thermal stability than nonbonded phases.

The other approach is to optimize the column polarity as a function of the most abundant and frequently observed classes of components in air. In this case, low or moderately polar columns should be preferred because they allow sufficiently good resolutions for nonpolar compounds (*n*-alkanes), polarizable compounds (alkenes, alkynes, arenes), and moderately polar compounds (carbonyls, ethers, esters, and halogen-containing compounds) (Supelco Bulletin 875C, 1999). These columns also provide acceptable performance for some polar compounds (alcohols). They do not work well, however, for amines and acids because their chromatographic peaks are severely tailed and/or overloaded. This effect is particularly evident on the first members of the homologous series. The polarity indices of general-purpose columns range from approximately 20 to 90 (low polar) or 70 to 170 (moderately polar). Such polarities can be obtained with dimethyl siloxane fluids containing small amounts of diphenylsiloxane (5–20 percent) in the polymer. These stationary phases can be bound chemically within the tubing. In addition to low bleeding, these types of columns provide high resistance to water, organic solvents, acids, and bases. In contrast with nonbonded phases, they can be rinsed with liquid solvents to remove nonvolatile material accumulated at the column inlet.

The Efficiency, Capacity, and Phase Ratio of the Column

Although important, the polarity of the stationary phase is not the only factor that can be used to optimize the resolution of a chromatographic column. It is in fact possible to increase R by increasing the number of theoretical plates of the column. Under isothermal conditions, the dependence of R on N is, in fact, regulated by the following equation (Bruner, 1993):

$$R = \tfrac{1}{4}\left(\frac{\alpha - 1}{\alpha}\right)\left(\frac{k'}{k' + 1}\right)N^{1/2} \tag{21.21}$$

where α and k' are terms closely related to the polarity of stationary phase and of the solute. In using the column efficiency to increase R, we must always remember that the resolution depends on the square root of N. This means that we need to increase the number of theoretical plates by a factor of approximately 4 to fully separate compounds that have a resolution of 0.75.

The efficiency effectively can be improved by increasing the column length L. Since N is linearly dependent on L, we can double the number of theoretical plates by doubling the column length. With capillary columns, such linear dependence holds for values of L going from approximately 15 to approximately 100 m. Above this value, N is usually smaller than that predicted by the theory.

Another way to increase N is to decrease the internal diameter of the column d_c because

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narrow-bore columns show a more favorable *L/N* ratio (also called the *height equivalent of a theoretical plate,* or HETP) than wide-bore or packed columns. A reduction in d_c is also advantageous in terms of flow rates because the best efficiency is reached at lower gas velocities of the carrier gas through the column (u). Efficiency curves of *L/N* versus u show indeed that the smaller d_c is, the lower is the flow rate at which the maximum efficiency is obtained. Although it is possible to use chromatographic columns at flow rates different from the one giving the maximum efficiency, substantial losses of N are observed for values of u deviating more than 30 percent from the optimal value (u_{opt}). This happens because the dependence of *L/N* on u is described by a hyperbolic curve (also called the *Van Deemter curve*) characterized by a distinct minimum (Freeman, 1981; Rouessac, 1992; Bruner, 1993).

Data reported in Table 21.5 show that a great advantage in efficiency and resolution is obtained by selecting columns with very small internal diameters for the analysis of VOCs, but this is severely paid for in terms of column capacity. In practice, the amount of matter that can be injected into narrow-bore columns can be so low as to hinder a full exploitation of *R*. Since N is measured by

$$N = 5.54\ (\mathrm{t}r_n'/\mathrm{w}_{1/2})^{\,2} \tag{21.22}$$

where $\mathrm{t}r_n'$ is the retention time of an eluted compound with $k' > 3$ and $w_{1/2}$ is the peak width at half height, any distortion of the gaussian band due to mass effects results in drastic losses in efficiency and, consequently, in column resolution. Due to easy overloading or tailing of the chromatographic peak, the efficiency produced by very narrow bore columns in the analysis of air samples can be comparable with or even lower than that of larger columns.

Because of this, the flow limitations associated with the use of the MS and the difficulties in minimizing the dead volume of the cryofocusing unit with very small bore columns, the best performance in the analysis of VOCs by GC-MS is obtained with long columns (60 m) having an internal diameter of 0.32 mm. Good performance also can be obtained with 30-m columns with $d_c = 0.25$, provided that dead volumes of the injection system are minimized and the bulk of water is eliminated completely by the trap.

The capacity and retention of these columns can be further optimized by selecting the proper amount of liquid coating inside the column. Larger capacities indeed can be obtained by increasing the thickness of the liquid film (d_f) deposited on the internal walls of the capillary tube because more solute molecules can be dissolved in the stationary

TABLE 21.5 Efficiency, Capacity, and Resolution Given by Capillary Columns Characterized by Different Internal Diameters d_c

Internal Diameter (mm)	Number of theoretical plates per meter (*N*/m)	*L/N* (HETP) (mm)	Optimal flow rate of helium (ml/min)	Capacity* (ng of each component)	Resolution† given by a 60-m column (*R*)
0.20	5000	0.20	0.4	5–30	1.5
0.25	4170	0.24	0.7	50–100	1.36
0.32	3300	0.30	1.4	400–500	1.23
0.53	1670	0.60	2.5	1000–2000	0.85
0.75	1170	0.85	5.0	10,000–15,000	0.72

Note: Data refer to the efficiency measured at μ_{opt}.

*Values obtained with a film thickness of 0.25 μm on 0.25- and 0.32-mm ID columns and 0.5 μm on 0.53- and 0.75-mm ID columns.

†Calculations made by assuming a complete separation of two contiguous peaks with $k' >> 3$ on the most efficient column (0.2 mm ID).

Source: Data from the Supelco Bulletin 875 (1999).

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phase. However, this results in a parallel increase in retention of all components present in the organic mixture because more time is spent by the solute molecules in the liquid phase. The use of large d_f values is thus particularly suitable if we need to better separate the more volatile fraction of the organic mixture. The increase in retention, however, can be so large as to make elution of the heaviest compounds difficult.

A parameter that greatly helps in the proper selection of d_f is the phase ratio ß of the column (Rouessac, 1992; Bruner, 1993). It is defined by the ratio between the void volume of the column V_0 and that of the liquid phase V_{st} and is inversely related to the column retention ($ß = K_p/k'$). Since empty tubes are used in capillary GC and the liquid phase can be homogeneously distributed around the internal walls, it is possible to calculate ß from simple geometric considerations by knowing d_c and d_f (Rouessac, 1992). Its value is given by

$$ß = \frac{d_c}{4d_f} \tag{21.23}$$

Being related to d_f and k', the value of ß provides indications on the amount of phase necessary to separate a complex organic mixture as a function of the hydrocarbon composition present in it. Figure 21.13 reports the changes in ß and C as a function of d_f for columns having inner diameters of 0.2, 0.25, and 0.32 mm. We also have indicated in Fig. 21.13 the values of ß that are more suitable for separating organic mixtures with different hydrocarbon distributions.

For general purposes, ß values ranging between 100 and 400 should be preferred (Supelco Bulletin 875, 1999). With columns having internal diameters of 0.32 mm, this corresponds to values of d_f ranging from 0.2 to 0.8. Since these columns provide the best performances for VOCs ranging in volatility from C_4 to C_{30}, subambient temperatures (0–5°C) must be used to separate and detect light components.

For specific applications, a wide selection of columns is available. They include capillary columns internally coated with porous layers of adsorbent materials (PLOT columns). A full list of columns used for the analysis of VOCs in air can be found in the literature (Helmig 1999). We would like to add to this list columns internally coated with chiral phases (ß-cyclodextrins). One such column has been used recently by Yassaa et al. (2001) to separate enantiomeric VOCs in vegetation emissions and in atmospheric samples. This is a rather new approach that might open new possibilities to clarify the origin of monoterpenes in plants and their fate in the atmosphere.

IDENTIFICATION OF VOCs IN AIR BY GC-MS

The Full Scan and Selected Ion Detection in Electron Impact MS

With direct coupling, the whole effluent of the column is sent to the ion source of the mass spectrometer, where molecules are ionized and the products formed transferred by an electrical field to a mass analyzer for separation (Bruner, 1993). Depending on the potential applied to the ion repeller, negative or positive ions can be expelled by the source. They can be separated with filters using magnetic and/or electrical fields. The latter can be generated statically (sector-based filters) or dynamically (quadrupole and ion-trap filters). The mass and composition of ions are determined by recording them with an ion detector (usually an electron multiplier) after selective passage through the analyzer. By programming the ion filter in a certain mass range, the intensity of the fragments can be recorded sequentially into a data system, and a matrix reporting the ion intensity versus the value of m/z is generated. The fragmentation pattern as well as the intensity of the ions produced strictly depends on the type of ionizing medium adopted.

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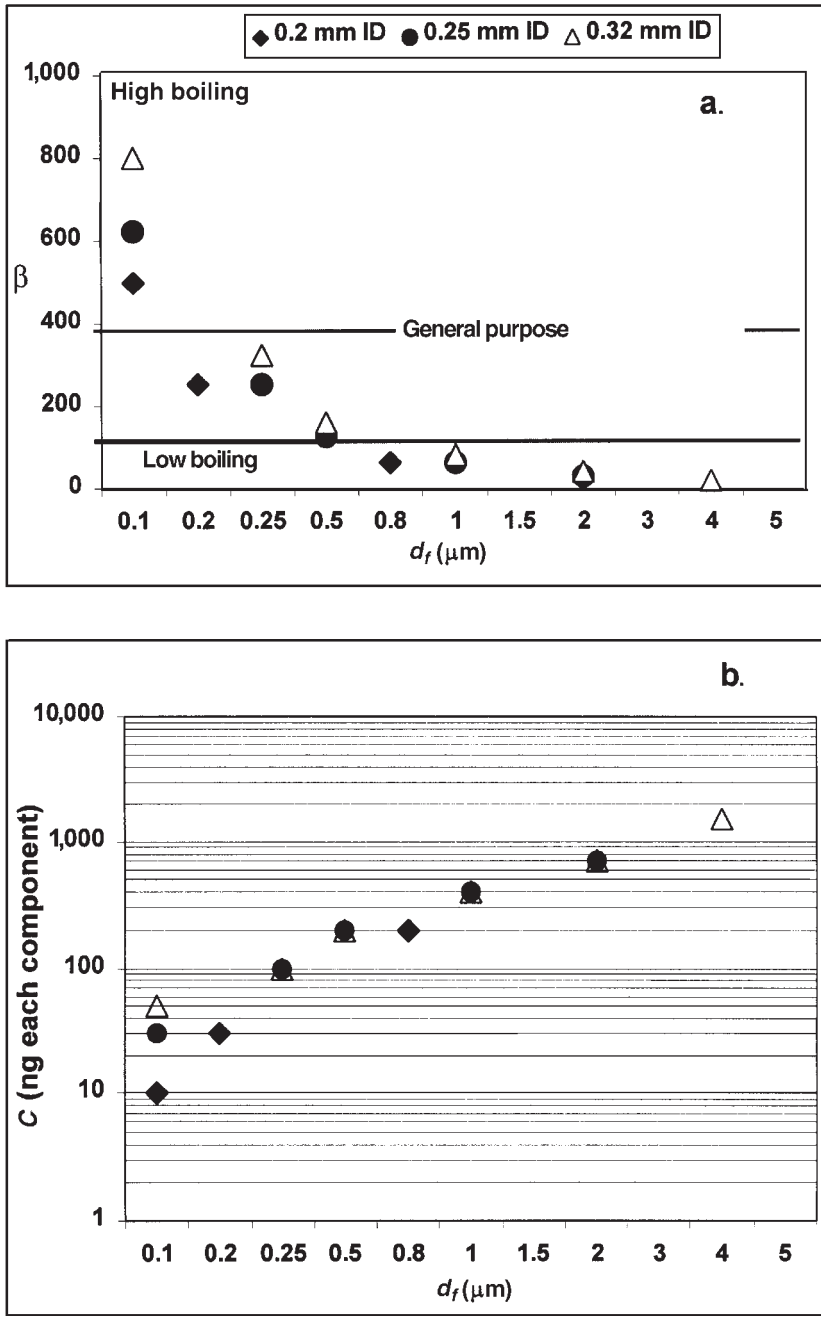

FIGURE 21.13 Changes of the phase ratio (ß) and capacity (C) of narrow-bore columns with different internal diameters as a function of the film thickness of the liquid phase (d_f).

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The GC-MS detection exploits the fact that the ion collection in a wide range of masses is one order of magnitude faster than the elution of the peak, and several scans can be made during the elution of a single component (Bruner, 1993). The signal from individual ions and that of the total current acquired during each scan are stored sequentially in a data system. By plotting them against time, the so-called mass-chromatogram is generated. Since the total current and individual signals can be retrieved, it is possible to reconstruct the GC profile for the total ion current (TIC) and for any one of the individual masses that have been recorded in each scan (Budde and Eichelberger, 1979). Spectra collected also can be reprocessed, and a subtraction technique can be applied to them to separate the contribution of the eluted compound from that of column bleeding. This is particularly important in that part of the chromatogram where high temperatures are reached. Subtraction techniques are also needed in the case of partial overlapping between eluted components.

The sensitivity obtained in reconstructed mass-chromatography is in the nanogram range because substantial amounts of ions are lost during the scanning process. It might be greater or lesser as a function of the fragmentation pattern of the compound investigated and the type of ionization and filter used. Much better sensitivities (picogram or even subpicogram level) can be obtained by fast recording a limited set of ions (usually 3 to 5) that are specific to the compound to be detected. To do this, the fragmentation pattern of the compound must be known in advance. Since only a limited number of masses are stored in the data system, it is impossible with this method to get the full spectrum of eluted components. For this reason, selective ion monitoring (SIM) is used preferentially for the detection and quantification of target compounds present at trace levels in complex mixtures. It is the preferred technique for monitoring highly toxic pollutants in air and in complex matrices. Full-scan and SIM analyses represent at least 95 percent of the analyses performed today. The former technique is by far the preferred one when unknown samples are analyzed and the full picture of VOCs present in air needs to be obtained. Once the composition of VOCs in a certain area is assessed, it possible to develop a SIM approach for studying the spatial and temporal evolution of priority compounds in that specific area. To do this, we must identify the largest number of components possible.

Positive identification by MS is linked primarily to the possibility of deriving information on the structure and molecular weight of eluted compounds and on the presence of functional groups in them. Among the various ionization techniques used in MS, the one exploiting impact with high-energy electrons (70 eV) provides the best structural information because it gives rise to the largest number of fragments in the spectrum. Chemical rules to rationalize their formation from the molecular ion have been known for several years, and methods to interpret mass spectral data are well consolidated (Biemann, 1962; Mclafferty, 1963; Budzikiewicz et al., 1967). Moreover, reference spectra for almost all stable organic compounds known in nature are available in the literature. The identification of compounds through their electron impact spectra is greatly simplified today because reliable algorithms have been developed to compare data collected in GC-MS with those of pure compounds. Even the most simple benchtop mass spectrometer is now equipped with reference libraries containing more than 200,000 spectra and with a specific software to help in the identification of eluted compounds. It should be noted, however, that computer programs do not follow chemical rules, and a careful interpretation of the spectra is always necessary to confirm that the most probable structure indicated by the program is actually the right one.

Other MS Ionization Techniques for VOC Identification

Not always, however, can compounds eluted by the column be identified unambiguously by electron impact. Some of them may have similar fragmentation patterns, and others do not provide enough information for a clear identification. In this case, high-resolution analyzers, such as those based on magnetic and electric sectors set in series, can be of great

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help for positive identification. Since these mass spectrometers can detect differences in mass units lower than 10^{-4}, it is possible to identify the eluted compounds by using the exact chemical composition of the ions formed by electron impact.

Another way to gain decisive information on the chemical structure of an unknown component is to use the collision of its ions with argon or helium. With this technique (called MS-MS), another mass filter is necessary to analyze the daughter ions formed by ion-molecule reactions. The recent development of low-cost ion-trap mass spectrometers has further stimulated the use of MS-MS techniques for identification purposes because such instruments have intrinsic MS-MS capabilities. The ions formed by electron impact, in fact, can be confined inside the mass filter as long as defined values of the quadrupolar field are applied to it (March and Todd, 1995). To dampen the oscillation of the ions and keep them in the center of the electrical field, a moderator gas, usually helium, is introduced into the chamber. By increasing the collision path of the ions inside the trap above a certain value, ion-molecule reactions can be induced. Daughter ions formed by collision with helium can be extracted and analyzed. Through their study, fundamental information for unambiguous identification of the unknown compound can be obtained (Johnson et al., 1990).

Another approach commonly used for peak identification is chemical ionization (Munson and Field, 1966; Harrison, 1992). It is particularly useful for those compounds in which the energy transferred by electron impact is too large when compared with their ionization potentials, and only ions characterized by low m/z values are observed in the mass spectra. By using ion-molecule reactions for the ionization process, a lower amount of energy can be transmitted to the molecule, and fragmentation of the molecular ion can be reduced drastically. The reagent species usually is generated by electron impact. Its preferential formation is obtained by maintaining inside the source a high pressure (approximately 0.2–1 torr) of the ionizing gas. When the unknown component is added to the reagent species, acid-base reactions take place, and a proton (or hydride) transfer is observed between the neutral molecule and the reagent. In chemical ionization, this ion is often the base peak. The mass of the parent ion will be $(M + 1)^+$ when the reagent acts as a Brønsted acid. A parent ion with $m/z = (M - 1)^+$ will be generated instead when the reagent behaves as a Brønsted base. Preferred gases in chemical ionization are the ones whose ions act as strong Brønsted acids (methane, water, iso-butane). Proton transfer using water as the ionizing gas has been used (Lindinger et al., 1998) to build an MS analyzer of VOCs in air.

Electron capture of thermal electrons also can be exploited for the selective detection of strong electrophylic compounds, such as those organics containing halogen atoms in the molecule. Thermal electrons (a few electronvolts of energy) are produced inside the source by collision of a gas (such as methane) with high-energy electrons. The experimental setup is quite similar to the one used in chemical ionization except for the fact that negative ions are recorded.

The Combined Use of Selected Ions and Retention Indices for the Identification of VOCs by Electron Impact MS

Due to their high selectivity and complexity, these techniques cannot be used on a routine basis for the GC-MS analysis of VOCs in air. Therefore, once the unknown component has been identified, electron impact fragments are selected and used for routine identification. Full-scan and SIM analyses in electron impact can be performed with any one of the mass filters available on the market. Since the highest molecular weight of VOCs in air never exceeds a value of 350 mass units, reliable results can be obtained with a benchtop MS equipped with quadrupole or ion trap analyzers. It is strongly debated today whether one option is better than the other. From a practical viewpoint, both are suitable for this type of analysis as long as they are used correctly. Since mass spectra obtained with quadrupole-based MS better match those recorded in existing libraries, these instruments are easy to

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SAMPLING OF ATMOSPHERIC VOLATILE ORGANIC COMPOUNDS (VOCS) WITH SORBENT TUBES AND THEIR ANALYSIS BY GC-MS

use by people who have only a limited background in mass spectrometry. Ion-trap-based MS provides better sensitivities and MS-MS capabilities than quadrupole-based MS, but a deeper knowledge is needed to interpret the data and to exploit the full potential of these instruments. Recently, ion-trap detection has been applied successfully to the identification of precursors and products of photochemical smog pollution in air (Daughtrey et al., 1998).

For positive identification, the best situation occurs when all mass spectra acquired by GC-MS are sufficiently clear to closely match the ones of pure compounds listed in known libraries. This is possible in practice when the column is able to sufficiently separate all compounds present in the mixture. Despite the high efficiency of columns used today, the composition of VOCs in air is often so complex that many constituents are coeluted or show substantial overlapping of their chromatographic peaks. If subtraction techniques are unable to clearly separate the contributions of the ions coming from overlapping compounds, mass spectra obtained in GC-MS will never match those of pure substances, and positive identification becomes very difficult.

There is still a chance to positively identify these compounds if some of the ions generated by one component do not appear in the fragmentation pattern of the other component. In this case, it is possible to generate mass chromatographic profiles substantially free from interferences by plotting the current profiles of the ions that are specific to one of the two components (Budde and Eichelberger, 1979; Bruner, 1993). The ratios between the areas of the chromatographic peaks obtained using specific ions can be used for identification purposes as long as their ratios match those of the ion intensities observed in the mass spectrum of the pure component. By recalling that for the compound *n,* the area of the peak recorded in full-scan mode (A_n^{TIC}) is given by the contribution of all ions produced by the ionization of *n,* we can write

$$\text{RF}_n^{\text{TIC}} = \frac{A_n^{\text{TIC}}}{Q_n} \tag{21.24}$$

where Q_n and RF_n^{TIC} are the amount injected and the response factor of *n,* respectively. Since each ion contributes to the total ion current for a fraction *f,* we have

$$\text{RF}_n^x = f_n \times \text{RF}_n^{\text{TIC}} \tag{21.25}$$

$$\text{RF}_n^y = (f_n^y / f_n^y)\, \text{RF}_n^x \tag{21.26}$$

where f_n^x and f_n^y are the percentage contribution to the total ion current of the ions *x* and *y,* respectively, and RF_n^x, RF_n^y and RF_n^{TIC} are the response factors measured with *x, y,* and the total ion current.

By combining the various equations, we have

$$\frac{A_n^x}{A_n^y} = \frac{f_n^x}{f_n^y} \tag{21.27}$$

$$\frac{A_n^x}{A_n^{TIC}} = f_n^x \tag{21.28}$$

Equation (21.28) holds also in the case in which the signal of TIC does not cover the entire mass range. To limit interference from permanent gases and to have more clear signals, it is a common practice to acquire the ions starting from values of *m*/*z* equal to or higher than 20. In this case, a proper value should be used for f_n^x.

Since few components exist in nature whose fragments are so specific as not to be produced by other molecules, it is possible to use this method for unambiguous identification only when the relative retention of a compound on the GC column is consistent with the appearance of its specific ions in the mass chromatogram. Since 1985, libraries exist that provide RI values for different components on columns having different polarities.

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Together with data reported in the literature, they can help greatly in the identification of eluted VOCs (Helmig et al., 1996, 1998). If the same column is used, a matrix can be developed for a search for the specific ions in various sectors of the chromatographic profile (Ciccioli et al., 1993b). For positive identification, it is important that data are collected under the same experimental conditions and that all information acquired through the analysis of different samples is stored into the data system. A good example of this approach can be found in the papers by Helmig et al. (1996, 1998, 1999b), who have used RI extensively and selected ions for the identification of VOCs in the remote station installed at Mauna Loa, Hawaii, and in forest areas of the United States. The use of RI is fundamental in the case of enantiomeric components because they show exactly the same mass spectra (Yassaa et al., 2001).

If the RI and the mass spectrum of an unknown peak are recorded accurately, it is possible to proceed to its identification when the pure compound will be isolated and its distinctive features confirmed. This is a common process in the analysis of VOCs in air because new products emitted from biogenic or anthropogenic sources or formed by their photochemical degradation in the atmosphere are continuously identified by GC-MS.

Following this approach, a database has been created in our institute that allows identification of 600 different components in air by GC-MS. It has been built over more than 10 years by combining data obtained from the literature with the direct information acquired from the analysis approximately 5000 air and emission samples collected worldwide (Ciccioli et al., 1999). Table 21.6 lists the retention indices of these components together with the three most selective ions to be used for positive identification by mass chromatography or SIM. They are reported together with the CAS number (when available or clearly defined) and the molecular formula. To make the exploitation of retention data possible by readers, we have summarized in Table 21.7 the capillary column and experimental conditions with which the database has been created. Additional information on the temporal sequence of ions to be used for positive identification of the various classes of VOCs can be found in Ciccioli et al. (1993).

A practical example of the application of the data reported in Table 21.6 is shown in Fig. 21.14 where the total ion profile of a VOC sample collected in the city of Algiers is plotted together with the mass chromatographic profile generated for the selective detection of monoterpene compounds (m/z 93), trimethylbenzenes (m/z 12), alcohols (m/z 31), aldehyde (m/z 44), and acids (m/z 60). For sake of clarity, in Fig. 21.14, we have numbered only some key components for each class investigated. A complete list of compounds identified in this samples can be found in Yassaa et al. (2000). This application highlights the different levels of specificity that can be obtained by using the ions listed in Table 21.6 for the identification of VOCs in air. While a very clean profile is obtained for acids, monoterpenes, alcohols, and trimethylbenzenes, some interference is observed on the aldehyde profile because of the lower specificity of the m/z 44. The occurrence of this interference explains why the RI and three different ions must be combined for the positive identification of a given component.

QUANTIFICATION OF VOCs BY MASS SPECTROMETRY

General Problems

The main difficulty encountered in the quantitative analysis of VOCs by GC-MS is that the molar response of individual compounds in electron impact essentially depends on the first ionization potential of the molecule. This parameter is a function the number of carbon

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TABLE 21.6 List of Relative Retention Indices (RI) and Selected Ions for the Positive Identification of VOCs in Air by GC-MS

					Relative Abundance							
					MW ion		Ion 1		Ion 2		Ion 3	
No.	CAS number	Compound	RI	Molecular formula	*m/z*	%	*m/z*	%	*m/z*	%	*m/z*	%
1	74-90-8	Hydrocyanic acid		CHN	27	100	27	100	26	24		
2	75-07-0	Acet aldehyde		C_2H_4O	44	46	29	100	44	46	43	28
3	67-56-1	Methanol		CH_4O	32	63	31	100	32	63	29	78
4	74-98-6	*n*-C_3	300.0	C_3H_8	44	27	29	100	28	59	27	47
5	75-28-5	Propane, 2-methyl-	346.7	C_4H_{10}	58	3	43	100	41	43	27	30
6	106-98-9	1-Butene	388.9	C_4H_8	56	38	41	100	56	38	39	42
7	106-99-0	1,3-Butadiene	393.3	C_4H_6	54	90	54	90	39	100	27	70
8	106-97-8	*n*-C4	400.0	C_4H_{10}	58	12	43	100	58	12	29	43
9	689-97-4	1-Buten-3-yne	405.8	C_4H_4	52	100	52	100	51	50	50	42
10	74-83-9	Methane, bromo-	408.0	CH_3Br	94	100	94	100	96	90	79	32
11	624-64-6	*trans*-2-Butene	408.7	C_4H_8	56	48	41	100	56	48	39	36
12	107-00-6	1-Butyne	413.4	C_4H_6	54	100	54	100	39	91	53	48
13	74-93-1	Methanethiol	416.8	CH_4S	48	90	47	100	48	90	45	47
14	107-01-7	*cis*-2-Butene	419.9	C_4H_8	56	48	41	100	56	48	39	42
15	107-31-3	Formic acid, methyl ester	422.0	$C_2H_4O_2$	60	25	31	100	29	84	60	25
16	460-12-8	1,3-Butadiene	430.6	C_4H_2	50	100	50	100	49	39		
17	590-19-2	1,2-Butadiene	439.1	C_4H_6	54	100	54	100	27	62	39	44
18	563-45-1	1-Butene, 3-methyl-	457.4	C_5H_{10}	70	25	55	100	70	25	39	26
19	64-17-5	Ethanol	459.7	C_2H_6O	46	10	31	100	45	35	46	10
20	591-93-5	1,4-Pentadiene	465.6	C_5H_8	68	100	68	100	67	84	53	57
21	75-05-8	Acetonitrile	466.9	C_2H_3N	41	100	41	100	40	54	39	21
22	123-38-6	Propanal	469.7	C_3H_6O	58	63	29	100	58	64	28	63
23	107-02-8	2-Propenal	472.4	C_3H_4O	56	66	27	100	56	66	26	59
24	78-78-4	Butane, 2-methyl-	473.9	C_5H_{12}	72	3	43	100	41	95	57	49
25	591-95-7	1,2-Pentadiene	477.5	C_5H_8	68	51	68	51	67	83	39	100

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TABLE 21.6 List of Relative Retention Indices (RI) and Selected Ions for the Positive Identification of VOCs in Air by GC-MS (*Continued*)

					Relative Abundance							
					MW ion		Ion 1		Ion 2		Ion 3	
No.	CAS number	Compound	RI	Molecular formula	*m/z*	%	*m/z*	%	*m/z*	%	*m/z*	%
26	67-64-1	2-Propanone	479.0	C_3H_6O	58	26	43	100	58	26		
27	75-69-4	Methane, trichlorofluoro-	482.6	CCl_3F	136	0	101	100	103	66		
28	503-17-3	2-Butyne	484.3	C_4H_6	54	100	54	100	53	43	39	25
29	109-67-1	1-Pentene	489.3	C_5H_{10}	70	34	42	100	55	68	70	34
30	1717-00-6	Ethane,1,1-dichloro-1-fluoro-	490.2	$C_2H_3Cl_2F$	116	1	81	100	83	32	61	26
31	110-00-9	Furan	490.6	C_4H_4O	68	75	68	75	39	100		
32	563-46-2	1-Butene, 2-methyl-	496.5	C_5H_{10}	70	35	55	100	70	35	42	31
33	107-13-1	2-Propenenitrile	498.6	C_3H_3N	53	100	53	100	52	79	26	85
34	109-66-0	*n*-C5	500.0	C_5H_{12}	72	8	43	100	57	15	42	60
35	109-94-4	Formic acid, ethyl ester	502.2	$C_3H_6O_2$	74	14	31	100	45	26	74	14
36	67-63-0	2-Propanol	502.3	C_3H_8O	60	1	45	100	59	4		
37	60-29-7	Ethyl ether	504.9	$C_4H_{10}O$	74	23	31	100	45	32	59	38
38	78-79-5	Isoprene	506.1	C_5H_8	68	63	67	100	68	63	53	82
39	75-18-3	Sufide, dimethyl-	508.2	C_2H_6S	62	83	47	100	62	83	45	59
40	646-04-8	*trans*-2-Pentene	509.5	C_5H_{10}	70	36	55	100	70	36	42	38
41	627-20-3	*cis*-2-Pentene	517.4	C_5H_{10}	70	34	55	100	70	34	42	47
42	513-35-9	2-Butene, 2-methyl-	522.5	C_5H_{10}	70	36	55	100	70	36	42	30
43	75-09-2	Methane, dichloro-	524.0	CH_2Cl_2	84	86	49	100	84	86	86	55
44	79-20-9	Acetic acid, methyl ester	524.6	$C_3H_6O_2$	74	16	43	100	74	16	59	7
45	2004-70-8	*trans*-1,3-Pentadiene	525.0	C_5H_8	68	65	68	65	67	95	39	100
46	75-15-0	Carbon disulfide	525.5	CS_2	76	100	76	100	78	9	44	17
47	75-65-0	2-Propanol, 2-methyl-	526.1	$C_4H_{10}O$	74	0	59	100	31	43		
48	78-80-8	1-Buten-3-yne, 2-methyl-	531.8	C_5H_6	66	100	66	100	40	55	51	36
49	76-13-1	Ethane,1,1,2-trichloro-1,2,2-trifluoro-	533.9	$C_2Cl_3F_2$	186	0	101	100	151	69	103	64

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50	542-92-7	1,3-Cyclopentadiene	534.9	C_5H_6	66	100	66	100	65	69	39	50
51	107-12-0	Propanenitrile	536.3	C_3H_5N	55	10	54	62	28	100	55	10
52	75-83-2	Butane,2,2-dimethyl-	536.7	C_6H_{14}	86	0	43	100	57	83	71	64
53	1574-41-0	*cis*-1,3-Pentadiene	537.5	C_5H_8	68	65	68	65	67	98	39	100
54	2206-23-7	3-Penten-1-yne	544.2	C_5H_6	66	89	66	89	65	61	39	100
55	75-52-5	Nitromethane	544.4	CH_3NO_2	61	39	30	100	61	50	46	34
56	78-84-2	Propanal, 2-methyl-	548.9	C_4H_8O	72	38	43	100	72	38	41	80
57	142-29-0	Cyclopentene	553.9	C_5H_8	68	38	67	100	68	38	39	52
58	78-85-3	2-Propenal, 2-methyl-	559.1	C_4H_6O	70	82	41	100	70	82	39	67
59	760-20-3	1-Pentene, 3-methyl-	559.1	C_6H_{12}	84	39	55	100	69	86	41	64
60	287-92-3	Cyclopentane	564.4	C_5H_{10}	70	14	42	100	55	38	70	14
61	109-99-9	Furan, tetrahydro-	565.3	C_4H_8O	72	31	42	100	72	31	71	28
62	126-98-7	2-Propenenitrile-2-metil-	566.5	C_4H_5N	67	56	41	100	67	56	52	19
63	79-29-8	Butane, 2,3-dimethyl-	566.5	C_6H_{14}	86	3	43	100	42	90	71	18
64	563-78-0	1-Butene, 2,3-dimethyl-	567.7	C_6H_{12}	84	30	69	100	41	85	84	30
65	71-23-8	1-Propanol	568.7	C_3H_8O	60	7	31	100	59	11	42	7
66	1634-04-4	Propane, 2-metoxy-2-methyl-	570.0	$C_5H_{12}O$	88	0	73	100	41	20	57	20
67	107-83-5	Pentane, 2-methyl-	571.2	C_6H_{14}	86	3	43	100	42	58	57	10
68	558-37-2	1-Butene, 3.3-dimethyl-	573.2	C_6H_{12}	84	24	41	100	69	80	84	24
69	108-05-4	Acetic acid, ethenyl ester	574.1	$C_4H_6O_2$	86	9	43	100	86	9		
70	646-05-9	1-Penten-3-yne	576.2	C_5H_6	66	99	66	99	65	55	39	100
71	78-94-4	3-Buten-2-one	576.3	C_4H_6O	70	29	43	77	55	96	70	29
72	592-42-7	1,5-Hexadiene	579.1	C_6H_{10}	82	1	67	89	41	100	54	51
73	123-72-8	Butanal	579.8	C_4H_8O	72	30	44	67	41	69	72	30
74	1066-40-6	Silanol, trimethyl-	583.9	$C_3H_{10}OSi$	90	0	75	100	45	25		
75	96-14-0	Pentane, 3-methyl-	584.1	C_6H_{14}	86	2	57	86	56	84	41	100
76	630-19-3	Propanal, 2,2-dimethyl-	584.6	$C_5H_{10}O$	86	34	57	100	41	83	86	34
77	78-93-3	2-Butanone	587.0	C_4H_8O	72	17	43	100	72	17	57	9
78	763-29-1	1-Pentene, 2-methyl-	589.0	C_6H_{12}	84	21	56	88	41	100	69	30
79	14092-20-7	2-Hexen-4-yne	590.1	C_6H_8	80	42	79	100	80	42	77	60
80	78-82-0	Propanenitrile, 2-metil-	590.3	C_4H_7N	69	2	68	43	42	100	54	21

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TABLE 21.6 List of Relative Retention Indices (RI) and Selected Ions for the Positive Identification of VOCs in Air by GC-MS (*Continued*)

					Relative Abundance							
					MW ion		Ion 1		Ion 2		Ion 3	
No.	CAS number	Compound	RI	Molecular formula	*m/z*	%	*m/z*	%	*m/z*	%	*m/z*	%
81	592-41-6	1-Hexene	590.4	C_6H_{12}	84	13	56	62	41	100	69	19
82	534-22-5	Furan, 2-methyl-	596.9	C_5H_6O	82	100	82	100	81	71	53	86
83	110-54-3	*n*-C6	600.0	C_6H_{14}	86	6	41	100	57	75	43	64
84	78-92-2	2-Butanol	602.4	$C_4H_{10}O$	74	0	45	100	31	27	59	20
85	7642-09-3	*cis*-3-Hexene	603.3	C_6H_{12}	84	29	55	94	41	100	69	25
86	108-20-3	Propane, 2,2'-oxybis	603.8	$C_6H_{14}O$	102	1	45	100	87	19	59	10
87	4050-45-7	*trans*-2-Hexene	605.9	C_6H_{12}	84	28	55	100	41	57	69	19
88	930-27-8	Furan, 3-methyl-	606.8	C_5H_6O	82	100	82	100	81	59	53	91
89	67-66-3	Methane, trichloro-	607.8	$CHCl_3$	118	2	83	100	85	60	35	28
90	96-33-3	2-Propenoic acid, methyl ester	608.0	$C_4H_6O_2$	86	0	55	100	27	88	85	17
91	2787-43-1	1,3-Pentadiene, 3-methyl-	608.2	C_6H_{10}	82	40	67	100	82	40	39	38
92	691-38-3	2-Pentene, 4-methyl-	608.7	C_6H_{12}	84	19	41	100	69	57	84	19
93	141-78-6	Acetic acid, ethyl ester	608.8	$C_4H_8O_2$	88	2	43	100	61	12	70	9
94	115-18-4	3-Buten-2-ol, 2-methyl-	610.4	$C_5H_{10}O$	86	5	71	87	43	100	59	31
95	616-12-6	2-Pentene, 3-methyl-, *trans*-	611.3	C_6H_{12}	84	24	41	100	69	49	55	34
96	1120-62-3	Cyclopentene, 3-methyl-	611.9	C_6H_{10}	82	21	67	100	82	21	39	35
97	7688-21-3	*cis*-2-Hexene	616.2	C_6H_{12}	84	29	55	100	41	61	69	23
98	4786-20-3	2-Butenenitrile	616.3	C_4H_5N	67	34	67	34	41	100	66	18
99	1118-58-7	1,3-Pentadiene, 2-methyl-	619.2	C_6H_{10}	82	47	67	100	39	61	41	54
100	109-75-1	3-Butenenitrile	622.1	C_4H_5N	67	36	67	36	41	100	39	43
101	922-62-3	2-Pentene, 3-methyl-, *cis*-	623.4	C_6H_{12}	84	25	41	100	69	53	55	35
102	64-18-6	Formic acid	624.0	CH_2O_2	46	61	29	100	46	61	45	48
103	554-12-1	Propanoic acid, methyl ester	625.5	$C_4H_8O_2$	88	21	29	100	57	76	59	25
104	75-85-4	2-Butanol, 2-methyl-	625.8	$C_5H_{12}O$	88	0	59	100	73	55	45	43
105	590-35-2	Pentane, 2,2-dimethyl-	626.2	C_7H_{16}	100	0	43	78	57	100	85	30

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106	96-37-7	Cyclopentane, methyl-	627.9	C_6H_{12}	84	7	56	100	41	80	69	41
107	107-06-2	Ethane, 1,2-dichloro-	632.2	$C_2H_4Cl_2$	98	14	62	100	27	91	49	40
108	10420-90-3	1,3-Hexadien-5-yne	632.4	C_6H_6	78	100	78	100	52	37	63	23
109	108-08-7	Pentane, 2,4-dimethyl-	633.7	C_7H_{16}	100	0	43	100	57	66	56	41
110	625-27-4	2-Pentene, 2-methyl-	634.4	C_6H_{12}	84	24	41	100	69	52	84	24
111	109-74-0	Butanenitrile	634.5	C_4H_7N	69	0	41	100	29	62	27	37
112	78-83-1	1-Propanol, 2-methyl-	634.6	$C_4H_{10}O$	74	7	43	100	31	77	41	89
113	7319-00-8	*trans*-1,4-Hexadiene	636.2	C_6H_{10}	82	41	67	100	82	41	39	79
114	628-41-1	1,4-Cyclohexadiene	637.1	C_6H_8	80	76	80	76	79	100	77	59
115	15798-64-8	2-Butenal	637.7	C_4H_6O	70	100	70	100	39	87	69	45
116	71-55-6	Ethane,1,1,1-trichloro-	638.7	$C_2H_3Cl_3$	0	132	97	100	99	63	117	15
117	7318-67-4	*cis*-1,4-Hexadiene	640.1	C_6H_{10}	82	41	67	100	82	41	39	68
118	592-57-4	1,3-Cyclohexadiene	641.5	C_6H_8	80	52	80	52	79	100	77	46
119	13721-54-5	1-Hexen-3-yne	644.0	C_6H_8	80	85	80	85	79	100	77	68
120	590-86-3	Butanal, 3-methyl-	645.0	$C_5H_{10}0$	86	5	44	100	58	44	41	93
121	563-80-4	2-Butanone, 3-methyl-	650.8	$C_5H_{10}O$	86	10	43	100	86	10		
122	5194-50-3	2,4-Hexadiene	651.2	C_6H_{10}	82	24	67	100	82	24	39	54
123	1076-43-3	Hexadeuterobenzene	651.7	C_6D_6	84	100	84	100	56	21	54	19
124	693-89-0	Cyclopentene, 1-methyl-	652.1	C_6H_{10}	82	23	67	100	82	23	41	26
125	71-43-2	Benzene	653.5	C_6H_6	78	100	78	100	51	24	52	20
126	513-42-8	2-Propen-1-ol, 2-methyl-	654.2	C_4H_8O	72	21	57	100	39	68	31	35
127	96-17-3	Butanal, 2-methyl-	655.3	$C_5H_{10}O$	86	11	58	58	41	100	57	89
128	110-02-1	Thiophene	656.6	C_4H_4S	84	100	84	100	58	65	45	56
129	562-49-2	Pentane, 3,3-dimethyl-	657.6	C_7H_{16}	100	0	43	100	71	37	85	9
130	56-23-5	Methane, tetrachloro-	658.8	CCl_4	152	0	117	100	119	88	47	28
131	110-82-7	Cyclohexane	660.6	C_6H_{12}	84	64	56	100	84	64	41	62
132	108-21-4	Acetic acid, isopropyl ester	660.6	$C_5H_{10}O_2$	102	0	43	100	61	12	87	6
133	814-78-8	3-Buten-2-one, 3-methyl-	663.7	C_5H_8O	84	29	43	100	84	29	69	35
134	107-98-2	2-Propanol, 1-methoxy-	664.4	$C_4H_{10}O_2$	90	1	45	100	47	23	31	12
135	2235-12-3	1,3,5-Hexatriene	665.0	C_6H_8	80	44	80	44	79	100	77	46
136		Cyclopentene, 3-methylene-	666.6	C_6H_8	80	40	80	40	79	100	77	32
137	64-19-7	Acetic acid	667.9	$C_2H_4O_2$	60	43	43	100	45	99	60	43
138	928-49-4	3-Hexyne	668.3	C_6H_{10}	82	35	67	83	82	35	41	100
139	74-95-3	Methane, dibromo-	669.2	CH_2Br_2	172	51	174	100	93	91	95	76

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TABLE 21.6 List of Relative Retention Indices (RI) and Selected Ions for the Positive Identification of VOCs in Air by GC-MS (*Continued*)

					Relative Abundance							
					MW ion		Ion 1		Ion 2		Ion 3	
No.	CAS number	Compound	RI	Molecular formula	*m/z*	%	*m/z*	%	*m/z*	%	*m/z*	%
140	71-36-3	1-Butanol	670.2	$C_4H_{10}O$	74	0	31	100	56	57	41	85
141	591-76-4	Hexane, 2-methyl-	671.5	C_7H_{16}	100	2	43	100	57	28	85	25
142	1629-58-9	1-Penten-3-one	674.2	C_5H_8O	84	14	55	100	84	14	27	55
143	107-87-9	2-Pentanone	675.3	$C_5H_{10}O$	86	11	43	100	58	7	86	11
144	110-83-8	Cyclohexene	675.8	C_6H_{10}	82	35	67	100	82	35	54	69
145	994-05-8	Butane,2-methoxy-2-methyl-	676.6	$C_6H_{14}O$	102	0	73	100	87	22	55	31
146	589-34-4	Hexane, 3-methyl-	679.1	C_7H_{16}	100	2	43	100	57	39	70	39
147	116-09-6	2-Propanone, 1-hydroxy-	679.6	$C_3H_6O_2$	74	7	43	100	31	23	74	7
148	600-14-6	2,3-Pentanedione	680.9	$C_5H_8O_2$	100	18	43	100	57	39	29	65
149	617-78-7	Pentane, 3-ethyl-	681.4	C_7H_{16}	100	3	43	100	70	52	71	50
150	110-62-3	Pentanal	682.5	$C_5H_{10}O$	86	0	44	100	41	54	58	29
151	616-25-1	1-Penten-3-ol	682.7	$C_5H_{10}O$	86	2	57	100	31	18	29	67
152	78-87-5	Propane,1,2-dichloro-	682.7	$C_3H_6Cl_2$	112	5	63	100	76	57	41	85
153	822-50-4	Cyclopentane,1,2-dimethyl-, *trans*-	683.0	C_7H_{14}	98	6	56	84	41	100	70	89
154	111-43-3	Propane,1,1'-oxybis	683.8	$C_6H_{14}O$	102	7	43	100	73	17	102	7
155	96-22-0	3-Pentanone	684.8	$C_5H_{10}O$	86	18	57	92	29	100	86	18
156	2453-00-1	Cyclopentane, 1,3-dimethyl-	685.2	C_7H_{14}	98	5	56	84	41	100	70	77
157	1192-18-3	Cyclopentane, 1,2-dimethyl-, *cis*-	687.7	C_7H_{14}	98	11	56	90	41	100	70	66
158	540-84-1	Pentane, 2,2,4-trimethyl-	688.7	C_8H_{18}	114	0	57	100	41	50	56	38
159	79-01-6	Ethene, trichloro-	689.6	C_2HCl_3	130	90	97	64	132	89	95	100
160	591-87-7	Acetic acid, 2-propenyl ester	690.5	$C_5H_8O_2$	100	0	43	100	58	9	41	17

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161	592-76-7	1-Heptene	691.1	C_7H_{14}	98	5	41	100	56	64	70	30
162	3208-16-0	Furan, 2-ethyl-	694.0	C_6H_8O	96	42	81	100	96	42	53	43
163	4038-04-4	1-Pentene, 3-ethyl-	695.6	C_7H_{14}	98	18	41	100	55	41	69	86
164	6032-29-7	2-Pentanol	697.2	$C_5H_{12}O$	88	0	45	100	55	21	73	6
165	75-97-8	2-Butanone, 3,3-dimethyl-	698.1	$C_6H_{12}O$	100	19	41	93	57	100	100	19
166	625-86-5	Furan, 2,5-dimethyl-	699.2	C_6H_8O	96	100	96	100	95	80	53	67
167	142-82-5	*n*-C7	700.0	C_7H_{16}	100	6	43	100	57	44	71	35
168	110-80-5	Ethanol, 2-ethoxy-	701.1	$C_4H_{10}O_2$	90	1	31	100	59	68	72	22
169	592-78-9	3-Heptene	701.6	C_7H_{14}	98	14	41	100	56	23	69	33
170	105-37-3	Propanoic acid, ethyl ester	702.1	$C_5H_{10}O_2$	102	12	29	100	57	60	102	12
171	3683-22-5	2-Hexene, 4-methyl-	702.6	C_7H_{14}	98	19	41	100	69	76	98	19
172	80-62-6	2-Propenoic acid 2-methyl-, methyl ester	703.5	$C_5H_8O_2$	100	30	41	100	69	66	39	40
173	556-61-6	Methane, isothiocyanato-	704.1	C_2H_3NS	73	100	73	100	72	47	45	25
174	4914-89-0	3-Hexene, 3-methyl-	704.1	C_7H_{14}	98	41	69	100	41	86	98	41
175	14686-13-6	*trans*-2-Heptene	706.0	C_7H_{14}	98	38	41	100	56	81	69	56
176	109-60-4	Acetic acid, propyl ester	706.1	$C_5H_{10}O_2$	102	0	43	100	61	20	73	11
177	142-83-6	2,4-Hexadienal	706.5	C_6H_8O	96	100	96	100	95	46	67	85
178	15840-60-5	3-Hexene, 2-methyl-	706.9	C_7H_{14}	98	44	41	100	55	78	69	70
179	592-84-7	Formic acid, butyl ester	710.5	$C_5H_{10}O_2$	102	14	56	100	31	75	41	80
180	3404-72-6	1-Pentene, 2,3-dimethyl-	711.0	C_7H_{14}	98	24	41	100	55	41	69	77
181	107-21-1	1,2-Ethanediol	711.9	$C_2H_6O_2$	62	0	31	100	33	28	29	22
182	623-42-7	Butanoic acid, methyl ester	714.5	$C_5H_{10}O_2$	102	1	43	100	74	68	87	17
183	6443-92-1	*cis*-2-Heptene	715.7	C_7H_{14}	98	28	41	100	55	85	69	34
184	290-37-9	Pyrazine	717.8	$C_4H_4N_2$	80	100	80	100	26	90	53	60
185	111-28-4	2,4-Hexadien-1-ol	718.9	$C_6H_{10}O$	98	55	55	47	83	41	41	100
186	108-87-2	Cyclohexane, methyl-	719.4	C_7H_{14}	98	27	41	85	55	100	83	76
187	3102-33-8	3-Penten,2-one	722.5	C_5H_8O	84	22	69	100	41	95	84	22
188	763-32-6	3-Buten-1-ol, 3-methyl-	726.3	$C_5H_{10}O$	86	14	68	65	31	85	56	80
189	1115-11-3	2-Butenal, 2-methyl-	726.8	C_5H_8O	84	97	55	100	84	97	29	80
190	108-10-1	2-Pentanone, 4-methyl-	728.3	$C_6H_{12}O$	100	8	43	100	58	31	100	8
191	624-92-0	Disulfide, dimethyl-	728.5	$C_2H_6S_2$	94	100	94	100	79	55	45	67
192	565-61-7	2-Pentanone, 3-methyl-	729.4	$C_6H_{12}O$	100	13	43	100	57	30	72	21
193	590-36-3	2-Pentanol, 2-methyl-	731.0	$C_6H_{14}O$	102	0	59	100	45	49	87	23

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TABLE 21.6 List of Relative Retention Indices (RI) and Selected Ions for the Positive Identification of VOCs in Air by GC-MS (*Continued*)

					Relative Abundance							
					MW ion		Ion 1		Ion 2		Ion 3	
No.	CAS number	Compound	RI	Molecular formula	*m/z*	%	*m/z*	%	*m/z*	%	*m/z*	%
194	110-86-1	Pirydine	732.0	C_5H_5N	79	100	79	100	52	80	51	50
195	1640-89-7	Cyclopentane, ethyl-	732.4	C_7H_{14}	98	6	41	100	68	63	69	77
196	592-13-2	Hexane, 2,5-dimethyl -	735.3	C_8H_{18}	114	2	43	100	57	77	99	11
197	589-43-5	Hexane, 2,4-dimethyl-	737.0	C_8H_{18}	114	2	43	100	57	58	85	34
198	123-51-3	1-Butanol, 3-methyl-	737.6	$C_5H_{12}O$	88	0	31	54	70	51	55	100
199	109-49-9	5-Hexen-2-one	738.4	$C_6H_{10}O$	98	2	43	100	55	13	83	9
200	110-59-8	Pentanenitrile	740.1	C_5H_9N	83	0	41	100	43	99	54	50
201	79-09-4	Propanoic acid	740.8	$C_3H_6O_2$	74	37	28	98	45	50	29	69
202	109-97-7	1H-Pyrrole	740.9	C_4H_5N	67	100	67	100	41	66	40	59
203	4850-28-6	Cyclopentane, 1,2,4-trimethyl-	741.5	$C_8H_{16}6$	112	4	70	100	55	94	41	55
204	565-69-5	3-Pentanone, 2-methyl-	741.5	$C_6H_{12}O$	100	14	43	100	57	96	100	14
205	137-32-6	1-Butanol, 2-methyl-	742.1	$C_5H_{12}O$	88	0	57	100	70	40	56	85
206	560-21-4	Pentane, 2,3,3-trimethyl-	743.2	C_8H_{18}	114	0	43	100	57	33	71	34
207	57-55-6	1,2-Propanediol	749.4	$C_3H_8O_2$	76	0	45	100	31	29	43	22
208	2613-69-6	Cyclopentane, 1,2,3-trimethyl-	749.6	C_8H_{16}	112	8	70	100	55	70	56	53
209	565-75-3	Pentane, 2,3,4-trimethyl-	752.0	C_8H_{18}	114	0	43	100	57	15	71	43
210	123-15-9	Pentanal, 2-methyl-	752.8	$C_6H_{12}O$	100	2	43	100	58	80	41	43
211	1569-59-1	4-Penten-2-ol, 3-methyl-	752.9	$C_6H_{12}O$	100	0	45	100	56	87	41	58
212	1576-87-0	*trans*-2-Pentenal	753.0	C_5H_8O	84	65	55	100	84	65	83	50
213	1569-02-4	2-Propanol, 1-ethoxy-	753.4	$C_5H_{12}O_2$	104	1	45	100	59	79	31	58
214	15877-57-3	Pentanal, 3-methyl-	753.5	$C_6H_{12}O$	100	1	56	100	41	69	43	42
215	120-92-3	Cyclopentanone	753.9	C_5H_8O	84	31	55	100	28	48	41	45

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216	2037-26-5	Octadeuterotoluene	754.7	C_7D_8	100	65	98	100	100	65	54	11
217	108-88-3	Toluene	758.1	C_7H_8	92	57	91	100	92	57	65	14
218	108-11-2	2-Pentanol, 4-methyl-	760.1	$C_6H_{14}O$	102	0	45	100	69	18	41	22
219	25044-01-3	1-Penten-3-one, 2-methyl-	760.9	$C_6H_{10}O$	98	18	69	70	41	100	98	18
220	110-19-0	Acetic acid, 2-methyl-propyl ester	761.5	$C_6H_{12}O_2$	116	0	43	100	56	20	73	15
221	124-48-1	Methane, dibromochloro-	763.0	$CHBr_2Cl$	206	2	129	100	127	78	131	26
222	616-44-4	Tiophene, 3-methyl-	763.6	C_5H_6S	98	55	97	100	98	55	45	27
223	15045-43-9	Furan, tetrahydro-2,2,5,5-tetramethyl-	763.7	$C_8H_{16}O$	128	0	43	100	55	45	113	35
224	584-94-1	Hexane, 2,3-dimethyl-	765.4	C_8H_{18}	114	0	43	100	70	53	71	40
225	554-14-3	Tiophene, 2-methyl-	767.8	C_5H_6S	98	56	97	100	98	56	45	19
226	123-54-6	2,4-Pentanedione	767.9	$C_5H_8O_2$	100	32	43	100	85	56	100	32
227	71-41-0	1-Pentanol	768.0	$C_5H_{12}O$	88	0	31	89	42	100	70	28
228	592-27-8	Heptane, 2-methyl-	770.7	C_8H_{18}	114	3	43	100	57	86	99	9
229	590-50-1	2-Pentanone, 4,4-dimethyl-	771.2	$C_7H_{14}O$	114	5	43	100	58	32	57	39
230	589-53-7	Heptane, 4-methyl-	772.1	C_8H_{18}	114	0	43	100	71	35	70	35
231	589-38-8	3-Hexanone	773.3	$C_6H_{12}O$	100	19	43	100	57	70	71	25
232	60-35-5	Acetamide	775.5	C_2H_5NO	59	84	59	84	44	100	43	70
233	556-82-1	2-Buten-1-ol, 3-methyl-	776.0	$C_5H_{10}O$	86	11	71	100	53	29	86	11
234	96-41-3	Cyclopentanol	776.3	$C_5H_{10}O$	86	9	57	100	44	33	86	9
235	591-78-6	2-Hexanone	776.3	$C_6H_{12}O$	100	7	43	100	58	46	100	7
236	2207-04-7	Cyclohexane, 1,4-dimethyl-, *trans*-	777.0	C_8H_{16}	112	16	97	73	55	100	41	74
237	589-81-1	Heptane, 3-methyl-	777.4	C_8H_{18}	114	0	43	100	57	54	85	29
238	5187-71-3	4-Pentenal, 2-methyl-	777.4	$C_6H_{10}O$	98	5	41	100	56	27	69	25
239	624-29-3	Cyclohexane, 1,4-dimethyl-, *cis*-	778.6	C_8H_{16}	112	21	97	69	55	100	41	64
240	6789-80-6	*cis*-3-Hexenal	779.3	$C_6H_{10}O$	98	8	41	100	55	41	69	36
241	109-49-9	5-Hexen-2-one	779.5	$C_6H_{10}O$	98	8	43	100	55	37	83	21
242	79-31-2	Propanoic acid, 2-methyl-	780.0	$C_4H_8O_2$	88	8	43	100	73	27	88	8
243	820-71-3	2-Propen-1-ol, 2-methyl-acetate	782.0	$C_6H_{10}O_2$	114	0	43	100	72	45	39	32
244	590-66-9	Cyclohexane, 1,1-dimethyl-	783.0	C_8H_{16}	112	3	97	100	55	99	69	53

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TABLE 21.6 List of Relative Retention Indices (RI) and Selected Ions for the Positive Identification of VOCs in Air by GC-MS (*Continued*)

					Relative Abundance							
					MW ion		Ion 1		Ion 2		Ion 3	
No.	CAS number	Compound	RI	Molecular formula	*m/z*	%	*m/z*	%	*m/z*	%	*m/z*	%
245	66-25-1	Hexanal	783.5	$C_6H_{12}O$	100	0	44	100	56	64	41	93
246	141-79-7	3-Penten-2-one, 4-methyl-	784.2	$C_6H_{10}O$	98	35	83	97	55	100	98	35
247	2613-65-2	Cyclopentane-1-ethyl-3-methyl-, *trans*-	786.9	C_8H_{16}	112	3	83	60	55	100	41	68
248	291-64-5	Cycloheptane	788.1	C_7H_{14}	98	26	56	63	41	100	70	50
249	2613-66-3	Cyclopentane,1-ethyl-3-methyl-, *cis*-	788.4	C_8H_{16}	112	3	83	60	55	100	41	77
250	564-04-5	3-Pentanone, 2,2-dimethyl-	788.7	C_7H_{14}	114	11	57	100	41	37	114	11
251	930-89-2	Cyclopentane, 1-ethyl-2-methyl-	789.7	C_8H_{16}	112	9	83	58	55	100	41	90
252	111-66-0	1-Octene	791.1	C_8H_{16}	112	4	41	100	55	79	70	47
253	105-54-4	Butanoic acid, ethyl ester	791.9	$C_6H_{12}O_2$	116	2	43	95	71	81	88	42
254	6876-23-9	Cyclohexane, 1,2-dimethyl-, *trans*-	792.9	C_8H_{16}	112	19	97	70	55	100	41	72
255	626-93-7	2-Hexanol	794.3	$C_6H_{14}O$	102	0	45	100	69	10	87	3
256	127-18-4	Ethene, tetrachloro-	797.9	C_2C_{14}	164	76	166	100	168	47	129	79
257	2207-01-4	Cyclohexane, 1,2-dimethyl-, *cis*-	798.7	C_8H_{16}	112	16	97	56	55	100	41	71
258	6144-93-0	2-Pentanol, 4,4-dimethyl-	799.5	$C_7H_{16}O$	116	0	45	79	57	100	101	12
259	111-65-9	*n*-C8	800.0	C_8H_{18}	114	4	43	100	57	30	71	15
260	123-86-4	Acetic acid, butyl ester	803.2	$C_6H_{12}O_2$	116	0	43	100	56	25	61	11
261	98-01-1	2-Furaldehyde	806.3	$C_5H_4O_2$	96	76	96	76	95	80	39	100
262		Furan, 2,3,5-trimethyl-	807.9	$C_7H_{10}O$	110	100	110	100	109	92	95	67
263	123-42-2	2-Pentanone, 4-hydroxy-4-methyl-	814.2	$C_6H_{12}O_2$	116	0	43	100	59	34	101	10

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264	624-24-8	Pentanoic acid, methyl ester	814.8	$C_6H_{12}O_2$	116	1	74	100	85	38	87	36
265	75-98-9	Propanoic acid, 2, 2-dimethyl-	818.4	$C_5H_{10}O_2$	102	2	57	100	41	52	29	32
266	20333-39-5	Disulfide, ethyl methyl	818.5	$C_3H_8S_2$	108	100	108	100	80	99	45	26
267	2517-43-3	1-Butanol, 3-methoxy-	821.1	$C_5H_{12}O_2$	104	0	59	100	31	27	89	8
268	107-92-6	Butanoic acid	821.3	$C_4H_8O_2$	88	0	60	100	73	29	45	26
269	4747-07-3	Hexane, 1-methoxy-	822.9	$C_7H_{16}O$	116	0	45	100	56	44	84	14
270	4126-78-7	Cycloheptane, methyl-	826.2	C_8H_{16}	112	14	97	47	55	100	41	90
271	2213-23-2	Heptane, 2,4-dimethyl-	827.2	C_9H_{20}	128	0	43	100	57	30	85	29
272	505-57-7	2-Hexenal	828.9	$C_6H_{10}O$	98	27	41	100	55	87	69	77
273	1678-91-7	Cyclohexane, ethyl-	832.6	C_8H_{16}	112	13	83	76	55	100	41	84
274	108-90-7	Benzene, chloro-	833.7	C_6H_5Cl	112	100	112	100	77	77	114	33
275	1072-05-5	Heptane, 2,6-dimethyl-	834.7	C_9H_{20}	128	2	43	100	57	45	71	30
276	2550-21-2	2-Hexanone, 3-methyl-	837.0	$C_7H_{14}O$	114	3	43	100	72	42	55	12
277	3073-66-3	Cyclohexane, 1,1,3-trimethyl-	837.8	C_9H_{18}	126	1	111	94	69	100	55	68
278	105-42-0	2-Hexanone, 4-methyl-	838.1	$C_7H_{14}O$	114	3	43	100	58	51	85	6
279	2216-30-0	Heptane, 2,5-dimethyl -	841.7	C_9H_{20}	128	1	43	43	57	100	71	11
280	928-96-1	3-Hexen-1-ol	845.6	$C_6H_{12}O$	100	2	41	100	67	70	82	30
281	539-82-2	Pentanoic acid, ethyl ester	846.6	$C_7H_{14}O_2$	130	1	29	100	88	58	85	57
282	628-73-9	Hexanenitrile	846.6	$C_6H_{11}N$	97	0	41	100	54	68	55	55
283	110-12-3	2-Hexanone, 5-methyl-	848.2	$C_7H_{14}O$	114	4	43	100	58	38	81	7
284	98-00-0	2-Furanmethanol	849.0	$C_5H_6O_2$	98	89	39	100	81	68	53	61
285	75-25-2	Methane, tribromo-	850.6	$CHBr_3$	250	4	173	100	175	50	252	12
286	503-74-2	Butanoic acid, 3-methyl-	851.0	$C_5H_{10}O_2$	102	0	60	100	43	50	87	20
287	100-41-4	Benzene, ethyl-	854.3	C_8H_{10}	106	30	91	100	106	30		
288	928-94-9	2-Hexen-1-ol	854.7	$C_6H_{12}O$	100	0	57	100	67	28	82	28
289	872-55-9	Thiophene, ethyl-	856.2	C_6H_8S	112	40	97	100	112	40	45	32
290	108-94-1	Cyclohexanone	857.3	$C_6H_{10}O$	98	28	55	100	98	28	42	85
291	107-88-0	1,3-Butanediol	857.7	$C_4H_{10}O_2$	90	0	43	100	45	74	72	20
292	3074-71-3	Heptane, 2,3-dimethyl-	858.2	C_9H_{20}	128	0	85	29	57	25	71	18
293	565-80-0	3-Pentanone, 2,4-dimethyl-	860.2	$C_7H_{14}O$	114	5	43	100	71	31	114	5
294	108-38-3	*m*-Xylene	862.7	C_8H_{10}	106	45	91	100	106	45	105	22

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TABLE 21.6 List of Relative Retention Indices (RI) and Selected Ions for the Positive Identification of VOCs in Air by GC-MS (*Continued*)

					Relative Abundance							
					MW ion		Ion 1		Ion 2		Ion 3	
No.	CAS number	Compound	RI	Molecular formula	*m/z*	%	*m/z*	%	*m/z*	%	*m/z*	%
295	106-42-3	*p*-Xylene	863.4	C_8H_{10}	106	43	91	100	106	43	105	25
296	123-19-3	4-Heptanone	864.0	$C_7H_{14}O$	114	17	43	100	71	79	58	7
297	536-74-3	Ethynil benzene	866.1	C_8H_6	102	100	102	100	76	30		
298	108-93-0	Cyclohexanol	866.8	$C_6H_{12}O$	100	2	57	100	82	33	67	25
299	638-02-8	Thiophene, 2,5-dimethyl-	868.3	C_6H_8S	112	78	111	100	112	78	97	55
300	111-27-3	1-Hexanol	868.6	$C_6H_{14}O$	102	0	31	65	56	100	43	79
301	2216-34-4	Octane, 4-methyl-	870.2	C_9H_{20}	128	1	43	100	57	23	85	18
302	3221-61-2	Octane, 2-methyl-	871.0	C_9H_{20}	128	1	43	100	57	46	71	26
303	106-35-4	3-Heptanone	874.7	$C_7H_{14}O$	114	8	57	100	72	19	85	24
304	96-48-0	2(3H)-Furanone, dihydro-	874.8	$C_4H_6O_2$	86	25	42	100	28	88	86	25
305	108-48-5	Pirydine, 2,6-dimethyl-	875.8	C_7H_9N	107	100	107	100	106	51	66	47
306	488-97-1	Cyclofenchene	876.6	$C_{10}H_{16}$	136	12	93	100	121	19	77	17
307	110-43-0	2-Heptanone	877.2	$C_7H_{14}O$	114	2	43	100	58	40	71	10
308	56004-61-6	*o*-Xylene D_{10}	877.9	C_8D_{10}	116	40	98	100	116	40		
309	2216-33-3	Octane, 3-methyl-	877.9	C_9H_{20}	128	1	43	33	57	100	41	51
310	100-42-5	Styrene	879.5	C_8H_8	104	100	104	100	78	62	103	52
311	2407-43-4	2(5*H*)-Furanone, 5-ethyl-	880.0	$C_6H_8O_2$	112	14	83	100	55	63	27	57
312	95-47-6	*o*-Xylene	882.8	C_8H_{10}	106	44	91	100	106	44	105	20
313	111-71-7	Heptanal	885.5	$C_7H_{14}O$	114	0	44	100	41	96	70	63
314	2370-12-9	1-Pentanol, 2,2-dimethyl-	886.1	$C_7H_{16}O$	116	0	43	100	56	39	69	15
315	589-82-2	3-Heptanol	889.2	$C_7H_{16}O$	116	0	59	100	69	70	87	30
316	626-96-0	Pentanal, 4-oxo-	889.6	$C_5H_8O_2$	100	8	43	100	72	45	84	29
317	638-00-6	Thiophene, 2,4-dimethyl-	889.8	C_6H_8S	112	80	111	100	112	80	97	60
318	124-11-8	1-Nonene	890.2	C_9H_{18}	126	1	41	100	56	90	70	38
319	543-49-7	2-Heptanol	893.2	$C_7H_{16}O$	116	0	45	100	55	16	70	5

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320	5161-14-8	Tiophene, tetrahydro-2, 5-dimethyl-	895.2	$C_6H_{12}S$	116	38	101	100	59	40	74	30	
321	110-13-4	2,5-Hexanedione	896.1	$C_6H_{10}O_2$	114	3	43	100	99	15	71	9	
322	109-52-4	Pentanoic acid	897.8	$C_5H_{10}O_2$	102	1	60	100	73	36			
323	930-68-7	2-Cyclohexen-1-one	898.3	C_6H_8O	96	23	68	100	96	23	39	45	
324	3240-09-3	5-Hexen-2-one, 5-methyl-	898.4	$C_7H_{12}O$	112	5	43	100	69	30	97	17	
325	111-84-2	*n*-C9	900.0	C_9H_{20}	128	3	43	100	57	72	71	15	
326	108-29-2	2(3H)-Furanone, dihydro, 5-methyl-	910.0	$C_5H_8O_2$	100	6	56	100	85	60	100	6	
327	106-70-7	Hexanoic acid, methyl ester	912.2	$C_7H_{14}O_2$	130	1	74	100	43	71	87	31	
328	108-86-1	Benzene, bromo-	913.6	C_6H_5Br	156	67	156	67	158	63	77	100	
329	98-82-8	Benzene, isopropyl-	914.0	C_9H_{12}	120	25	105	100	120	25	77	20	
330	104-93-8	Benzene,1-methoxy-4-methyl-	914.1	$C_8H_{10}O$	122	100	122	100	121	50	107	40	
331	20019-64-1	2(5H)-Furanone, 5, 5-dimethyl-	916.0	$C_6H_8O_2$	112	18	97	100	69	90	43	78	
332	292-64-8	Cyclooctane	916.2	C_8H_{16}	112	30	56	61	41	100	70	29	
333	111-76-2	Ethanol, 2-buthoxy	917.4	$C_6H_{14}O_2$	118	0	57	100	45	52	87	20	
334	2436-90-0	Isocitronellene	919.5	$C_{10}H_{18}$	138	1	83	61	55	100	41	69	
335	508-32-7	Tricyclene	921.7	$C_{10}H_{16}$	136	16	93	100	79	22	121	20	
336	6137-06-0	2-Heptanone, 4-methyl-	925.8	$C_8H_{16}O$	128	2	43	100	58	51	59	22	
337	2867-05-2	α-Thujene	926.6	$C_{10}H_{16}$	136	8	93	100	77	46	121	3	
338	1678-92-8	Cyclohexane, propyl-	929.6	C_9H_{18}	126	16	83	100	55	90	82	56	
339	80-56-8	α-Pinene	934.4	$C_{10}H_{16}$	136	6	93	100	77	30	121	12	
340		Benzene, isopropenyl-	934.9	C_9H_{10}	118	68	118	68	117	100	91	43	
341	100-52-7	Benzaldehyde	936.9	C_7H_6O	106	79	106	79	105	82	77	100	
342	123-05-7	Hexanal, 2-ethyl-	941.3	$C_8H_{16}O$	128	3	72	99	57	100	41	90	
343	928-68-7	2-Heptanone, 6-methyl-	941.3	$C_8H_{16}O$	128	1	43	100	58	46	110	7	
344	629-08-3	Heptanenitrile	945.3	$C_7H_{13}N$	111	3	41	100	82	68	83	52	
345	103-65-1	Benzene, *n*-propyl-	946.1	C_9H_{12}	120	19	91	100	120	19			
346	471-84-1	α-Fenchene	946.3	$C_{10}H_{16}$	136	18	93	100	79	74	121	40	
347	598-16-3	Ethene, tribromo-	946.6	C_2HBr_3	262	34	264	100	266	95	185	95	
348	62-53-3	Benzenamine	947.1	C_6H_7N	93	100	93	100	66	32			

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TABLE 21.6 List of Relative Retention Indices (RI) and Selected Ions for the Positive Identification of VOCs in Air by GC-MS (*Continued*)

					Relative Abundance							
					MW ion		Ion 1		Ion 2		Ion 3	
No.	CAS number	Compound	RI	Molecular formula	*m/z*	%	*m/z*	%	*m/z*	%	*m/z*	%
349	79-92-5	Camphene	948.0	$C_{10}H_{16}$	136	14	93	100	121	72	67	39
350	13861-97-7	2(3*H*)-Furanone, dihydro-4,4-dimethyl-	948.6	$C_6H_{10}O_2$	114	7	43	100	99	66	55	45
351	3123-97-5	2(3*H*)-Furanone, dihydro-5,5-dimethyl-	949.6	$C_6H_{10}O_2$	114	1	55	100	99	33	70	41
352	3658-80-8	Trisulfide, dimethyl-	951.1	$C_2H_6S_3$	126	51	79	100	94	32	45	61
353	620-14-4	Benzene, 1-ethyl-3-methyl-	954.0	C_9H_{12}	120	30	105	100	120	30	91	12
354	69441-16-3	Benzene, 1,3,5-trimethyl-(D_{12})	954.5	C_9D_{12}	132	51	114	100	132	51		
355	622-96-8	Benzene, 1-ethyl-4-methyl-	955.8	C_9H_{12}	120	27	105	100	120	27	91	13
356	100-47-0	Benzonitrile	956.4	C_7H_5N	103	100	103	100	76	38	50	20
357	5435-64-3	Hexanal, 3,5,5-trimethyl-	961.3	$C_9H_{18}O$	142	1	57	100	83	55	109	19
358	108-67-8	Benzene, 1,3,5-trimethyl-	961.6	C_9H_{12}	120	44	105	100	120	44	91	14
359	76-01-7	Ethane, pentachloro-	962.0	C_2HCl_5	200	0	167	100	165	85	119	93
360	15869-85-9	Nonane, 5-methyl-	964.2	$C_{10}H_{22}$	142	0	43	100	57	29	85	33
361	111-70-6	1-Heptanol	964.3	$C_7H_{16}O$	116	0	31	60	70	64	41	100
362	17301-94-9	Nonane, 4-methyl-	966.0	$C_{10}H_{22}$	142	0	43	62	57	100	71	25
363	871-83-0	Nonane, 2-methyl-	968.3	$C_{10}H_{22}$	142	0	43	100	57	80	71	29
364	473-55-2	*trans*-Pinane	968.6	$C_{10}H_{18}$	138	1	95	80	67	56	55	85
365	3387-41-5	Sabinene	969.4	$C_{10}H_{16}$	136	15	93	100	77	38	121	5
366	110-93-0	5-Hepten-2-one, 6-methyl-	970.8	$C_8H_{14}O$	126	2	43	100	108	17	111	8
367	611-14-3	Benzene,1-ethyl-2-methyl-	970.9	C_9H_{12}	120	26	105	100	120	26	91	3
368	100-80-1	Benzene, 1-ethenyl-3-methyl-	971.5	C_9H_{10}	118	100	118	100	117	90	115	30

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369	106-68-3	3-Octanone	972.1	$C_8H_{16}O$	128	2	43	100	57	87	72	37
370	18402-82-9	3-Octe*n*-2-one	973.2	$C_8H_{14}O$	126	13	43	100	55	98	111	56
371		Thiophene, 2,3,5-trimethyl-	973.2	$C_7H_{10}S$	126	77	111	100	126	77	125	79
372	111-13-7	2-Octanone	974.0	$C_8H_{16}O$	128	4	43	100	58	61	71	12
373	5911-04-6	Nonane, 3-methyl-	974.7	$C_{10}H_{22}$	142	1	43	68	57	100	71	59
374	127-91-3	β-Pinene	974.8	$C_{10}H_{16}$	136	8	93	100	41	77	69	45
375	103-73-1	Benzene, ethoxy-	978.3	$C_8H_{10}O$	122	32	94	100	122	32	66	34
376	111-90-0	Etanol,2-(2-ethoxyethoxy)-	978.8	$C_6H_{14}O_3$	134	0	45	100	59	40	31	33
377	108-95-2	Phenol	979.2	C_6H_6O	94	100	94	100	66	51	65	37
378	6876-13-7	*cis*-Pinane	979.6	$C_{10}H_{18}$	138	1	95	46	67	63	55	81
379		Benzene, isopropenyl-	981.0	C_9H_{10}	118	71	118	71	117	100	115	44
380	20324-32-7	2-Propanol, 1-(2-methoxy-1-methylethoxy)-	981.4	$C_7H_{16}O_3$	148	0	59	100	45	63	31	22
381	271-89-6	Benzofuran	982.2	C_8H_6O	118	100	118	100	89	53	90	45
382	98-06-6	*tert*-Butylbenzene	983.3	$C_{10}H_{14}$	134	26	119	100	134	26	91	46
383		Benzene, isopropenyl-	983.5	C_9H_{10}	118	83	118	83	117	100	115	37
384	55956-25-7	2-Propanol,1-(1-methyl-2-(2-propenyloxy)ethoxy)-	983.5	$C_9H_{18}O_3$	174	0	59	100	45	45	31	20
385		Benzene, isopropenyl-	984.8	C_9H_{10}	118	90	118	90	117	100	115	20
386	95-36-3	Benzene, 1,2,4-trimethyl-	984.9	C_9H_{12}	120	41	105	100	120	41	91	13
387	142-62-1	Hexanoic acid	985.3	$C_6H_{12}O_2$	116	0	60	100	73	45	87	12
388	124-13-0	Octanal	986.2	$C_8H_{16}O$	128	0	44	78	56	61	84	29
389	142-92-7	Acetic acid, hexyl ester	986.3	$C_8H_{16}O_2$	144	0	43	100	56	34	61	16
390		Benzene, isopropenyl-	986.5	C_9H_{10}	118	77	118	77	117	100	115	38
391	123-66-0	Hexanoic acid, ethyl ester	986.7	$C_8H_{16}O_2$	144	1	43	97	88	100	99	48
392	123-35-3	Myrcene	986.8	$C_{10}H_{16}$	136	3	93	75	41	100	69	68
393	273-53-0	Benzoxazole	989.7	C_7H_5NO	119	100	119	100	64	52	63	44
394	872-05-9	1-Decene	989.9	$C_{10}H_{20}$	140	5	41	77	55	100	70	41
395	541-73-1	Benzene, 1,3-dichloro-	990.2	$C_6H_4Cl_2$	146	100	146	100	148	68	111	42
396	3681-71-8	3-Hexen-1-ol, acetate	990.3	$C_8H_{14}O_2$	142	0	43	100	67	64	82	37
397	106-46-7	Benzene, 1,4-dichloro-	990.6	$C_6H_4Cl_2$	146	100	146	100	148	70	111	38
398	13429-07-7	2-Propanol,1-(2-methoxypropoxy)-	993.3	$C_7H_{16}O_3$	148	0	59	100	45	16		
399	95-50-1	Benzene, 1,2-dichloro-	996.8	$C_6H_4Cl_2$	146	100	146	100	148	70	111	52

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TABLE 21.6 List of Relative Retention Indices (RI) and Selected Ions for the Positive Identification of VOCs in Air by GC-MS (*Continued*)

					Relative Abundance							
					MW ion		Ion 1		Ion 2		Ion 3	
No.	CAS number	Compound	RI	Molecular formula	*m/z*	%	*m/z*	%	*m/z*	%	*m/z*	%
400	538-93-2	Benzene, isobutyl-	997.5	$C_{10}H_{14}$	134	23	91	100	134	23	92	53
401	99-83-2	α-Phellandrene	998.6	$C_{10}H_{16}$	136	21	93	100	77	41	136	21
402	1795-04-6	Thiophene, 2,3,4-trimethyl-	998.7	$C_7H_{10}S$	126	80	111	100	126	80	125	78
403	135-98-8	sec-Butylbenzene	999.7	$C_{10}H_{14}$	134	16	105	100	134	16	91	17
404	124-18-5	*n*-C10	1000.0	$C_{10}H_{22}$	142	3	43	100	57	87	71	29
405	1073-11-6	2(3*H*)-Furanone, 5-etenyldihydro-5-methyl-	1002.7	$C_7H_{10}O_2$	126	10	111	100	55	62	99	26
406	542-28-9	2*H*-Pyran-2-one, tetrahydro-	1006.2	$C_5H_8O_2$	100	11	42	100	41	82	56	37
407	13466-78-9	Δ-3-Carene	1007.8	$C_{10}H_{16}$	136	20	93	100	77	34	121	20
408	106-73-0	Heptanoic acid, methyl ester	1010.6	$C_8H_{16}O_2$	144	0	74	100	87	38	43	50
409	99-86-5	α-Terpinene	1011.0	$C_{10}H_{16}$	136	43	93	85	121	100	77	34
410	526-73-8	Benzene, 1,2,3-trimethyl-	1011.7	C_9H_{12}	120	40	105	100	120	40	91	15
411	535-77-3	Benzene, 1-methyl-3-isopropyl-	1012.2	$C_{10}H_{14}$	134	25	119	100	134	25	91	40
412	695-06-7	2(3H)-Furanone, 5-ethyldihydro-	1012.7	$C_6H_{10}O_2$	114	0	85	100	42	28	29	80
413		Benzene, isopropenyl-	1013.6	C_9H_{10}	118	67	118	67	117	100	115	44
414	99-87-6	Benzene, 1-methyl-4-isopropyl-	1015.6	$C_{10}H_{14}$	134	24	134	24	119	100	91	35
415	100-51-6	Benzenemethanol	1017.3	C_7H_8O	108	65	108	65	107	48	79	100
416	1195-31-9	1-Menthene	1021.2	$C_{10}H_{18}$	138	23	95	100	67	80	81	35
417	77-73-6	endo-Bicyclopentadiene	1021.6	$C_{10}H_{12}$	132	9	66	100	132	9	39	21
418	104-76-7	1-Hexanol, 2-ethyl-	1023.7	$C_8H_{18}O$	130	0	57	100	41	66	31	29

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419	555-10-2	β-Phellandrene	1024.5	$C_{10}H_{16}$	136	18	93	100	77	27	121	5
420	496-11-7	Indane	1024.7	C_9H_{10}	118	53	117	100	118	53	115	43
421	470-82-6	1,8-Cineol	1025.3	$C_{10}H_{18}O$	154	17	43	100	154	17	108	28
422	138-86-3	Limonene	1025.8	$C_{10}H_{16}$	136	23	68	100	93	77	67	80
423	27400-71-1	*cis*-β-Ocimene	1030.1	$C_{10}H_{16}$	136	2	93	100	77	34	121	11
424	527-84-4	Benzene, 1-methyl-2-isopropyl-	1030.2	$C_{10}H_{14}$	134	32	119	100	134	32	91	32
425	95-13-6	1*H*-Indene	1031.9	C_9H_8	116	77	116	77	115	100	89	16
426	1678-93-9	Cyclohexane, butyl-	1033.5	$C_{10}H_{20}$	140	12	83	83	82	57	55	100
427	141-93-5	Benzene, 1,3-diethyl-	1041.2	$C_{10}H_{14}$	134	42	105	100	119	91	91	29
428	3779-61-1	*trans*-β-Ocimene	1041.5	$C_{10}H_{16}$	136	4	93	100	77	35	121	13
429	98-86-2	Acetophenone	1043.1	C_8H_8O	120	22	77	81	105	100	120	22
430	1074-43-7	Benzene, 1-methyl-3-propyl-	1044.0	$C_{10}H_{14}$	134	23	105	100	134	23	91	12
431	105-05-5	Benzene, 1,4-diethyl-	1047.8	$C_{10}H_{14}$	134	42	119	100	105	82	91	19
432	1074-55-1	Benzene, 1-methyl-4-propyl-	1048.2	$C_{10}H_{14}$	134	20	105	100	134	20	91	8
433	104-51-8	Benzene, butyl-	1048.8	$C_{10}H_{14}$	134	19	91	100	134	19	92	55
434	124-12-9	Octanenitrile	1049.7	$C_8H_{15}N$	125	2	82	100	96	45	54	41
435		Benzene, dimethyl,ethyl	1050.8	$C_{10}H_{14}$	134	30	119	100	134	30	91	21
436	135-01-3	Benzene, 1,2-diethyl-	1053.5	$C_{10}H_{14}$	134	47	105	100	119	77	91	48
437	99-85-4	γ-Terpinene	1055.5	$C_{10}H_{16}$	136	31	93	100	77	37	121	25
438	91-17-8	Naphthalene, decahydro-	1056.0	$C_{10}H_{18}$	138	90	138	90	67	100	96	70
439	1074-17-5	Benzene, 1-methyl-2-propyl-	1059.7	$C_{10}H_{14}$	134	22	105	100	134	22	91	9
440	98-95-3	Benzene, *nitro*-	1060.7	$C_6H_5NO_2$	123	44	123	44	77	100	51	73
441	111-87-5	1-Octanol	1062.6	$C_8H_{18}O$	130	0	31	46	41	100	56	90
442	5989-33-3	*cis*-Linalool oxide	1064.9	$C_{10}H_{18}O_2$	170	0	93	22	59	100	111	23
443	67-72-1	Ethane, hexachloro-	1068.1	C_2Cl_6	234	0	201	93	117	100	166	48
444	617-94-7	Benzenemethanol, alpha, alpha-dimethyl-	1068.7	$C_9H_{12}O$	136	2	43	100	121	75	103	6
445		Benzene, dimethyl, ethyl-	1069.8	$C_{10}H_{14}$	134	29	119	100	91	23	105	15
446		Benzene, dimethyl, ethyl-	1071.4	$C_{10}H_{14}$	134	26	119	100	91	13	105	5
447	925-78-0	3-Nonanone	1072.0	$C_9H_{18}O$	142	1	43	100	57	69	72	44

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TABLE 21.6 List of Relative Retention Indices (RI) and Selected Ions for the Positive Identification of VOCs in Air by GC-MS (*Continued*)

					Relative Abundance							
					MW ion		Ion 1		Ion 2		Ion 3	
No.	CAS number	Compound	RI	Molecular formula	*m/z*	%	*m/z*	%	*m/z*	%	*m/z*	%
448	4695-62-9	Fenchone	1075.9	$C_{10}H_{16}O$	152	9	81	100	69	56	41	66
449	111-14-8	Heptanoic acid	1076.0	$C_7H_{14}O_2$	130	1	60	100	73	43	87	17
450		Benzene, dimethyl, ethyl-	1077.1	$C_{10}H_{14}$	134	27	119	100	91	27	105	9
451	821-55-6	2-Nonanone	1077.2	$C_9H_{18}O$	142	4	43	100	58	73	71	15
452	34995-77-2	*trans*-Linalool oxide	1078.4	$C_{10}H_{18}O_2$	170	0	93	23	59	100	111	23
453		Benzene, dimethyl, ethyl-	1083.2	$C_{10}H_{14}$	134	30	119	100	91	19	105	6
454	586-62-9	α-Terpinolene	1084.7	$C_{10}H_{16}$	136	68	93	100	121	78	136	68
455	124-19-6	Nonanal	1088.0	$C_9H_{18}O$	142	0	44	55	41	100	57	79
456	821-95-4	1-Undecene	1089.5	$C_{11}H_{22}$	154	7	41	100	55	80	70	67
457	78-70-6	Linalool	1089.6	$C_{10}H_{18}O$	154	1	93	60	71	100	41	80
458	546-80-5	α-Thujone	1092.6	$C_{10}H_{16}O$	152	4	81	100	110	58	67	77
459		Benzene, dimethyl, ethyl-	1096.2	$C_{10}H_{14}$	134	22	119	100	91	27	105	13
460	1120-21-4	*n*-C11	1100.0	$C_{11}H_{24}$	156	3	43	100	57	94	71	40
461	876-18-6	Rose oxide, *trans*-	1100.7	$C_{10}H_{18}O$	154	9	139	100	69	88	83	36
462	471-15-8	β-Thujone	1103.1	$C_{10}H_{16}O$	152	2	81	85	110	65	67	60
463	95-93-2	Benzene, 1,2,4,5-tetramethyl-	1108.6	$C_{10}H_{14}$	134	38	119	100	134	50	91	22
464	149-57-5	Hexanoic acid, 2-ethyl-	1109.5	$C_8H_{16}O_2$	144	0	73	100	88	82	116	14
465	111-11-5	Octanoic acid, methyl ester	1110.1	$C_9H_{18}O_2$	158	1	74	100	87	40	43	39
466	38651-65-9	Nopinone	1110.6	$C_9H_{14}O$	138	6	83	100	55	60	95	37
467	527-53-7	Benzene, 1,2,3,5-tetramethyl-	1112.5	$C_{10}H_{14}$	134	43	119	100	134	43	91	16
468	105-21-5	2(3*H*)-Furanone, dihydro-5-propyl-	1114.8	$C_7H_{12}O_2$	128	3	85	100	56	21	110	8
469	4501-58-0	α-Campholene aldehyde	1118.8	$C_{10}H_{16}O$	152	1	93	80	108	100	67	51

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470	876-17-5	Rose oxide, *cis*-	1119.8	$C_{10}H_{18}O$	154	8	139	100	69	98	154	8
471	673-84-7	Alloocymene	1120.0	$C_{10}H_{16}$	136	41	93	21	121	100	136	41
472	76-22-2	Camphor	1131.2	$C_{10}H_{16}O$	152	23	95	100	81	70	108	34
473	106-23-0	Citronellal	1132.3	$C_{10}H_{18}O$	154	11	41	100	69	64	95	30
474	547-61-5	Pinocarveol	1134.0	$C_{10}H_{16}O$	152	0	92	82	55	100	83	47
475	59905-53-2	Isopulegol	1139.1	$C_{10}H_{18}O$	154	3	41	100	67	51	93	25
476	464-45-9	1-Borneol	1141.9	$C_{10}H_{18}O$	154	1	95	100	110	20	139	8
477	491-07-6	Isomenthone	1142.4	$C_{10}H_{18}O$	154	17	112	64	69	69	154	17
478	93-55-0	1-Propanone, 1-phenyl-	1145.0	$C_9H_{10}O$	134	13	105	100	77	50	134	13
479	488-23-3	Benzene, 1,2,3,4-tetramethyl-	1146.3	$C_{10}H_{14}$	134	39	119	100	134	39	91	19
480	547-60-4	Pinocamphone	1148.3	$C_{10}H_{16}O$	152	7	83	85	55	100	41	87
481	65-85-0	Benzoic acid	1148.6	$C_7H_6O_2$	122	94	122	94	105	100	77	82
482	16812-40-1	Pinocarvone	1149.4	$C_{10}H_{14}O$	150	4	53	100	81	70	108	38
483	507-70-0	endo-Borneol	1151.0	$C_{10}H_{18}O$	154	1	95	100	110	17	139	4
484	120-82-1	Benzene, 1,2,4-trichloro-	1151.3	$C_6H_3Cl_3$	180	100	180	100	182	96	184	30
485	89-80-5	*p*-Menthone	1152.0	$C_{10}H_{18}O$	154	13	112	65	69	69	55	64
486	119-64-2	Naphthalene, 1,2,3,4-tetrahydro	1153.5	$C_{10}H_{12}$	132	42	132	42	104	100	91	34
487	87-61-6	Benzene,1,2,3-trichloro-	1154.7	$C_6H_3Cl_3$	180	100	180	100	182	96	184	30
488	112-41-4	1-Dodecene	1155.7	$C_{12}H_{24}$	168	8	41	100	55	81	70	56
489	494-90-6	Menthofuran	1156.6	$C_{10}H_{14}O$	150	28	108	100	150	28	79	36
490	491-01-0	Neomenthol	1160.5	$C_{10}H_{20}O$	156	0	71	100	95	70	81	48
491	143-08-8	1-Nonanol	1162.2	$C_9H_{20}O$	144	0	31	30	70	60	41	100
492	124-07-2	Octanoic acid	1167.0	$C_8H_{16}O_2$	144	2	60	100	73	59	101	14
493	89-78-1	Menthol	1168.0	$C_{10}H_{20}O$	156	0	71	100	95	62	81	79
494	112-34-5	Ethanol, 2-(2-butoxy-ethoxy)-	1169.2	$C_8H_{18}O_3$	162	0	45	100	57	85	75	16
495	562-74-3	4-Terpineol	1172.0	$C_{10}H_{18}O$	154	8	93	45	71	100	111	50
496	1146-65-2	Octadeuteronaphthalene	1172.0	$C_{10}D_8$	136	100	136	100	108	11	137	11
497	928-80-3	3-Decanone	1173.1	$C_{10}H_{20}O$	156	1	57	100	72	43	127	21
498	91-20-3	Naphthalene	1173.9	$C_{10}H_8$	128	100	128	100	102	11		
499	693-54-9	2-Decanone	1177.5	$C_{10}H_{20}O$	156	2	43	100	58	80	71	24
500	11095-43-5	Benzothiophene	1179.7	C_8H_6S	134	100	134	100	89	10	108	8

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TABLE 21.6 List of Relative Retention Indices (RI) and Selected Ions for the Positive Identification of VOCs in Air by GC-MS (*Continued*)

					Relative Abundance							
					MW ion		Ion 1		Ion 2		Ion 3	
No.	CAS number	Compound	RI	Molecular formula	*m/z*	%	*m/z*	%	*m/z*	%	*m/z*	%
501	98-55-5	α-Terpineol	1182.4	$C_{10}H_{18}O$	154	0	93	48	59	100	136	22
502	122-99-6	Ethanol, 2-phenoxy-	1183.5	$C_8H_{10}O_2$	138	25	94	100	45	12		
503	586-81-2	γ-Terpineol	1187.6	$C_{10}H_{18}O$	154	6	93	59	121	100	136	49
504	112-31-2	Decanal	1189.8	$C_{10}H_{20}O$	156	0	44	44	41	100	82	22
505	112-14-1	*n*-Octyl acetate	1196.0	$C_{10}H_{20}O_2$	172	0	43	100	56	25	70	19
506	112-40-3	*n*-C_{12}	1200.0	$C_{12}H_{26}$	170	4	43	100	57	99	71	49
507	95-16-9	Benzothiazole	1205.7	C_7H_5NS	135	100	135	100	108	31	69	25
508	104-50-7	2(3*H*)-Furanone, 5-butyldihydro-	1222.4	$C_8H_{14}O_2$	142	1	85	100	56	9	100	4
509	89-82-7	Pulegone	1225.8	$C_{10}H_{16}O$	152	55	81	100	67	96	109	35
510	2244-16-8	Carvone	1227.2	$C_{10}H_{14}O$	150	5	82	100	54	62	93	30
511	89-81-6	Piperitone	1239.3	$C_{10}H_{16}O$	152	12	82	100	110	65	95	41
512	4292-75-5	Cyclohexane, hexyl-	1242.1	$C_{12}H_{24}$	168	2	83	100	82	73	55	85
513	106-25-2	Nerol	1242.7	$C_{10}H_{18}O$	154	0	69	80	41	100	93	15
514	115-95-7	Linalyl acetate	1245.1	$C_{12}H_{20}O_2$	196	0	43	100	93	40	80	20
515		Pinon aldehyde	1251.1	$C_{10}H_{16}O_2$	168	0	83	58	43	100	69	44
516	141-27-5	Geranial	1251.9	$C_{10}H_{16}O$	152	2	41	100	69	68	84	17
517	112-05-0	Nonanoic acid	1261.6	$C_9H_{18}O_2$	158	5	60	100	73	77	129	17
518	106-22-9	Citronellol	1262.9	$C_{10}H_{20}O$	156	1	41	100	69	65	95	24
519	112-30-1	1-Decanol	1263.3	$C_{10}H_{22}O$	158	0	31	45	55	100	70	68
520	2437-56-1	1-Tridecene	1264.1	$C_{13}H_{26}$	182	7	41	100	55	82	70	56
521	112-12-9	2-Undecanone	1278.8	$C_{11}H_{22}O$	170	2	43	100	58	82	71	23
522	125-12-2	Isobornyl acetate	1279.5	$C_{12}H_{20}O_2$	196	0	95	100	121	50	136	50
523	76-49-3	Endobornyl acetate	1281.7	$C_{12}H_{20}O_2$	196	0	95	92	43	100	136	40
524	16409-45-3	Menthyl acetate	1284.6	$C_{12}H_{22}O_2$	198	0	95	80	81	45	138	20

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525	90-12-0	Naphthalene, 1-methyl-	1287.6	$C_{11}H_{10}$	142	100	142	100	141	95	115	44
526	112-44-7	Undecanal	1291.9	$C_{11}H_{22}O$	170	0	44	41	41	100	82	30
527	629-50-5	*n*-C13	1300.0	$C_{13}H_{28}$	184	5	43	99	57	100	71	50
528	91-57-6	Naphthalene, 2-methyl-	1303.8	$C_{11}H_{10}$	142	100	142	100	141	90	115	47
529	110-42-9	Decanoic acid, methyl ester	1308.9	$C_{11}H_{22}O_2$	186	2	74	100	87	42	186	2
530	136-60-7	Benzoic acid, butyl ester	1313.6	$C_{11}H_{14}O_2$	178	0	123	57	105	100	77	58
531	717-74-8	Benzene, 1,3,5-triisopropyl-	1329.1	$C_{15}H_{24}$	204	28	189	100	161	63	204	28
532	104-61-0	2(3*H*)-Furanone, dihydro-5-pentyl-	1329.4	$C_9H_{16}O_2$	156	0	85	100	100	5	114	4
533	294-62-2	Cyclododecane	1337.1	$C_{12}H_{24}$	168	2	55	75	69	52	83	33
534	80-26-2	Terpinyl acetate	1342.1	$C_{12}H_{20}O_2$	196	0	93	56	121	59	136	30
535	141-12-8	Neril acetate	1347.8	$C_{12}H_{20}O_2$	196	0	69	100	93	40	41	70
536	334-48-5	Decanoic acid	1357.4	$C_{10}H_{20}O_2$	172	3	60	100	73	87	129	33
537	17699-14-8	α-Cubebene	1357.5	$C_{15}H_{24}$	204	25	161	98	119	88	204	25
538	112-42-5	1-Undecanol	1361.1	$C_{11}H_{24}O$	172	0	31	33	55	100	69	90
539	105-87-3	Geranyl acetate	1365.4	$C_{12}H_{20}O_2$	196	0	69	83	93	30	41	100
540	22469-52-9	Cycloisosantivene	1381.8	$C_{15}H_{24}$	204	62	161	100	119	74	204	62
541	110-38-3	Decanoic acid, ethyl ester	1383.0	$C_{12}H_{24}O_2$	200	2	88	100	101	40	73	28
542	3856-25-5	α-Copaene	1387.0	$C_{15}H_{24}$	204	20	119	100	161	96	105	95
543	6175-49-1	2-Dodecanone	1391.5	$C_{12}H_{24}O$	184	1	43	100	58	76	71	22
544	112-54-9	Dodecanal	1394.0	$C_{12}H_{24}O$	184	0	44	39	41	100	82	36
545	5208-59-3	β-Bourbonene	1396.1	$C_{15}H_{24}$	204	2	81	100	123	57	161	25
546	13744-15-5	β-Cubebene	1396.8	$C_{15}H_{24}$	204	15	161	100	105	50	204	15
547	515-13-9	β-Elemene	1398.2	$C_{15}H_{24}$	204	2	93	100	81	86	107	67
548	629-59-4	*n*-C14	1400.0	$C_{14}H_{30}$	198	4	43	79	57	100	71	62
549	1135-66-6	Isolongifolene	1404.1	$C_{15}H_{24}$	204	18	161	100	175	58	133	54
550	118-65-0	Isocaryophyllene	1418.0	$C_{15}H_{24}$	204	6	41	100	93	78	161	24
551	475-20-7	Longifolene (Junipene)	1422.2	$C_{15}H_{24}$	204	33	161	100	189	48	204	33
552	131-11-3	*o*-Dimethylphthalate	1424.8	$C_{10}H_{10}O_4$	194	4	163	100	194	4	135	11
553	79120-98-2	β-Funebrene	1429.7	$C_{15}H_{24}$	204	10	161	71	93	61	204	10
554	87-44-5	β-Caryophyllene	1432.7	$C_{15}H_{24}$	204	4	93	100	133	83	161	25
555	3796-70-1	Geranylacetone	1436.6	$C_{13}H_{22}O$	194	0	43	100	69	27	107	8

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TABLE 21.6 List of Relative Retention Indices (RI) and Selected Ions for the Positive Identification of VOCs in Air by GC-MS (*Continued*)

					Relative Abundance							
					MW ion		Ion 1		Ion 2		Ion 3	
No.	CAS number	Compound	RI	Molecular formula	*m/z*	%	*m/z*	%	*m/z*	%	*m/z*	%
556	706-14-9	2(3*H*)-Furanone, 5-hexyldihydro-	1436.6	$C_{10}H_{18}O_2$	170	0	85	100	56	9	128	8
557	546-28-1	β-Cedrene	1436.8	$C_{15}H_{24}$	204	100	204	100	161	87	93	47
558	23986-74-5	Germacene D	1441.4	$C_{15}H_{24}$	204	12	161	100	93	28	204	12
559	61826-55-9	Pinonic acid	1441.6	$C_{10}H_{16}O_3$	184	0	83	68	43	100	69	46
560	18794-84-8	β-Farnesene	1452.3	$C_{15}H_{24}$	204	4	41	100	69	90	93	38
561	112-37-8	Undecanoic acid	1454.6	$C_{11}H_{22}O_2$	186	12	60	100	73	95	129	25
562	112-53-8	1-Dodecanol	1463.2	$C_{12}H_{26}O$	186	0	31	20	55	100	69	86
563	6753-98-6	α-Humulene	1466.9	$C_{15}H_{24}$	204	4	93	100	80	34	121	25
564	25246-27-9	Alloaromadendrene	1474.8	$C_{15}H_{24}$	204	70	161	92	93	81	204	70
565	120-61-6	Dimethyl p-phtalate	1479.0	$C_{10}H_{10}O_4$	194	22	163	100	194	22	135	23
566	593-08-8	2-Tridecanone	1480.2	$C_{13}H_{26}O$	198	3	43	100	58	92	71	29
567	1459-93-4	Dimethyl m-phtalate	1480.5	$C_{10}H_{10}O_4$	194	24	163	100	194	24	135	43
568	10486-19-8	Tridecanal	1494.4	$C_{13}H_{26}O$	198	0	41	73	82	70	96	34
569	629-62-9	*n*-C15	1500.0	$C_{15}H_{32}$	212	3	43	73	57	100	71	68
570	4630-07-3	Valencene	1504.8	$C_{15}H_{24}$	204	63	161	100	204	63	105	46
571	31983-22-9	α-Muurolene	1508.4	$C_{15}H_{24}$	204	15	105	100	93	46	161	32
572	111-82-0	Dodecanoic acid, methyl ester	1510.9	$C_{13}H_{26}O_2$	214	8	74	100	87	57	214	8
573	483-76-1	δ-Cadinene	1528.8	$C_{15}H_{24}$	204	51	161	100	134	54	204	51
574	143-07-7	Dodecanoic acid	1555.2	$C_{12}H_{24}O_2$	200	15	60	100	73	98	129	27
575	112-70-9	1-Tridecanol	1564.8	$C_{13}H_{28}O$	200	0	31	45	55	100	41	75
576	84-66-2	Diethyl phthalate	1566.5	$C_{12}H_{14}O_4$	222	1	149	100	177	22		
577	124-25-4	Tetradecanal	1567.6	$C_{14}H_{28}O$	212	0	41	100	82	80	96	47
578	2345-27-9	2-Tetradecanone	1581.7	$C_{14}H_{28}O$	212	5	43	96	58	100	71	35

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579	106-33-2	Dodecanoic acid, ethyl ester	1582.5	$C_{14}H_{28}O_2$	228	5	88	100	101	44	73	20
580	544-76-3	*n*-C16	1600.0	$C_{16}H_{34}$	226	4	43	82	57	100	71	79
581	638-53-9	Tridecanoic acid	1656.5	$C_{13}H_{26}O_2$	214	25	60	100	73	85	129	30
582	112-72-1	1-Tetradecanol	1666.4	$C_{14}H_{30}O$	214	0	31	18	55	100	69	82
583	2765-11-9	Pentadecanal	1670.9	$C_{15}H_{30}O$	226	0	41	76	82	100	96	64
584	2345-28-0	2-Pentadecanone	1683.6	$C_{15}H_{30}O$	226	4	43	65	58	100	71	34
585	629-78-7	*n*-C17	1700.0	$C_{17}H_{36}$	240	2	43	80	57	100	71	59
586	124-10-7	Tetradecanoic acid, methyl ester	1713.6	$C_{15}H_{30}O_2$	242	11	74	100	87	54	143	16
587	544-63-8	Tetradecanoic acid	1759.3	$C_{14}H_{28}O_2$	228	12	60	100	73	97	129	25
588	124-06-1	Tetradecanoic acid, ethyl ester	1782.4	$C_{16}H_{32}O_2$	256	3	88	100	101	53	73	15
589	593-45-3	*n*-C18	1800.0	$C_{18}H_{38}$	254	4	43	78	57	100	71	75
590	84-69-5	Diisobutyl phthalate	1815.5	$C_{16}H_{22}O_4$	278	0	149	100	57	30	223	6
591	149-57-5	Pentadecanoic acid	1835.1	$C_{15}H_{30}O_2$	242	27	60	92	73	100	129	27
592	112-39-0	Hexadecanoic acid, methyl ester	1888.2	$C_{17}H_{34}O_2$	270	6	74	100	87	73	143	16
593	84-74-2	Dibutyl phthalate	1891.8	$C_{16}H_{22}O_4$	278	1	149	100	205	4	223	5
594	629-92-5	*n*-C19	1900.0	$C_{19}H_{40}$	268	2	57	100	71	66	85	38
595	57-10-3	Hexadecanoic acid	1915.7	$C_{16}H_{32}O_2$	256	44	60	90	73	97	129	33
596	112-95-8	*n*-C20	2000.0	$C_{20}H_{42}$	282	2	57	100	71	65	85	40
597	7683-64-9	Squalene	2036.8	$C_{30}H_{50}$	410	1	69	100	81	46	137	12
598	27554-26-3	Diisoctyl phthalate	2085.3	$C_{24}H_{38}O_4$	390	0	149	100	167	38	279	10
599	629-94-7	*n*-C21	2100.0	$C_{21}H_{44}$	296	2	57	100	71	70	85	55

Note: For column and experimental conditions, see Table 21.7.

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TABLE 21.7 GC Column and Experimental Conditions Used for Generating the Data Reported in Table 21.6

Type	CP SIL 5-MS; DB-5; SPB-5 or equivalent
Polarity Indices (McReynolds numbers)	$x' = 19$; $y' = 74$; $z' = 64$; $u' = 93$; $s' = 62$ Total = 312
Length (m)	50
d_c (mm)	0.32
d_f (μm)	0.4
ß	200
C (ng each compound)	200–300
Φ (ml/min)	1.0
Carrier gas	Helium
Minimum temperature (°C)	−20
Maximum temperature (°C)	370
Initial isothermal step (°C)	5
Time (min)	3
First linear program (°C min)	3
Second isothermal step (°C)	50
Time (min)	0
Second linear program (°C min)	5
Final isothermal temperature (°C)	250
Time (min)	2

atoms present in the molecule and the type, number, and position of functional groups present in it. Branching and cycling of the molecule also affect the first ionization potential. Because of this, the use of interpolation techniques to predict the response factors on the basis of the number of carbon atoms in the molecule, commonly used with the FID (Ciccioli et al., 1997), is limited in MS to the case in which a compound belongs to a homologous series showing a very close similarity in the fragmentation pattern. Differences in signal imply that response factors (RFs) must be determined for a large number of components.

Another difficulty is represented by the critical dependence of the RFs on the conditions existing in the source, the analyzer, and the detector. The yield of the electron impact reaction is greatly affected by the absolute and relative concentrations of reagents in the source and the thermodynamic conditions (such as pressure and temperature) established in it. To obtain a constancy in the mass spectrum, and hence in the RF, it is important that ion-molecule reactions do not substantially interfere with the primary processes unless they are provoked intentionally for selective detection purposes (i.e., MS-MS detection or chemical ionization). This is the reason why a precise limit exists on the amount of carrier gas that can be introduced into the ion source. Another condition to meet is constancy in concentration and energy of electrons generated inside the source. Slow consumption of the tungsten filament and contamination of the ion source with carbon residues can greatly affect both the amount and energy of electrons, thus changing the RF of VOCs. These residues normally are produced inside the source by the ionization of eluted substances and the stationary phase of the GC column. Decays in response also are observed when deposits of carbon material occur in the ion repeller and the mass filter of the MS. Changes in the working conditions of the ion detector also can affect the response in GC-MS.

All these considerations indicate that the quantitative analysis of VOCs by GC-MS is not easy and may be affected by large errors if specific procedures are not followed strictly. First of all, it is extremely important that the working conditions of the source, the analyzer, and the detector are checked and recorded before any GC-MS analysis. Today, almost all

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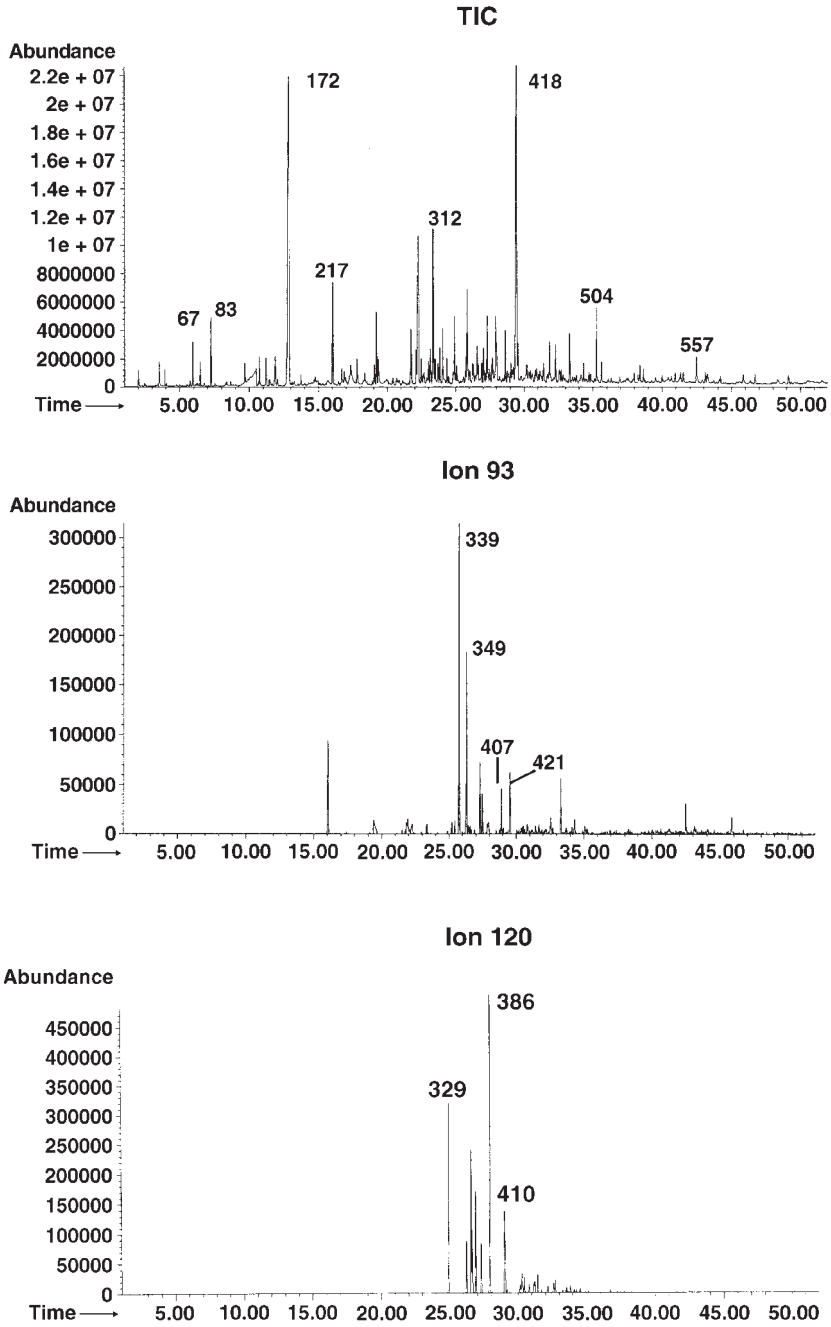

FIGURE 21.14 TIC and selected ion profiles obtained in the GC-MS analysis of an air sample collected in the city of Algiers. The TIC was obtained by collecting the ions from *m/z* 20 to 300. The mass chromatograms at *m/z* 93, 120, 31, 44, and 60 were used for the selective detection of monoterpenes, trimethylbenzenes, alcohols, carbonyl compounds, and carboxylic acids. The GC-MS run was performed using the experimental conditions reported in Table 21.7. For peak assignment, refer to Table 21.6.

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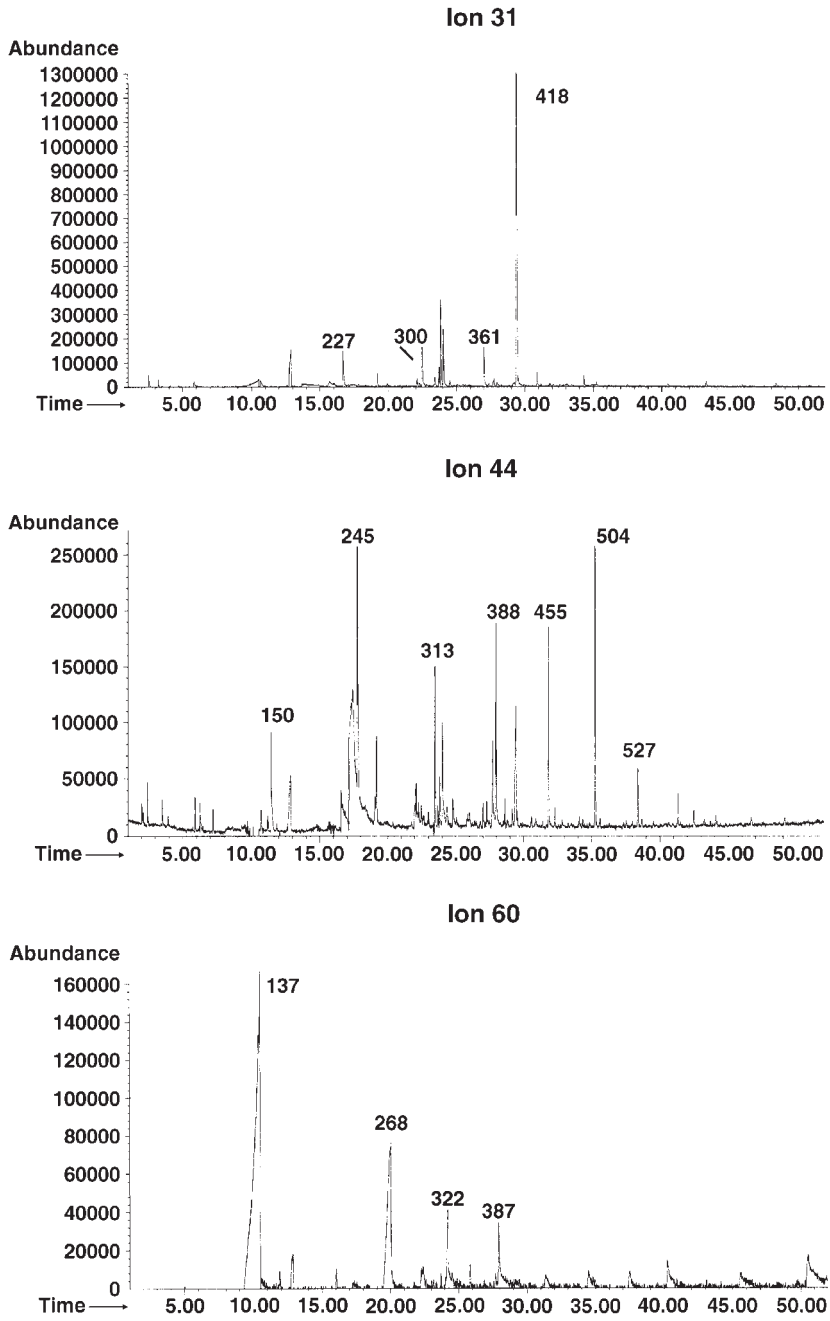

FIGURE 21.14 *(Continued)* TIC and selected ion profiles obtained in the GC-MS analysis of an air sample collected in the city of Algiers. The TIC was obtained by collecting the ions from *m*/*z* 20 to 300. The mass chromatograms at *m*/*z* 93, 120, 31, 44, and 60 were used for the selective detection of monoterpenes, trimethylbenzenes, alcohols, carbonyl compounds, and carboxylic acids. The GC-MS run was performed using the experimental conditions reported in Table 21.7. For peak assignment, refer to Table 21.6.

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mass spectrometers are equipped with specific software that helps to achieve constant conditions inside the source and the analyzer. This tuning process (also called *autotuning*) usually is performed with substances (such as perfluorinated fluids) that allow control not only of the efficiency of the ionization process but also of the exact mass assignment of the analyzer and, in the case of magnetic-sector or ion-trap instruments, the desired resolution. These compounds are introduced into the source through a molecular leak, ensuring a constant flow of vapors into the source. The tuning process allows also one to check the status of the ion detector. If the instrument is in good condition but bad results are obtained in the tuning process, intrusion of air into the carrier gas or the MS source can be suspected. If the intensity of the ions generated by nitrogen and oxygen is more than 10 percent higher than that generated by the water peak, air is entering into the source. The removal of leakage usually restores the correct ionization in a rather short time (a few hours). Another important point to check is that the cryofocusing unit or the column does not introduce compounds into the columns that can interfere with the analysis. This can be done by making sure that no peaks appear in the chromatogram when pure helium is passed through the trap.

Because of the large number of factors influencing the response of the MS, it is a common practice to calibrate the instrument regularly (every 1 or 2 weeks) and check the performance daily. This allows one to get good quantitative results even when maximum performance is not achieved.

Liquid Standard Solutions for the Calibration of VOCs

The simplest way to calibrate a GC-MS system for the analysis of VOCs is to use liquid standard mixtures as primary standards. After dissolving weighted amounts of pure components in methanol (or methylene chloride if solutes react with methanol or are not soluble in it), small aliquots (1–2 μl) are injected into the sorbent tube under a constant flow rate of helium (usually 100 ml/min). If light adsorbents are used, the bulk of solvent can be eliminated by passing small volumes of helium (approximately 1 liter) through the trap, and the standard mixture can be analyzed by GC-MS using thermal desorption.

To be sure that the results are not affected by artifacts, it always advisable to use at least two different types of sorbent tubes. When possible, RFs should be compared with those obtained by direct injection of the solution into the capillary column. On-column injectors or pressure-temperature vaporizers (PTV) are preferred for direct analysis because they ensure a more quantitative transfer of VOCs into the column. If RFs of high-boiling compounds need to be determined, a hot injector must be used to transfer the standard liquid solution into the trap. By considering the high flow rates of helium used during transfer, a temperature of 150°C usually is sufficient for the vaporization of the sample.

In controlling the performances of the mass spectrometer with liquid solutions, it is important to remember that the linearity range of the instrument is quite limited in the scan mode. Although differences are observed as a function of the geometry of the ionization source and the type of ion detector used, amounts larger than 100 ng usually saturate the detection system, and the area of the GC-MS peaks is not proportional to the amount injected anymore. By considering that the minimum detectable amount is on the order of 1 ng, the linear range is at least 2 order of magnitudes smaller than the FID. Good care must then be paid in the preparation of the standard solutions to avoid saturation of the GC-MS signal. In SIM mode, the linearity range is more extended because the minimum detectable amounts reach picogram levels, but much more diluted solutions must be used for the calibration.

To get reliable values of RF, at least five different amounts need to be injected into the system. The final value is given by the slope of the curve obtained by plotting the area of the peak versus the amount injected. Figure 21.15 shows an example of the calibration curves obtained with standard liquid solutions. It refers to the calibration of some carbonyl

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compounds obtained by using the ion at *m/z* 44 for selective detection. It is worth noting that the signal decreases with the number of carbon atoms in the molecule. This effect is caused by the decreased contribution of the ion with *m/z* 44 to the ionization process and should not be taken as an indication that the total ion current also follows this trend. Indeed, an opposite trend is observed using the sum of the ions with *m/z* going from 20 to 300.

Since the area of the chromatographic peak is the parameter used to measure the response factor, overloading or tailing of the peak does not affect the final result too much as long as the amount injected falls inside the linearity range of the ion detector. The quantitative analysis of compounds exhibiting nonlinearity of the partition isotherm will be affected, however, by a slightly larger uncertainty than that of peaks characterized by a perfect gaussian shape.

Table 21.8 lists compounds used in our laboratory to calibrate the GC-MS system with liquid standard solutions and to check its performances daily before the analysis of air samples. The list has been specifically designed for the quantification of precursors and products of photochemical smog pollution. It is based on the observations made in different tropospheric sites (Ciccioli et al., 1999). Other combinations can be used according to the specific aim for which the GC-MS analysis of VOCs is required. The calibration is performed by injecting liquid standard solutions containing different combinations of the compounds listed in Table 21.8. To compare results, it is useful to add an internal standard to each calibration mixture and normalize the response of different compounds with respect to the internal standard. By calling RF_{is}^{TIC} the response factor of the internal standard (IS) measured on the peak generated with the total ion current, the RRF_n^{TIC} of a compound *n* of the mixture is given by

$$RRF_n^{TIC} = \frac{RF_n^{TIC}}{RF_{is}^{TIC}} \tag{21.29}$$

Of course, RF and RRF obtained using selected ions of *n* and IS also can be used for quantification purposes. It is possible to convert any one of them into the others using Eqs. (21.24) through (21.28), provided that the mass spectra of *n* and IS are known. The

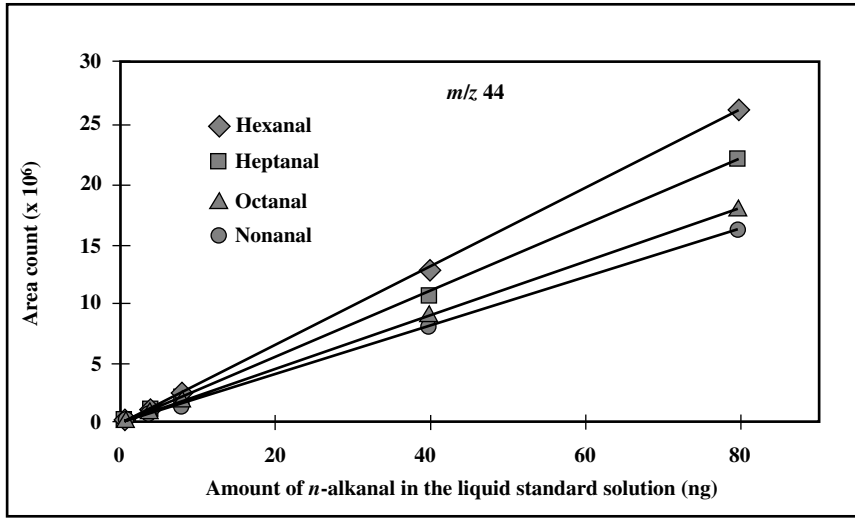

FIGURE 21.5 Calibration curves for determination of the RF of al kanals at *m/z* 44 obtained using liquid standard solution.

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TABLE 21.8 Compounds Suitable for the Calibration of VOCs in Air by GC-MS in Full Scan Using Liquid Standard Solutions

1	Acetone	42	Eethyl butanoate
2	Propanal	43	Tetrachloroethene
3	2-Propanol	44	Butanoic acid
4	*n-Pentane*	45	*n-Octane*
5	2-Methyl propanol	46	Methylpentanoate
6	Methyl acetate	47	Ethylbenzene
7	2-Methyl propanal	48	3-Methyl butanoate
8	1-Propanol	49	*p-xylene and/or perdeutero p-xylene*
9	Butanal	50	1-Hexanol
10	2-Butanone	51	3-Heptanone
11	2-Butanol	52	2-Heptanone
12	*n-Hexane*	53	Heptanal
13	Isopropyl ether	54	Pentanoic acid
14	Ethyl acetate	55	*n-Nonane*
15	Methyl propanoate	56	Methyl hexanoate
16	1-Methyl-2-propanol	57	Benzaldehyde
17	2-Methyl-2-butanol	58	*1,3,5-Trimethyl benzene and/or perdeutero 1,3,5-trimethylbenzene*
18	3-Methyl-butanal	59	1-Heptanol
19	*Benzene and/or perdeuterobenzene*	60	2-Octanone
20	Carbon tetrachloride	61	Octanal
21	Acetic acid	62	Hexanoic acid
22	1-Butanol	63	Ethyl hexanoate
23	2-Pentanone	64	α-phellandrene
24	Pentanal	65	*n-Decane*
25	3-Pentanone	66	1,2,3-Trimethyl benzene
26	Trichloroethene	67	Methyl heptanoate
27	*n*-Propyl ether	68	Limonene
28	2,2,4-Trimethyl pentane	69	1-Octanol
29	3-Pentanol	70	2-Nonanone
30	2-Pentanol	71	Nonanal
31	Propyl acetate	72	*n-Undecane*
32	*n-Heptane*	*73*	1,2,3,5-Tetramethyl benzene
33	Methyl butanoate	74	Methyl octanoate
34	Propanoic acid	75	1,2,3,4-Tetramethyl benzene
35	3-Methyl butanol	76	1-Nonanol
36	2-Methyl butanol	77	Ocatanoic acid
37	*Toluene and/or perdeuterotoluene*	78	*n-Dodecane*
38	1-Pentanol	79	*Naphtalene or perdeute r-onaphatelene*
39	2-Hexanone	80	1-Decanol
40	Hexanal	81	Nonanoic acid
41	2-Methyl propanoate	82	*Tridecane*

Note: Italicized compounds are the ones suggested to be used as internal standards. For their relative retention and ions for selective detection, see Table 21.6. Note that labeled compounds have different RIs than the unlabeled ones.

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presence of the internal standard is also useful to check the constancy of the retention indices given by the column.

Figure 21.16 reports the TIC profiles obtained by injecting four different standard solutions containing some of the compounds listed in Table 21.8 into the GC-MS system. Compounds are numbered according to sequence reported in the table. For their relative retention and specific ions used for selective detection and quantification, refer to Table 21.6. In this specific case, toluene (peak no. 37) was used as internal standard. The common practice suggests, however, that more accurate calibrations can be obtained using more than one component as an internal standard. In addition to reducing the uncertainty through a cross-checking of RF and RRF, this strategy also allows a better check of the constancy of the retention indices. Among the compounds proposed, the labeled ones offer some decisive advantages over the unlabeled ones. Since these compounds are not released or formed in air, they can be used as internal standards for the quantification of air samples. This can be done by loading the trap with the internal standard before sample collection. Helmig (1996) has used this procedure to check whether preparation, transport, and storage of traps was causing contamination of sampling tube.

For daily checks, the analysis of two of the standard solutions displayed in Fig. 21.16 usually is sufficient to test if the column meets the resolution and sensitivity requirements for the identification and quantification of VOCs in air. These analyses are necessary to verify if problems occur in the thermal desorption system, the cryofocusing unit, and the column. In this respect, it is important to mention that chemically bonded phases, although more stable than the ones attached to the fused silica tube, are also subjected to aging processes with use. Changes in the film thickness arising from chemical decomposition of the stationary phase result in changes in polarity of the column, giving rise to larger retention and tailing of polar compounds relative to the nonpolar ones.

Permeation and Diffusion Devices for the Calibration of VOCs

Due to evaporation problems, liquid standard solutions are unsuitable for calibrating VOCs exhibiting high vapor pressures at ambient temperature. In this case, permeation and diffusion devices (O'Keefe and Ortman, 1966; Scaringelli et al., 1970; Lucero, 1971; Fielden and Greenway, 1989; Staudt et al., 1995; Gautrois and Koppmann, 1999) can be used as primary standards.

Permeation tubes exploit the capability of a gas to dissolve into a membrane and diffuse into the air by passing through it. Compounds in the liquid phase are stored inside a tube made of an ethylene-propylene copolymer (FEP), Teflon, or even silicon whose ends are closed tightly (Fig. 21.17*a*). By keeping the temperature of the tube constant, a steady state is reached in which a constant permeation of the analyte through the walls is obtained. In these conditions, the permeation rate P_r of the compound can be measured with the gravimetric method. P_r is given by the slope of the curve obtained by plotting the weight of the tube against time (Scaringelli et al., 1970). Permeation rates ranging from nanograms to micrograms per minute can be obtained as a function of the size of the tube, the chemical nature of the analyte, the physicochemical properties of the membrane, and the temperature. The following equation describes the dependence of P_r on these parameters, provided that tubes are used at temperatures much lower than the critical temperature and in a limited range (approximately 30°C) (Lucero, 1971).

$$P_r = P_r' \, (p/760) \, (273.16/T) \, (M/22.4146) \, z^2 \, [1 - (p_i/p_o)] \, 10^{-3} \qquad (21.30)$$

where p is the atmospheric pressure in torrs, p_i and p_o are the pressures in torrs of the analyte inside and outside the tube, respectively, T is the temperature of the tube in degrees

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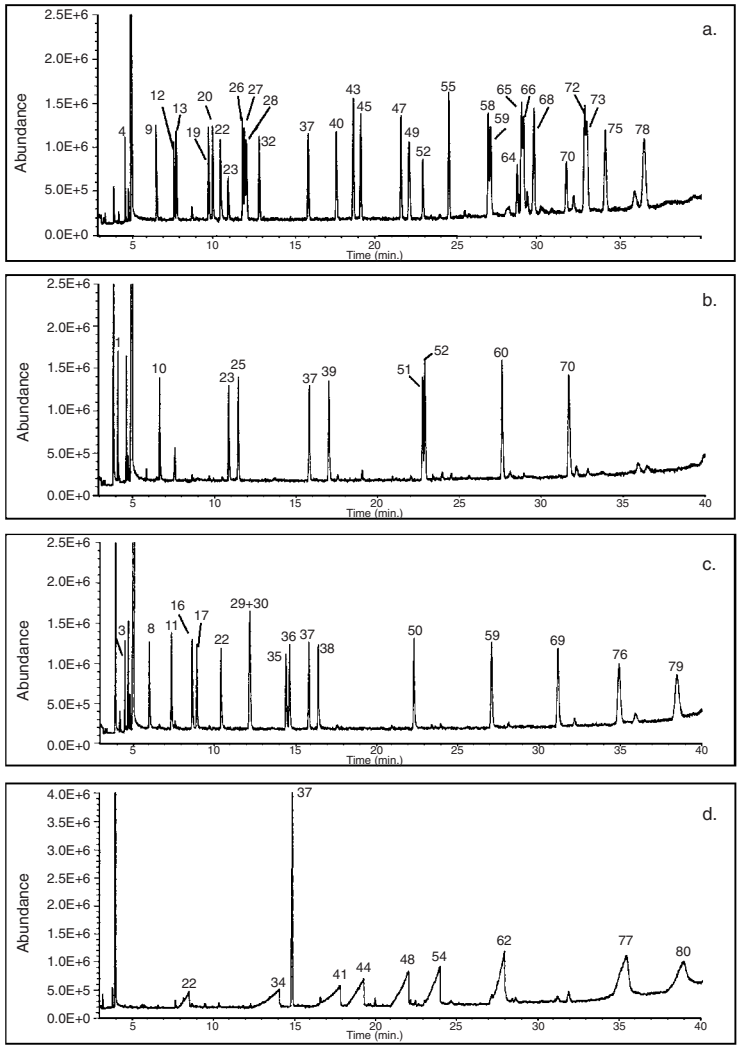

FIGURE 21.6 (a–d) TIC profiles of different liquid standard solutions used for the calibration of the GC-MS and for daily checks of its performances. For peak identification, see Table 21.8. Toluene (peak no. 37) was used as internal standard for measuring RRF.

Kelvin, M is the molecular weight of the analyte in grams, z^2 is a compressibility factor accounting for the deviation from ideal behavior (usually close to 1 for many gases), and P_r is the permeation rate in milliliters per minute at 760 torr and 273.16 K. It can be demonstrated that in the case of the cylindric tube shown in Fig. 21.16*a*,

$$P'_r = \frac{2\pi LP\,(p_i - p_o)}{\ln\,(r_o/r_i)} \tag{21.31}$$

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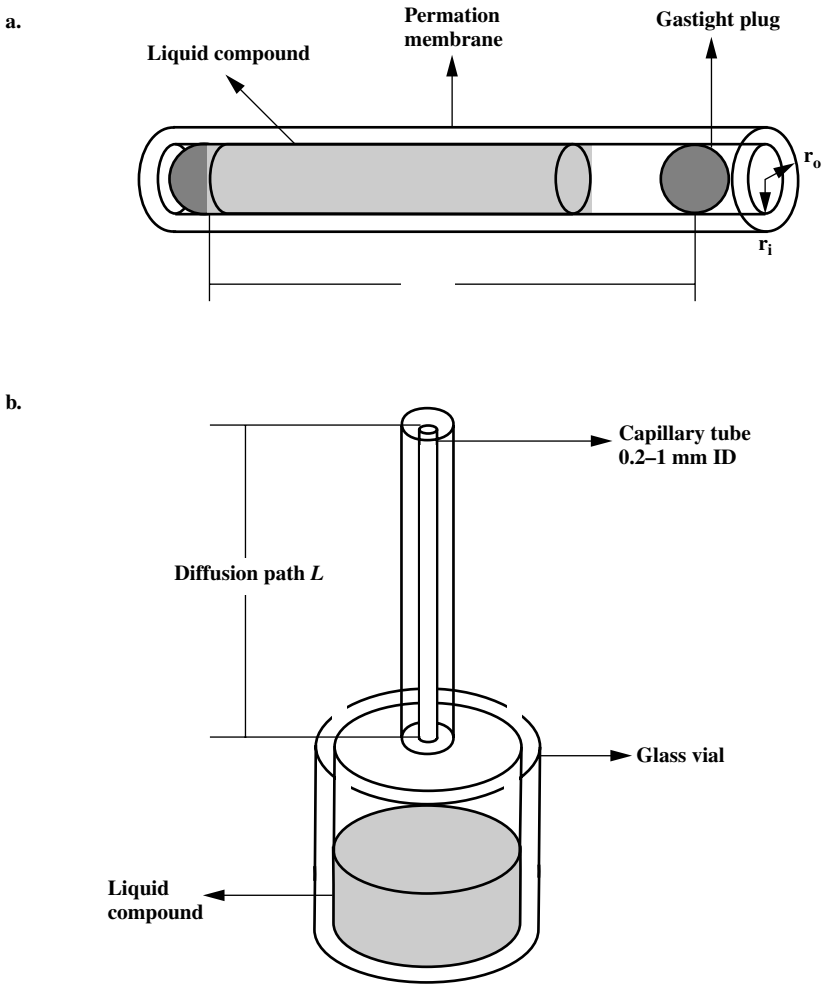

FIGURE 21.17 Schematic diagrams of permeation (*a*) and diffusion devices (*b*) for the calibration VOCs by GC-MS.

where L is the tube length in centimeters, r_o and r_i are the external and internal radius of the tube in centimeters, and P is the so-called permeability constant in milliliters per second per torr per centimeter. Equation (21.31) suggests that it is possible to modify the permeation rate by changing the length of the tube or the thickness of its walls. Since the dependence of p_i and P on the temperature is described by a Clausius-Clayperon type of equation, P_r also can be increased by increasing the temperature of the tube.

Owing to the exponential dependence of the permeation rate on the temperature, an accurate control ($\pm 0.1°C$) is required to maintain P_r at the desired value. Standard atmospheres can be generated dynamically by placing the permeation device in a thermostatic chamber in which a constant flow of air (Φ in liters per minute) is passed. The concentration of the analyte in the gas in nanograms per liter will be given by

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$$C = \frac{P_r}{\Phi} \tag{21.32}$$

Different concentrations can be obtained by changing the flow rate through the chamber or by diluting the effluent. Figure 21.18 shows a schematic diagram of the apparatus needed for the dynamic generation of standard atmospheres with permeation (or diffusion) devices. The system is also equipped with a humidifier and an ozone generator to simulate the collection of VOCs under ambient conditions. For good calibration, all flow rates of gases should be controlled accurately, and the mixing chamber should be heated to avoid condensation of VOCs on the walls. The system is also suitable to test the performance of an ozone scrubber.

Permeation devices are particularly suitable for compounds ranging in volatility between C_2 and C_6 because it is possible to get good permeation rates at temperatures (27°C) not too far from the ambient value. The construction of permeation tubes is quite easy, especially with VOCs that are liquid at room temperature. The only critical point is perfect closure of the tube. Depending on the analyte, permeation devices can work for many years. Complex standard atmospheres can be obtained by placing several tubes in the same thermostatic system (see Fig. 21.18). This approach has been used for the calibration of CFC in the ppbv to pptv range by GC-MS (Bruner et al., 1981). Permeation devices are particularly suitable for checking the capacity of adsorption traps and for measuring the BTV, SSV, and SAV of VOCs under frontal chromatographic conditions.

Diffusion techniques also can be used for the dynamic generation of standard mixtures (Fielden and Greenway, 1989; Staudt et al., 1995; Gautrois and Koppmann, 1999; Possanzini et al., 2000). With respect to permeation devices, they offer the advantage that the amount of analyte released by the system can be varied over a wide range simply by changing the length

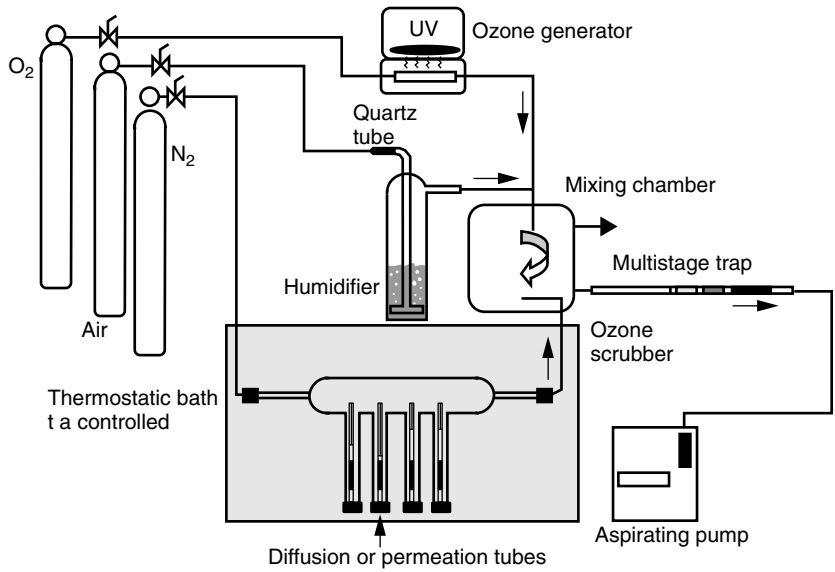

FIGURE 21.18 Schematic diagram of the apparatus for generating standard atmospheres using permeation and diffusion devices.

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SAMPLING OF ATMOSPHERIC VOLATILE ORGANIC COMPOUNDS (VOCS) WITH SORBENT TUBES AND THEIR ANALYSIS BY GC-MS

of the diffusion path and the internal diameter of the capillary tube. Diffusion tubes are made with vials containing a liquid or a solid and a capillary on the top as the diffusion path (see Fig. 21.16*b*). Capillary tubes ranging from 0.2 to 1 mm can be used to regulate the diffusion of vapors into the air. Their length can be adjusted between 1 and 10 cm as a function of the diffusion coefficient D of the gas and the vapor pressure of the compound. Using glass, fused silica, or metal capillary tubes, tight sealing of the vial can be obtained with standard Swagelock connectors or with silicon membranes covered by Teflon. The diffusion rate D_r in grams per second can be calculated by using the following equation:

$$D_r = \frac{D_0 p_0 MA}{LRT} \text{ ln bu} \left(\frac{p}{p - p_s} \right) \tag{21.33}$$

where D_0 is the diffusion coefficient of a gas at a standard pressure (p_0) of 101.325 hPa, M is the molecular mass in grams per mole, A is the cross-sectional area of the capillary in square centimeters, L is the length of the capillary tube in centimeters, R is the gas constant, T the temperature in degrees Kelvin, and p and p_s are the total pressure and the saturated vapor pressure of the analyte in pascals, respectively. A constancy of D_r is obtained by maintaining the diffusion device at constant pressure and temperature. To achieve this goal, diffusion tubes must be placed inside a thermostatic chamber like the one shown in Fig. 21.17 in which the pressure is maintained at 130 to 160 hPa above the ambient value (Gautrois and Koppmann, 1999).

Diffusion rates can be determined experimentally by measuring the loss of liquid from the vials or calculated theoretically by knowing the diffusion coefficient of the gas through the tube. In the former case, D_r is the slope of the curve obtained by plotting the weight of the tube against time. In many instances, theoretical values of D_r provide sufficiently accurate values for the calibration of VOCs by GC. Figure 21.19 shows the close relationship observed between GC-MS data obtained using liquid solutions and diffusion devices whose D_r values were calculated theoretically using Eq. (21.28). In theory, diffusion devices can be constructed for any VOC with volatility larger than C_5. However, the diffusion rates can be so low above a certain range of carbon atoms that more than 1 year is required to get reliable values of D_r.

Gas Cylinders for the Calibration of VOC

For stable components, cylinders filled with standard gaseous mixtures represent the easiest option for calibrating the GC-MS (U.S. EPA, 1997, 1999). They are used commonly for VOCs ranging in volatility from C_2 to C_6. This approach is quite useful for intercomparison purposes or calibration in the field because cylinders can be transported easily. However, their stability might not last very long because selective losses can be observed after a certain period of time (usually 3–6 months). The main problem with cylinders is that their content must be certified by the supplier or with primary standards to be sure that the concentrations given are the correct ones and that no losses have occurred on the walls during preparation and storage of the cylinder. For short periods and small volumes, standards also can be prepared by introducing known volumes of analytes into silcosteel canisters and by pressuring them with clean air.

Other Methods for Calibrating VOCs

Due to the large number of compounds that have been identified in the atmosphere, great difficulties still remain in the quantification of VOCs whose pure compounds are not avail-

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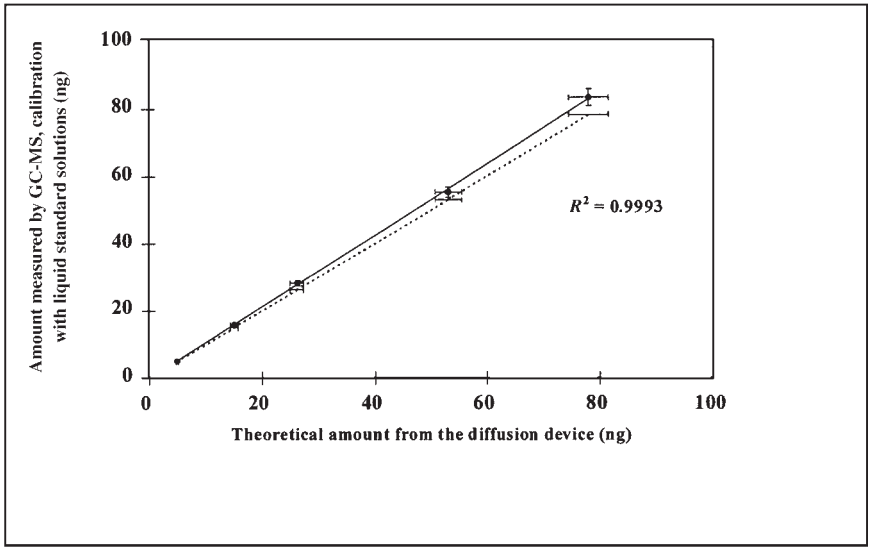

FIGURE 21.19 Correlation between the theoretical concentration of hexanal produced by a diffusion device and the one measured using standard liquid solutions. For the equation used for the calculations, see text.

able. If the RF or RRF values are nor reported in the literature, the only possible approach is to use the knowledge of mass spectrometry to estimate them. To get reasonable results, we must find one or more compounds with a known RF that gives the closest fragmentation pattern possible with the compound that needs to be quantified. In doing this, particular attention should be paid to the occurrence of neutral losses, branching of ions, and the presence of aromatic rings and functional groups in the molecule. Once the reference compounds are found, the total ion corrent can be estimated with interpolation or extrapolation techniques by assuming a linear increase in molar response of TIC with the number of carbon atoms in the molecule. The linearity of the TIC response can be assumed, however, only in a small interval of carbon atoms (3–4) because the actual trend is an exponential one. After the RF in total ion current has been estimated, the RF of selective ions can be calculated from the mass spectra obtained by GC-MS or stored in the library. RF also can be determined by GC-FID, provided that the component whose RF must be determined is separated adequately from the other constituents.

CONCLUSIONS

Although the use of GC-MS has contributed greatly to our knowledge of the emission, transformation, and deposition of VOCs in air, there are still very few laboratories around the world using this method. Many atmospheric chemists believe that this technique is too expensive and complex to be used on a routine basis, whereas others think that is too slow and, perhaps, obsolete.

The complexity bias is not justified because there are commercially available systems that are much easier to use in comparison with those of 20 years ago, and the time required for their operation is not substantially different from that of a GC equipped with a standard

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detection system. Any person with a good chemistry background can learn and properly use capillary GC-MS as long as he or she is aware of the potential problems and the limits associated with VOC collection with the trapping materials.

It is true that the technique is time-consuming and requires good training and considerable knowledge. Although faster alternatives to GC-MS have been developed (Ciccioli and Cecinato, 1992; Ciccioli, 1993b; Helmig, 1999), they cannot cover the same range of components. It is thus likely that this technique will be used for many years to come, especially if decisive improvements in sensitivity can be obtained with time-of-flight MS (Grix et al., 1989) and new software packages for automated data processing are developed. Even though the analysis time will remain the same, fast data processing could drastically reduce the time spent for calculations, and fundamental information could be available in a more reasonable time.

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SAMPLING OF ATMOSPHERIC VOLATILE ORGANIC COMPOUNDS (VOCS) WITH SORBENT TUBES AND THEIR ANALYSIS BY GC-MS

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CHAPTER 22
AEROSOL SAMPLING AND ANALYSIS

Paulo Artaxo

INTRODUCTION

Sampling and analysis of atmospheric aerosol particles are a particularly difficult task. The large diversity of particle types, sources, and processes that regulate the physical and chemical properties of atmospheric particles makes their environmental monitoring a challenging task. These particles come in many different forms, such as dust, fume, mist, smoke, fog, and others. Many of the aerosol particles are from natural sources such as soil dust, marine aerosols, and biogenic, volcanic, and other particles as well as anthropogenic particles such as sulfates, fly ash from power plant emissions, and automobile emissions, which are present in urban and remote areas of our planet. These aerosols affect human health and quality of life as well as visibility, radiation balance, climate, cloud formation, nutrient cycling, ecosystem health, and many other key aspects of the global earth system. These issues generate a need for accurate and widespread monitoring of atmospheric aerosols to characterize their diverse morphology, density, and elemental composition over their large size range that reaches about six orders of magnitude from 0.001 to 100 μm (1 μm is 10^6 m).

PHYSICAL AND CHEMICAL PROPERTIES OF AEROSOL PARTICLES

We can characterize particles by their physical and chemical properties, including shape and size, light scattering, elemental properties, and dynamic behavior. Characterizing particle size distributions is one of the most important elements of an aerosol monitoring program. The size of the particles governs much of the particle chemistry, filter collection efficiency, lung deposition, light scattering, and other key properties. The three size distributions that are normally expressed are the particle number, area, and volume size distribution. The smallest suspended particles are about 0.001 μm in diameter, which is just above the size of individual molecules. Particles of this size are produced by gas-to-particle conversion. Most of the aerosol particles that have significant resident times are in the size range of 0.1 to 10 μm. The size range of 0.1 to 2.5 μm is known as the *fine mode* and is also known as the *accumulation mode.* The size range 2.5 to 10 μm is known as the *coarse mode,* and all particles less than 10 μm are called *inhalable particles,* or PM_{10}. Particles smaller than 2.5 μm are

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also denoted $PM_{2.5}$, and those less than 100 μm are called *suspended particulate matter* (SPM). It is important to notice that this nomenclature is rather arbitrary, and it is common to find other names or size ranges. Instruments that separate particles using aerodynamic properties, such as cascade impactors, have a specified aerodynamic diameter d_a. The d_a is closely related to the physical diameter through the particle density, which is assumed to be that of a sphere of unit density.

Particle concentrations are expressed in different units, depending on the properties being measured. The most commonly used property is the aerosol mass concentration, expressed in micrograms per cubic meter. If particle number is measured, then concentration is expressed as particle number per cubic centimeter (no./cc). The pressure observed during a concentration measurement should be expressed in SI units as pascals (1 Pa = 1 N/m^2), although atmospheric pressure is also referred to as 1 atm (1 atm = 14.7 psig = 760 mmHg = 1040 cm H_2O = 408 in H_2O). Gas and particle properties are listed at normal temperature and pressure (NTP), which refers to 1 atm of pressure and 20°C (equivalent to 293 K = 68°F). Some handbooks also list values in STP (standard temperature and pressure), which is 1 atm and 0°C, but this is not recommended because most aerosol measurements in the environment are taken at temperatures closer to 20°C. It is important to always express the temperature and pressure conditions at which the measurement was taken.

AEROSOL MONITORING INSTRUMENTATION

There are a very large number of instruments available for collection and analysis of aerosol particles. The most suitable instrument depends on the objectives of the study, the monitoring and analysis strategies, and the desired products. For example, if the need is only to measure the 24-hour average aerosol mass concentrations, then a simple aerosol filter with gravimetric measurement of the mass deposited is sufficient. A normal filter is not suitable if the need is to obtain the mass concentration averaged over 30 to 60 minutes. In this case, a real-time mass monitor such as a TEOM or beta-gauge aerosol monitor will be needed. The appropriate instrumentation is a function of the needs but typically also will be limited by budget and resources. If the need includes speciation, such as nitrate, sulfate, or carbonaceous aerosol measurements, the choices are more restricted, and the sampling strategy must be balanced carefully.

Most aerosol measurements are performed by actively drawing aerosol into a sensor or onto a sampling surface by means of a pump. Commercially available pumps sample at 1 to 1000 liters/min, with a range of pressure drop and characteristics (e.g., available from GAST Manufacturing Co., SKC, Inc., and General Motor Works, Inc., among others). The measurements may be performed by collecting the particles onto a substrate and then analyzing them or by dynamically sensing them in the airborne state. In the first case, a filter generally is used to collect the particles for subsequent analysis. In real-time monitors, aerosols are measured with high time resolution using different physical properties. Sampling artifacts are always present in aerosol collection and analysis, so there is a need to carefully study the sampling artifacts and the effects on the desired final results.

It is important to consider carefully the location of the sampling site. Sites that are too close to traffic may overestimate the exposure to aerosol particles, whereas sampling sites at the tops of buildings may underestimate the ground concentrations. The site must be reasonably ventilated and not too close to high buildings, and ideally, the inlet should be located about 2 m from the ground.

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AEROSOL SAMPLING AND ANALYSIS

Inlet Requirements and Particle Cutoff Characteristics

The first issue to consider in a monitoring program or scientific study is to identify the aerosol size range that is of interest. Ten years ago, the sampling of suspended particle matter (SPM) was achieved using so-called high-volume sampling systems, which allowed the collection of particles up to 100 μm with no clear upper size limit and a flow rate of 1130 liter/min. Today, the use of these simple samplers is not recommended unless they are fitted with a 10-μm inlet head. Particles larger than 10 μm are too large for significant health effects or visibility alterations and so are typically not of interest. Current procedures collect either particles less than 10 μm (PM_{10}) or particles less than 2.5 μm ($PM_{2.5}$). Specially designed inlets with flow rates suitable for the instrument are used to collect only particles with these aerodynamic diameters. All major aerosol instrumentation manufacturers have inlets for both PM_{10} and $PM_{2.5}$ aerosol sampling.

Aerosol Sampling Systems for PM_{10} or $PM_{2.5}$

For the collection of PM_{10} or $PM_{2.5}$, there are several certified aerosol collection instruments. Some samplers, called *dichotomous aerosol samplers,* collect the two size fractions simultaneously, which are designated as the *coarse-mode* ($2.5 < d_p < 10\mu m$) and the *fine-mode fractions* ($d_p < 2.5$ μm). These samplers collect 10 percent of the fine particles on the coarse particle filter, so corrections must be made to the coarse particle concentrations. The Sierra-Andersen low-volume dichotomous sampler uses a flow rate of 16.7 liters/min through the inlet and a virtual impactor to separate fine- from coarse-mode particles. The Partisol plus automatic dichotomous sampler from Rupprecht and Patashnick, Inc., collects automatically 16 fine- and coarse-mode samples on Teflon filters for subsequent gravimetric and elemental analyses. A data logger collects detailed information about the flow rate for each sample and also records meteorological variables. The stacked filter unit (SFU) is used in many monitoring and research sampling programs because of the low cost, separation of the fine and coarse mode, and easy handling. The SFU uses Nuclepore filters and a 10-μm inlet. Manufacturers of aerosol monitoring equipment include Andersen Samplers, Inc., Gelman Instrument Co., General Metal Works, Wedding and Associates, and Rupprecht and Patashnick, among others. Most of these instruments use 47- or 37-mm-diameter Teflon or Nuclepore filters, but quartz, glass fiber, or other substrate also can be used in some samplers.

Filter Collection of Aerosol Particles

Filtration is by far the most common method for removing particles from the aerosol flow for subsequent analysis. The type of filter to be used depends on the sampling technique, the analytical methods, and the chemical species being characterized. Typical filters used for aerosol sampling consist of glass fibers, Teflon, cellulose, plastic fibers, porous membranes, or polycarbonate pore membranes, among others. There are a large number of filter holders and instruments, and each filter has advantages and disadvantages. Table 22.1 shows the main characteristics of some common filter substrates.

Numerous sources of errors may influence the accuracy of the measured aerosol mass or species concentrations. Both positive and negative sampling artifacts normally are present in most of the aerosol sampling systems. Semivolatile compounds are present in the gas and aerosol phases. The positive artifacts result from condensation of organic compounds in the collected aerosol particles or the filter itself, as well as absorption of acidic compo-

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TABLE 22.1 Summary of Characteristics of the Various Filters Commonly Used for Aerosol Collection

Filter type	Main characteristics	Some manufacturers
Fibrous filters	Mat or weave of fibers with diameters of 0.1–100 μm. Cellulose or paper, glass, quartz, and polymer fiber filters are available. Porosities 60–99%; thickness 0.15–0.5 mm. High particle collection efficiencies require low air velocity. Low pressure drop. Quartz filters ideal for organic determination.	Gelman (glass fiber, quartz); Whatman (cellulose fiber); Paliflex (quartz, teflon-coated); MSA
Porous membrane filters	Microporous membranes with tortuous pores throughout the surface. Pore sizes available in the range 0.02–10 μm. High collection efficiency, high pressure drop. Teflon has a very low trace metal content and is inert chemically.	Millipore filters (cellulose acetate and nitrate, PVC, Teflon); Metricel, Gelman (mixed ester, Teflon); Ghia (Teflon); Zefluor (Teflon); Sartorius (cellulose acetate, nylon); Nuclepore (PVC, silver membrane)
Straight-through pore filters	Thin polycarbonate films (10 μm), with cylindrical pores, with diameters of 0.1–8 μm. Low porosity (5–12%), low flow rate, high pressure drop. Very low trace metal content.	Nuclepore filters (polycarbonate); Poretics filters

nents such as sulfates by the alkaline aerosol particles already present in the filter. Retention of gaseous HNO_3, SO_2, and organic carbon creates some of the positive artifacts observed. The negative artifacts are mostly volatilization of semivolatile compounds such as NH_4NO_3 and polycyclic aromatic hydrocarbons (PAHs). In addition, losses of Cl^- in atmospheres high in SO_2 have been reported. A careful blank control can help to identify the sampling artifacts. Moreover, reducing the time between sampling and gravimetric and chemical analyses should help to minimize sampling artifacts. The collected filters must be handled carefully to avoid loss of particles, especially the coarse-mode particles. Accurate measurement of the flow rate at a given pressure and temperature is very important and frequently a neglected major source of errors in atmospheric sampling.

Gravimetric Analysis

Measurement of the increase in weight of a filter following exposure in a suitable sampler is the most common aerosol analysis. This is achieved by weighing the filter before and after sampling in a controlled environment (typically 15–20°C and 20–45 percent ± 5 percent relative humidity for 24 hours both before and after filter loading). Gravimetric analysis is very sensitive to humidity and temperature changes, as well as to electrostatic charge buildup. In addition, mechanical vibration must be kept at a minimum. Filters of cellulose fibers are the most affected by water vapor uptake, with glass and quartz filters together

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AEROSOL SAMPLING AND ANALYSIS

with Teflon and Nuclepore being less susceptible. Electrostatic charges are very difficult to control, and this makes handling of sampled filters very difficult, as well as producing large errors associated with weighing by microbalance. It is always necessary to expose the filter to a source of bipolar discharging ions such as polonium-210 or americium-241. These electrostatic eliminators are available commercially and have a short useful life, so it is necessary to change the static eliminators every 6 to 12 months. In any case, filter blanks must be part of the quality assurance/quality control (QA/QC) procedure of any measurement program. This consists of weighing a set of blank (i.e., not sampled) filters that travel and follow exactly the same procedures as the sampled filters. The difference in mass of these blank filters can be high (100–200 μg), and 10 percent of the sampled filters must be blanks. The average mass gain of the blank filters must be subtracted from the sampled filters to avoid bias in the gravimetric measurements. The microbalance used for the gravimetric mass measurement must have a high sensitivity and be compatible with the filter tare. For 37-mm Teflon or Nuclepore filters, a microbalance with 1-μg sensitivity is necessary to achieve good precision and accuracy. A sensitivity of 0.1 μg is ideal for weighing these filters. Several major balance manufacturers (Sartorius, Metler, Cahn, and others) can provide equipment with high sensitivity. Weighing of high-volume filters that are 20 × 25 cm in size and accumulate several milligrams of particulate matter is easier, but the humidity conditioning is very critical in obtaining high accuracy in the aerosol mass determination for high-volume aerosol sampling.

Elemental Analysis of Filters

Most modern studies of aerosols are aimed either at making a quantitative source apportionment using receptor modeling and similar approaches or at measuring specific heavy metals or major elements (such as sulfate or nitrate) after the filter is weighed. The type of filter used sometimes is critical to the possible range of analysis, so an integral approach taking into account the sampling equipment, filter substrate, and analysis must be done. For trace element determination, energy-dispersive x-ray fluorescence (ED-XRF) is one of the best methods. With Teflon and Nuclepore filters, XRF can routinely measure 10 to 15 elements from aluminum to lead. Because of x-ray absorption, corrections are required for the determination of Al, Si, S, and Cl. There are several manufacturers (Kevex, Philips, Rigaku, and others) that provide good analyzers with a cost in the range of US$40,000 to US$90,000. Blank filters must be measured carefully to subtract filter contaminations, which can be high for some elements and many filters. Another technique for trace element measurement is particle-induced x-ray emission (PIXE), which has a 5 to 10 times better detection limits than XRF but requires very expensive equipment and the use of a laboratory. With PIXE, in a routine analysis, about 20 to 25 elements from Al to Pb can be determined with detection limits of 0.1 ng/m^3. Sample preparation for XRF and PIXE is unnecessary, and the samples can be analyzed directly on the collection filter.

An alternative trace element method that is gaining acceptance is the use of the inductively coupled plasma—mass spectrometry (ICP-MS) method. In ICP-MS, the sample must be in a liquid form, so dissolution of the filter is needed. The soluble fraction of the aerosol can be extracted in a small container (a small Eppendorf vessel is used frequently), where the sampled filter is ultrasonically washed with Milli-Q water. This is enough to extract all the soluble components. In the case that a full elemental analysis is required, a microwave acid digestion with very pure HNO_3 acid must be used, which may bring contamination to the aerosol and makes the analysis very labor-intensive. The ICP-MS method can determine 30 to 40 elements in parts per trillion (ppt) levels. There are several new automated instruments for this analysis on the market, manufactured by Perkin Elmer, Varian, Fissons, Finingan, and others.

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For ionic component determination, ion chromatography (IC) is used to measure cations and anions in the aerosol filter. The filter must be dissolved in an ultrasonic bath in Milli-Q water for about 30 minutes and injected into an ion chromatography instrument after filtration using a 0.22-μm-pore-size filter. The method uses chemically suppressed ion chromatography with a conductivity detector. The choice of the eluent and the use of gradient pumping affect the detected species and detection limits. Determination of H^+, Na^+, NH_4^+, K^+, Mg^{+2}, Ca^{+2}, Cl^-, NO_2^-, NO_3^-, SO_4^{-2}, PO_4^{-2}, acetate, formate, and other organic acids is possible with excellent detection limits. Sulfates and nitrates are measured routinely by this method. Dionex and Shimadzu are two of the main manufacturers of IC instruments.

The carbonaceous component can be determined by collecting the aerosol in prefired Pallflex quartz filters, with subsequent analysis by a total carbon analyzer. This technique makes a complete combustion of the aerosol particles with subsequent analysis of the CO_2 produced. Elemental carbon or the so-called black carbon can be measured by light absorption analysis of the filter. This technique is suitable for Teflon and Nuclepore filters and uses a simple photometer that is calibrated against filters loaded with standard black carbon.

Real-Time Aerosol Monitors

Filters are used commonly to obtain average concentrations over 12 or 24 hours. It is sometimes necessary to measure aerosol concentrations at higher resolution (<30 minutes). For this purpose, several real-time aerosol monitors are available. The physical property most commonly used is the absorption of beta radiation through the loaded filter. This attenuation of beta radiation is related to the aerosol mass of the medium between the source and the detector. The increase in mass as the filter increases its aerosol loading is converted to atmospheric mass concentration. This type of instrument is not very sensitive, and the calibration can change according to the aerosol elemental composition.

Another important instrument for real-time aerosol mass measurement is the tapered-element oscillating microbalance (TEOM), manufactured by Rupprecht and Patashnick, Inc. The particle sample is collected on a filter mounted in a tapered oscillating element. The natural frequency of the tapered element changes with the mass loading. The instrument is very sensitive but has a problem in that the aerosol flow must be heated to 50 or 70°C, causing the loss of semivolatile compounds. In intercomparison experiments between real gravimetric measurements and the TEOM aerosol monitor, the TEOM sampler always provide values for PM_{10} that are 10 to 30 percent smaller than gravimetric measurement, which is expected to be more representative of the actual aerosol mass.

Real-Time Aerosol Speciation Instruments

The real-time monitoring of aerosol properties with high-time resolution is greatly extending the types of scientific studies and monitoring that are possible. The measurement of black carbon (BC) concentrations using the Aethalometer from Magee Scientific, Inc., has been in use for more than 10 years. The Aethalometer provides BC concentration by measuring the light absorption over a quartz filter tape automatically every 5 minutes. The instrument is very sensitive and is even capable of measuring black carbon in remote locations such as Antarctica. Recently, an organic and elemental carbon monitor was developed by Rupprecht and Patashnick, Inc.; the 5400 carbon monitor makes measurements of the absolute concentration of organic and elemental carbon every 30 minutes by converting the carbonaceous aerosol into CO_2. The same company recently introduced real-time sulfate and nitrate monitors, and detection limits are adequate for urban aerosol monitoring.

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AEROSOL SAMPLING AND ANALYSIS

Optical-Based Techniques for Aerosol Monitoring

With optical aerosol measurement instruments, the interaction of particles with incident light serves as a basis for the real-time measurement of particle concentration and size. Important advantages of these instruments include very fast response and high sensitivity. Light extinction by particles is measured with the Nephelometer instrument manufactured by TSI, Inc., Radiance Research, Inc., and others. Optical particle counters quantify individual particles with a minimum size of about 0.1 μm with the aid of a laser illumination system. Particle size distribution can be measured almost in real time with these advanced optical counter systems. A variation in these instruments is the time-of-flight aerodynamic particle sizer instrument (TSI APS 3300) that measures aerosol size distribution with high temporal resolution and great sensitivity. Particle Measuring Systems manufactures the aerosol LASAIR II particle counter that optically counts particles in the size range of 0.3 to 25 μm.

The lower particle size detection limit of an optical counter can be extended to about 3 to 10 nm by using a vapor condensation technique. In these instruments, the sampled aerosol is saturated with butanol vapor with subsequent detection by optical techniques. These instruments are called *condensation nucleus counters* and measure total particle concentration with a time resolution of seconds (TSI 3020, 3076 CNC).

Measurement of Aerosol Size Distribution

Cascade impactors have long been used to measure aerosol size distribution. Some models allow the determination of mass distribution, whereas others are focused on trace element or ionic distribution. One of the best cascade impactors is the so-called MOUDI (multiorifice uniform deposit cascade impactor) manufactured by MSP Corp. The MOUDI rotates the impactor plates so that a uniform deposit is obtained. It is a multijet impactor, which means that a low pressure drop is used along the stages, thereby minimizing the loss of semivolatile compounds. It has 8 or 10 size ranges, from 0.012 to 10 μm, with a flow rate of 28 liters/min. The Berner cascade impactor is also a low-flow-rate multijet impactor with 8 stages, allowing aerosol sizing in the range 0.1 to 10 μm. When high mass is required for analysis, such as for the determination of organic compounds, a high-volume cascade impactor is necessary. General Metal Works, Wedding, and Sierra Andersen manufacture high-volume cascade impactors that allow aerosol mass distribution to be measured for 5 or 6 size ranges.

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APPENDIX 22A

AEROSOL EQUIPMENT MANUFACTURERS AND FILTER SUPPLIERS

TSI Particle Instrumentation Home Page: *http://www.tsi.com/particle/cover/paid home.htm.*

Rupprecht and Patashnick, *http://www.rpco.com//index.htm.*

Magee Scientific (Aethalometer): *http://www.mageesci.com/.*

Andersen Instruments: *http://www.anderseninstruments.com/, http://www.graseby.com/.*

Particle Measurement Systems: *http://www.pmeasuring.com/.*

Whatman Filters: *http://www.whatman.plc.uk/.*

Mie Monitoring Instruments for the Environment, Inc.: *http://www.mieinc.com/.*

Ecotech World-Class Air and Water Monitoring Systems: *http://www.ecotech.com.au/.*

Millipore Corporation: *http://www.millipore.com/.*

Structure Probe, Inc.: *http://www.2spi.com/.*

Shimadzu Corp.: *http://www.shimadzu.com/.*

WWR Co.: *http://www.vwrsp.com/.*

Thomas Scientific Co.: *http://www.thomassci.com/.*

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CHAPTER 23
DEPOSITION FROM THE ATMOSPHERE

Stanislaw Cieslik

INTRODUCTION

Any constituent of the atmosphere (thus including air pollutants) may be removed and transferred to the earth's surface by a variety of mechanisms. This transfer is known under the generic term of *deposition.* The choice of this term is not very appropriate in so far as it covers a variety of processes that may be considerably different from each other. To give a few examples, gaseous molecules such as ozone are taken up by vegetation by penetration into the plant tissues or are destroyed at the surface by reaction. Such a process is not really *deposition,* but by convention, the term is used. Particulate matter (atmospheric aerosol) is really deposited as a consequence of two contributing processes: gravitational settling and atmospheric turbulence, which brings the particles in contact with the surface in a quasi-random way. Removal of dissolved matter may occur by precipitation; in this case, the term *fall* would be more appropriate. However, the term *deposition* is used widely. By convention, these processes are subdivided in two categories. The expression *dry deposition* is used for any transfer process of gaseous or particulate matter from the atmosphere to the surface. *Wet deposition* corresponds to the transfer of dissolved matter to the surface. I will deal with these two categories successively. Table 23.1 summarizes the deposition processes, the main mechanisms by which they occur, and the substances involved.

Obviously, nature is sensitive to *total* deposition. Dry and wet processes therefore must be summed, and the final result may be expressed in terms of, for example, tons of elemental sulfur (or nitrogen, or any other polluting substance) deposited per square kilometer and year. To obtain such figures over extended areas, measurement alone is insufficient because it is carried out at single stations (point values); it must be complemented by integration and extrapolation work, which can be made through modeling techniques.

DRY DEPOSITION

General

Interest in dry deposition dates back to the late 1970s, when it became clear that deposition processes must be integrated in air pollutant transport models, where they constitute a sink

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TABLE 23.1 The Different Deposition Processes

Process		Mechanism	Deposited substance
Dry deposition	Gas	Turbulence, uptake by vegetation, surface reaction	SO_2, HNO_3, O_3, NO_x, ammonia, etc.
	Particulate	Turbulence, gravitational settling	Sulfates, nitrates, metal salts, silica, soot, etc.
Wet deposition	Fog	Turbulence, gravitational settling	SO_2, HNO_3, etc.
	Rain	Gravity	H_2SO_4,O_3, NO_x, various ions

and lower boundary condition for both gaseous minor species and aerosol particles. Further, environmental concerns related to acid rain and forest dieback led to studying acid deposition as a whole because not all acidic substances removed from the atmosphere are deposited by rain (wet deposition) on the earth's surface; acids such as HCl, SO_2, and HNO_3 also may be deposited as gases. Nonacidic substances (e.g., ozone, nitrogen oxides, and ammonia) undergo dry deposition.

Early reviews of dry deposition may be found in Sehmel (1980), Hosker at al. (1982), and Voldner et al. (1986). A number of studies were devoted to particles, ammonia, and SO_2. Presently, the atmospheric concentrations of SO_2 have decreased considerably in most developed countries (western Europe and North America) due to air pollution abatement measures (e.g., elimination of sulfur in fuels), and there are fewer studies of dry deposition of SO_2 than in the past. Nowadays, our knowledge on SO_2 deposition is considered sufficient to allow its inclusion in long-range (regional) transport models (Stortenberg and Hov, 1995).

More emphasis has been given to ozone and nitrogen deposition in recent years. Dry deposition of ozone has been investigated for many years, the first available work having been carried out by Regener (1957). Subsequent significant investigations have been made by Galbally (1971), Galbally and Roy (1980), Wesely et al. (1978, 1982), Delany et al. (1986), Massman (1993), Padro (1995), Gusten and Heinrich (1996), and Sun and Massman (1999), to cite a few. The main features of ozone deposition are the increase in deposition during morning hours, a maximum at noon, followed by a decrease. Nighttime deposition is nearly absent. Such behavior has been observed on vegetated surfaces as well as on bare soils, indicating that contrary to what was stated in the past, uptake by vegetation is not the only pathway for ozone deposition.

Nitrogen oxides (mostly in the form of NO and NO_2) were considered initially as purely depositing substances. It appears since Delany et al. (1986) that the surface fluxes of these species may be directed both downward and upward. The situation is obscured by the rapid chemical reactions involving the triad NO-NO_2-O_3, causing artifacts during measurements. It is now well established that NO is emitted by soils due to microbiological processes. During its ascent through the atmospheric surface layer, the emitted NO is rapidly oxidized by ozone to NO_2. Consequently, an observation of upward NO_2 fluxes made at 10 m above ground in reality may be due to the presence of oxidized NO. Several attempts have been made to resolve the problem of chemically perturbed nitrogen oxide fluxes by modeling techniques (Kramm et al., 1991; Vila-Guerau et al., 1995; Galmarini et al., 1997; Kirstensen et al., 1997). In conclusion, it appears that surface fluxes of nitrogen oxides may be both upward or downward, mostly depending on the NO_2 concentration in air.

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DEPOSITION FROM THE ATMOSPHERE

Mechanisms

Dry deposition is best quantified by surface fluxes, denoted by F, i.e., quantities of matter vertically crossing a unit surface area per unit time. Deposition velocities are defined as

$$v_d = \frac{F}{C} \tag{23.1}$$

where C is the concentration. They are generally preferred to fluxes in modeling work for practical (numerical) reasons because their variations with time are smoother than those of fluxes. Thus, in the literature, deposition data generally are expressed in terms of velocities, which are in turn parameterized to make calculations easier.

A powerful parameterization of surface deposition is the resistance representation, where the deposition process is described as if it were an electric circuit governed by Ohm's law. The electric current is analogous to the deposition velocity, and voltage is analogous to the concentration difference between air and surface. This may be written as follows:

$$C_A - C_S = RF \tag{23.2}$$

where C_A and C_S are the air and soil concentrations, respectively, and R is an empirical quantity, the resistance. In the case of pure deposition, it is reasonable to consider C_S as negligible because the soil represents a sink for it. The resistance is decomposed into three resistances in series, according to

$$R = r_a + r_b + r_c \tag{23.3}$$

where r_a is the aerodynamic resistance to vertical transport of the substance through the turbulent air layer, r_b is the laminar sublayer resistance to diffusion of the substance through the laminar sublayer present near the surface (a few millimeters), and r_s is the surface resistance. It may be easily seen that

$$v_d = \frac{1}{r_a + r_b + r_c} \tag{23.4}$$

This scheme can be extended for a more complex air-surface interface, as is generally the case for a vegetation canopy. In such a case, more resistances may be introduced, mounted in series and in parallel, simulating the different pathways followed by the depositing substance. The resistance scheme is now used widely in modeling work as a parameterization.

Physically, deposition occurs by various pathways. One of the most important is penetration in plant tissues through the stomata present on the surfaces of the leaves. This process depends on air moisture, temperature, and sunlight intensity, which govern opening and closing of the stomata as an evaporation-regulating mechanism. The more open the stomata are, the more intense deposition is. In the resistance scheme, the stomatal aperture is simulated through the surface resistance. On bare soils, some substances (e.g., ozone) may be destroyed by a wall-like chemical reaction.

Atmospheric turbulence enhances vertical mixing and thus favors deposition because it brings more molecules of the substance in contact with the surface. Its influence is expressed by the aerodynamic resistance, which is defined by

$$r_a = \int_0^{z_M} \frac{dz}{K(z)} \tag{23.5}$$

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where z is the height variable, z_M is the height of measurement, and $K(z)$ is the turbulent diffusion coefficient, directly related to the intensity of turbulence.

In conclusion, knowledge of dry deposition is reasonably good as far as processes are concerned. Good modeling parameterizations exist for most environmentally relevant depositing substances. Some uncertainties subsist, especially for species undergoing rapid chemical reactions or species showing both upward and downward fluxes, such as nitrogen oxides.

MEASUREMENT TECHNIQUES

The methods used to measure dry deposition velocities of fluxes differ depending on whether the depositing matter is formed by aerosol particles or by a gaseous substance. Aerosols are sampled on surrogate surfaces (mainly filters). Sampling periods may be rather long (days to weeks) to increase measurement precision. Subsequent chemical analysis yields amounts of pollutants, which are readily converted into fluxes using the known area and integration times. These techniques are very similar to those used for wet deposition, where rainwater is sampled and subsequently analyzed (see next section). At monitoring stations, aerosol dry deposition and wet deposition generally are determined simultaneously by using dry/wet collectors. These facilities consist of two buckets, which open and close depending on whether it is raining or not. In case of rain, there is no aerosol dry deposition because particles are washed out by rain and thus incorporated into wet deposition. Thus the dry bucket closes, and the wet one opens. When rain ceases, the dry bucket opens and the wet one closes such that rainwater is collected.

Collection methods are not used for gaseous dry deposition because the deposited gas generally does not remain on the surface. Flux determination is made using micrometeorological methods, where the flux is measured in air at some height (several meters) above the surface. Micrometeorology assumes the existence of a *constant flux layer* (CFL) extending from the surface to a few tens of meters height, where vertical fluxes of scalar conservative quantities (such as enthalpy, humidity, and concentrations) are height-independent. It may be deduced from this hypothesis that a flux measured at any height inside the CFL is equal to the surface flux.

The three main micrometeorological methods are described briefly here and are discussed in more detail in Chap. 19.

EDDY CORRELATION

In the atmosphere, all variables are varying or *fluctuating* rapidly. Thus a physical variable X may be expressed as a sum of a time average $\overline{X}$ and a fluctuation X' in the form $X = \overline{X} + X'$. These fluctuations have an apparently random behavior, which characterizes a turbulent fluid. Turbulence is responsible for the vertical transport of substances that are eventually deposited. Since deposition is related to turbulent vertical air motion, it seems logical that the fluxes are in some way related to both the fluctuations of vertical air velocity w and of concentration C.

This is best expressed by

$$F = \overline{w'C'} \tag{23.6}$$

where w' and C' are the fluctuations of vertical wind (air) velocity and concentration, respectively. The method is based on the measurement of these fluctuations, and thus it requires the use of sensors that are fast enough to resolve them. A response time of at least

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5 Hz (number of measurements per second) is necessary. Vertical velocity can be measured quickly and accurately with a sonic anemometer; the concentration of the pollutant must be recorded by a fast-response chemical sensor. The most important depositing atmospheric constituents can be monitored very rapidly, including ozone, nitrogen and sulfur dioxide, and ammonia. The chemiluminescence method is used extensively for these measurements.

VERTICAL GRADIENT

This technique is based on the assumption that the deposition process is governed by vertical turbulent diffusion, thus obeying a Ficklike diffusion equation:

$$F = \mathrm{K}\,\frac{\partial \overline{C}}{\partial z} \tag{23.7}$$

where K is the vertical turbulent diffusion coefficient and z is the height above ground. The vertical gradient $\partial\overline{C}/\partial z$ is approximated by $\Delta\overline{C}/\Delta z$ because concentration measurements are made at discrete heights. More that two (three to six) heights are recommended to check the homogeneity of the vertical profile. The diffusion coefficient is deduced from meteorological observations. This method does not require fast-response sensors, so a wider variety of substances can be monitored, but it is less reliable. The substance can be sampled during successive averaging periods (e.g., semihourly) and then analyzed by any method (e.g., gas chromatography). The vertical gradient method can be used for the deposition of organic compounds.

EDDY ACCUMULATION

These measurements are made at a single level, eliminating any artifact due to distorted vertical concentration profiles (as in vertical gradient records), but does not require fast-response sensors. Thus this method combines the advantages of eddy covariance and vertical gradients. This technique consists of sampling air into two reservoirs (e.g., bags or adsorption tubes) according to the sign (direction) of the vertical air motion; one reservoir is filled when air goes up, and the other is filled when air goes down. At the end of an averaging period, the concentration is determined for the two reservoirs (referred to as C_+ and C_-) by some analytical procedure. A simplified form of eddy accumulation, called *relaxed eddy accumulation* or *conditional sampling,* estimates fluxes $F = ß\sigma_w(\mathrm{C}_+ - \mathrm{C}_-)$, where ß is a semiempirical coefficient (generally ranging between 0.55 and 0.65) and σ_w is the standard deviation of the vertical wind. This method requires the use of a sonic anemometer to determine the value of σ_w and because the sign of the vertical wind is needed to direct the air flow into the correct reservoir.

WET DEPOSITION

As stated earlier, wet deposition is the transfer of atmospheric constituents to the surface in dissolved form. In most cases, the term refers to precipitation (i.e., rain, hail, or snow), but it also applies to the deposition of fog droplets. In this case, it is sometimes called *occult wet deposition.*

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A number of substances may be dissolved in liquid or frozen water. Liquid water is present in the atmosphere in the form of cloud or fog droplets or raindrops. Frozen water is present in air as ice crystals, as well as in the form of snow and hail. There are a large variety of substances present in the atmosphere that can be incorporated into droplets (and then subsequently frozen). Sulfur dioxide, some nitrogen oxides, and hydrogen peroxide may be present in cloud droplets, as well as a wide variety of ions such as sulfates, nitrates, and metal ions.

After having been incorporated into cloud droplets, sulfur and nitrogen dioxides may undergo oxidation by other dissolved substances such as hydrogen peroxide or Fe^{3+} ions. These chemical reactions generally are slow, but the residence time of substances dissolved in droplets may be quite long (several days). Thus oxidation has sufficient time to occur, resulting in the formation of sulfuric and nitric acids. When the cloud precipitates, the presence of these species lowers the pH, and one can thus speak of *acid rain,* a phenomenon discovered in the 1970s in Scandinavia. A number of Norwegian lakes became so acidic that an important part of their fauna disappeared. Norway has few industries that could be responsible for the acidification process (e.g., through wastewater), and it was thus supposed that the acidity could come only from long-range atmospheric transport. Analyses of rainwater showed that this hypothesis was correct. "Pure" rainwater has a mean pH of 5.6, due to the presence of carbon dioxide (a slight acid) in air. In Norway, however, pH values were found to be in many cases less than 4. A map of atmospheric mean circulation in Europe shows that most trajectories of air masses arriving over Scandinavia come from the southwest and thus are likely to transport air pollution emitted over the British Isles and other parts of northwestern Europe, where heavy industry is present.

Nowadays, the term *wet deposition* is preferred to that of *acid rain* because it covers a broader range of effects. Getting a reliable picture of wet deposition is a matter of chemical analysis and long-term monitoring. During the last 20 years, monitoring networks have been established on local, regional, and worldwide scales. Among the most important long-term and large-scale programs on wet deposition, we can cite the National Atmospheric Deposition Program (NADP, United States), the Cooperative Program for Monitoring and Evaluation of the Long-Range Transmission of Air Pollutants in Europe (EMEP), and the Global Atmospheric Watch (worldwide).

The first step in wet deposition measurements is determination of the concentrations of pollutants present in rainwater. After collection, chemical analysis is carried out. For ions, the most suitable method is ion chromatography. By combining the concentrations obtained with rainfall quantities, one gets the amounts of pollutants deposited per unit area and time (equivalent to a flux). In addition to concentration measurements, some quantities characterizing the rainwater quality such as pH and electrical conductivity are also determined.

A major concern regarding wet deposition is the general trend. In eastern North America (including the United States and Canada), there is a decrease in sulfur deposition due to decreasing emission rates (1997 Canadian Acid Rain Assessment, Environment Canada Report, 1997). In 1980, about 10.2 million tons of sulfur were emitted over that area, whereas 8.3 million tons were emitted in 1993. The total wet deposition of sulfur was 3.6 million tons in 1980 and 2.8 million tons in 1993. This negative trend, which is still underway, is also observed in Europe and is due to the abatement measures regarding sulfur in fuels, which has been banned progressively by desulfurization of fuels. This trend is even more visible if we examine SO_2 concentrations, which decreased considerably in the last 20 years. For example, the average SO_2 concentration in the city of Zurich (Switzerland) was about 40 to 50 $\mu g/m^3$ in the years from 1980 to 1985 (NABEL Luftbelastung, 1999; Schriftreihe nr. 316, Federal Swiss Bureau for Environment, Forestry and Landscape, 1999) and is about 20 $\mu g/m^3$ presently.

For nitrogen oxides, the situation is more complex. For eastern North America, practically no trend is detectable for emissions as well as for wet deposition. During the period

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1980–1993, emissions were close to 3.8 million tons per year, whereas wet deposition amounted to about 1.3 million tons per year, remaining practically constant. This is due to the difficulty of reducing nitrogen oxides emitted by car exhaust. A general assessment of recent findings in wet deposition also may be found in Whelpdale and Kaiser (Global Acid Deposition Assessment, GAW Report No. 106, WMO, Geneva, 1996).

INTEGRATION

As stated in the Introduction, the final goal of deposition studies is to sum deposition estimates and to establish regional maps of amounts of pollutants deposited per unit area (square kilometer or hectare) and time (months or years). An important concept here is that of *critical load,* defined as the maximum deposition rate (expressed in tons per hectare and per year) tolerated by a given ecosystem (forest, lake, etc.) if, when exceeded, acute or chronic adverse effects result. For example, the pH critical load for a lake is the lowest pH value still able to buffer further addition of acid substances. Critical loads vary according to the chemical species deposited and ecosystem type such that its evaluation is a rather complex task. For example, the Appalachian Plateau in Maryland has a critical load for sulfates of 24 kg SO_4 per hectare per year, whereas the nearby Blue Ridge Region (also in Maryland) has a critical load of 96 kg/ha/yr because it has a limestone bedrock that has a greater buffering ability.

Atmospheric modeling is required for establishing maps of critical loads as well as deposited quantities. Models must integrate emissions, short- and long-range transport of pollutants, chemical transformation, meteorology, and finally, deposition. A good example of a recent regional deposition (dry and wet) assessment that integrates both observations and modeling can be found in the EMEP Report 1/2000 (ISSN 0332-9879), which gives a good overall picture of the entire European continent and its individual countries.

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CHAPTER 24
TRACE GAS EMISSION MEASUREMENTS

Alex Guenther

INTRODUCTION

The first chapter of this section described the important issues related to regional and global air quality. Trace gas emissions play a key role in the processes controlling these air quality phenomena and are also an important part of any potential solutions. In some cases, changes in trace gas emissions are due to obvious pollutant sources, including many technological sources. Technological sources include fossil fuel burning, industrial processes, and waste disposal. These sources are the major trace gas contributors in densely populated or industrial areas and also have a strong impact on the global atmosphere. Other sources, including biomass burning and biogenic sources, have a natural component but are strongly influenced by humans. There is widespread concern about the effect of human activities on the chemical composition of the current earth atmosphere. Human activities are the underlying cause of the current increase in pollutant levels on regional and global scales. In order to understand these increases and to predict future changes, we must quantify emissions from various sources and understand the natural and human-influenced processes that control emissions.

This chapter provides an overview of methods that can be used to investigate and monitor trace gas emissions into the atmosphere. Each technique is described in sufficient detail to give a basic understanding of the method and to enable the reader to determine the most suitable method(s) for a particular application. Additional references are provided to give further details on the selected techniques. Methods for measuring wet and dry deposition were described in Chap. 23.

EMISSION MEASUREMENT METHODS

There is no single measurement method that is preferred for all emission studies. The three major categories are micrometeorological, mass balance, and tracer ratio methods. These methods can be deployed on a variety of platforms, including handheld, tower, blimp, and aircraft-based. Figure 24.1 illustrates how various techniques can be applied to a range of spatial (from <1 cm^2 to the entire earth system) and time (from seconds to years) scales. In many cases, it is useful to characterize emissions on several different spatial and time scales in order to gain a complete understanding of the processes controlling emissions from a par-

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ticular source. Measurements of emissions from a specific component of a complex source are often the best way to investigate emission mechanisms. Other measurements, such as those provided by micrometeorological techniques, enable us to integrate over an entire source and understand the processes controlling net emissions, which may be more than just the sum of each component.

Micrometeorological Techniques

A trace gas or particle emitted into the atmospheric boundary layer is dispersed horizontally by the mean wind and vertically by the random movements of eddies through a process called *eddy diffusion.* A smoke plume mixing into the atmosphere on a sunny day provides an opportunity to observe these processes in the atmosphere. The plume travels horizontally in the direction of the mean wind flow and spreads out vertically at a rate determined by the strength of the turbulent eddies in the atmosphere. Atmospheric turbulence is generated primarily by heating and friction at the earth's surface. The random fluctuations that occur in turbulent flow move atmospheric constituents (such as smoke and trace gases) toward or away from the earth's surface. The upward movement of trace gases from the surface is an emission flux, whereas the downward movement is a deposition flux. The micrometeorological methods described below are used to quantify the net movement of a gas across a horizontal plane in the turbulent boundary layer. The major advantages of these methods are that they do not disturb the source and that they integrate over a large area. An overview of these methods and examples of their application are given in Table 24.1.

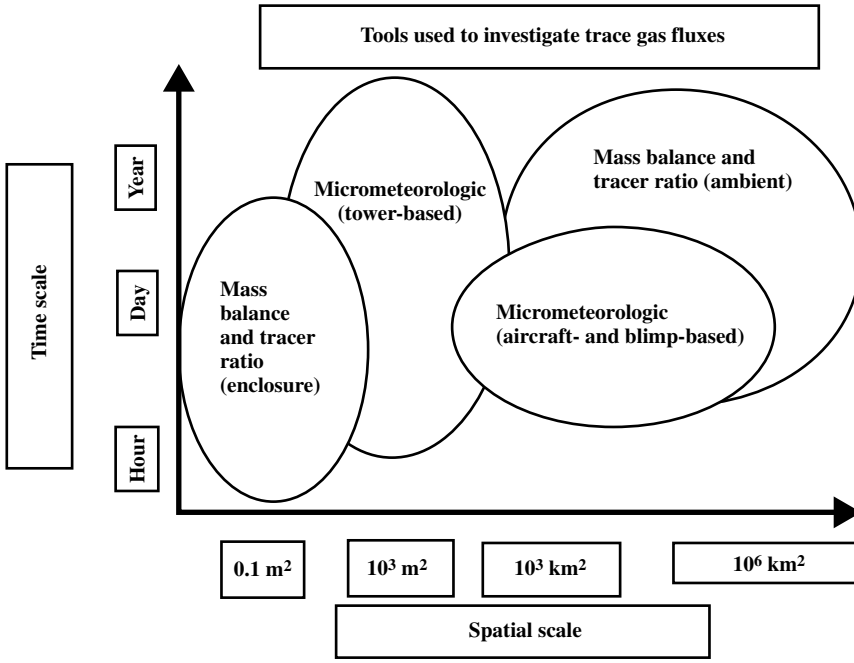

FIGURE 24.1 Spatial and time scales associated with different flux measurement methods.

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TABLE 24.1 Micrometeorological Flux Measurement Studies

Method	Species measured	Site	Reference
Eddy covariance (tower)	CH_4, CO_2	Subarctic tundra	Fan et al. (1992)
Eddy covariance (tower)	O_3, NO	Grassland	Stocker et al. (1993)
Eddy covariance (tower)	CO_2, H_2O	Temperate forest	Baldocchi et al. (1996)
Eddy covariance (tower)	Isoprene, O_3, CO_2, H_2O	Temperate forest	Guenther and Hills (1998)
Eddy covariance (tower)	NO	Agricultural field	Civerolo and Dickerson (1998)
Eddy covariance (tower)	N_2O	Agricultural field	Hargreaves et al. (1996)
Eddy covariance (tower)	Aerosol particles	Field	Buzorius et al. (1998)
Eddy covariance (aircraft)	H_2O, CO_2	Boreal forest	Dobosy et al. (1997)
Eddy covariance (aircraft)	O_3	Grassland	Massman et al. (1995)
Eddy accumulation, disjunct (tower)	Isoprene, monoterpenes	Temperate forest	Rinne et al. (2000)
Relaxed eddy accumulation (tower)	Isoprene	Temperate forest	Guenther et al. (1996b)
Relaxed eddy accumulation (tower)	Pesticides	Agricultural field	Majewski et al. (1993)
Relaxed eddy accumulation (tower)	CO_2	Agricultural field	Oncley et al. (1993)
Relaxed eddy accumulation (tower)	N_2O	Agricultural field	Hargreaves et al. (1996)
Relaxed eddy accumulation (tower)	Ammonia	Field	Zhu et al. (2000)
Relaxed eddy accumulation (aircraft)	Isoprene	Tropical forest	Greenberg et al. (1999b)
Relaxed eddy accumulation (aircraft)	Isoprene	Boreal forest	Zhu et al. (1999)
Gradient flux: eddy covariance tracer	Isoprene	Temperate forest	Guenther et al. (1996b)
Gradient flux: eddy covariance tracer	Pesticides	Agricultural field	Majewski et al. (1990)
Gradient flux: convective boundary layer	Isoprene, monoterpenes	Temperate forest	Guenther et al. (1996a,b,c)
Gradient flux: convective boundary layer	Isoprene, monoterpenes	Tropical forest	Davis et al. (1994)
Gradient flux: convective boundary layer	Isoprene, monoterpenes	Temperate forests	Greenberg et al. (1999a)
Gradient-flux: surface energy balance	Isoprene	Temperate forest	Guenther et al. (1996c)
Gradient-flux: surface energy balance	Pesticides	Agricultural field	Majewski et al. (1990)
Gradient flux: profile similarity	Pesticides	Agricultural field	Majewski et al. (1990, 1993)
Gradient flux: profile similarity	N_2O	Agricultural field	Hargreaves et al. (1996)
Variance	H_2O	Plain	De Bruin et al. (1993)

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There are a number of issues that must be considered before applying any micrometeorological technique, including sampling time, sensor requirements, and where to sample. A response time of about 1 s may be required for accurate (within 10 percent) daytime measurements with moderate to low wind speeds (<5 m/s), whereas faster sensors are needed at night. The averaging time used for micrometeorological flux measurements is typically between 15 and 60 minutes. The ideal terrain for these measurements is flat (slope <8 percent) and uniform within an upwind distance that is about 100 times greater than the measurement height. These constraints can be relaxed somewhat if uncertainties larger than 10 percent are acceptable. The measurement height is the vertical distance above the surface for bare ground, but a thick canopy or buildings effectively result in an elevated surface. Additional details regarding these considerations for micrometeorological flux measurements are given elsewhere (Hicks and McMillen, 1988; Stull, 1988; Wyngaard, 1990; Verma, 1990; Lenschow, 1995; Baldocchi, et al., 1996).

Micrometeorological measurements often are made with instruments mounted on towers above the source of interest. Other platforms that can be used to make these measurements include tethered-balloon sampling systems and aircraft (Desjardins and MacPherson, 1989).

Eddy Covariance. The preferred micrometeorological method for measuring trace gas fluxes in the turbulent boundary layer is eddy covariance. This approach is a direct measurement of the fluctuating vertical wind velocity and trace gas concentration. The flux is determined from the mean covariance between vertical wind velocity w and concentration c fluctuations and can be expressed as

$$\text{Flux} = w'c' \tag{24.1}$$

where w' is the difference between the instantaneous and mean vertical wind speed and c' is the difference between the instantaneous and mean trace gas concentration. Here we use $w'c'$ to represent the time average of the product of these two variables. For example, Fig. 24.2 includes a 70s record of trace gas concentration (Fig. 24.2*a*) and vertical wind speed (Fig. 24.2*b*) sampled in the air above a forest canopy. The instantaneous product of w' and c', shown in Fig. 24.2*c,* ranges from about -6 to 9 $\mu g/m^2$ per second, and the average $w'c'$ of about 1 $\mu g/m^2$ per second is the emission flux from the forest canopy during this time period.

The major components of an eddy covariance flux system are

1. An instrument that measures vertical wind speed with a fast (typically <100 ms) response time.
2. An instrument that measures the targeted atmospheric constituent with a fast response time.
3. A system to receive and store the data (e.g, data logger or computer).

Instruments with slower (>100 ms) response times can be used to measure the flux associated with lower frequencies but will underestimate the total flux. In some cases this may result in an acceptable error, whereas in other cases an attempt can be made to account for the loss of flux due to inadequate sensor response (Moore, 1986). The correction involves using another scalar that is measured with a fast-response sensor and then estimating the reduction in flux that results if a digital filter is used to simulate the response time of the slower instrument.

Eddy covariance is used extensively to measure sensible and latent heat fluxes and has been used recently for networks dedicated to quantifying carbon dioxide fluxes from various landscapes (Baldocchi et al., 1996). Commercial fast-response instruments are available for some compounds (e.g., CO_2, ozone, and isoprene), and others can be built for other chemical

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species (see references in Table 24.1). The eddy covariance method generally is preferred, but there are cases where other methods can be used. This includes measurements of compounds for which a fast response analyzer does not exist or is too expensive or difficult to maintain and operate. Alternative methods include eddy accumulation and gradient methods.

Eddy Accumulation. The eddy accumulation technique is based on eddy covariance and does not require any empirical factors (Desjardins, 1972). It is a valuable alternative to the standard eddy covariance method because it enables samples to be collected for later analysis using a wide variety of techniques including gas chromatography. Trace gases are collected into two reservoirs (corresponding to upward and downward airflow), and the volume rate at which the sample is collected is proportional to the vertical wind velocity. The flux then can be estimated from the difference in mass collected in each reservoir:

$$\text{Flux} = \overline{w'c'} = \frac{M_u - M_d}{2\kappa t} \tag{24.2}$$

where M_u is the mass collected into the up reservoir, M_d is the mass collected into the down reservoir, t is the time interval, and κ is a constant that is used to relate flow to w' such that

$$dV/dt = \kappa|w'| \tag{24.3}$$

where dV/dt is the flow rate and $|w'|$ is the absolute magnitude of the vertical wind speed. The trace gas concentration and vertical wind speed data shown in Fig. 24.2 illustrate the eddy accumulation technique. Based on the measured vertical wind speed, the trace gas is directed into the reservoir at rates ranging from 0 to about 4 μg/s.If we set κ at 2×10^{-5} m^{-2} then during the 70-s period shown in Fig. 24.2, the mass collected in the up reservoir (5.6 ng) is higher than that collected in the down reservoir (4 ng), and the flux calculated using Eq. (24.2) is about 1 μg/m^2 per second, which agrees with that calculated by eddy covariance using Eq. (24.1).

The major components of an eddy accumulation system are

1. An instrument that measures vertical wind speed with a fast response time.
2. A system that directs flow into the appropriate reservoir (separator).
3. A system to receive and store the wind data and control the separator (controller).
4. The storage reservoirs.
5. A system for analyzing the trace gases collected in the reservoirs.

If a measurement site has nonideal terrain, then it is possible that there is a significant mean offset in vertical wind velocity (i.e., the mean wind is not zero) that must be accounted for in real time. This can be accomplished at least partially by using a running mean or by characterizing the mean offset angles using data collected previously. There have been few attempts to apply the eddy accumulation method due to the difficulty of accurately separating the sample flow at a rate of 10 Hz. Periodic sampling, described below, is a useful method for bypassing these difficulties.

Periodic or Disjunct Sampling. Periodic sampling, also called *disjunct* or *intermittent sampling,* is a technique that enables a wider application of eddy covariance and eddy accumulation measurements by collecting a sample very quickly but not continuously. Rinne et al. (2000) describe a system that accomplishes this by quickly opening and then closing a valve attached to an evacuated cylinder. The sample is then proportionally directed into an up or down reservoir (for eddy accumulation) or analyzed directly (for eddy covariance).

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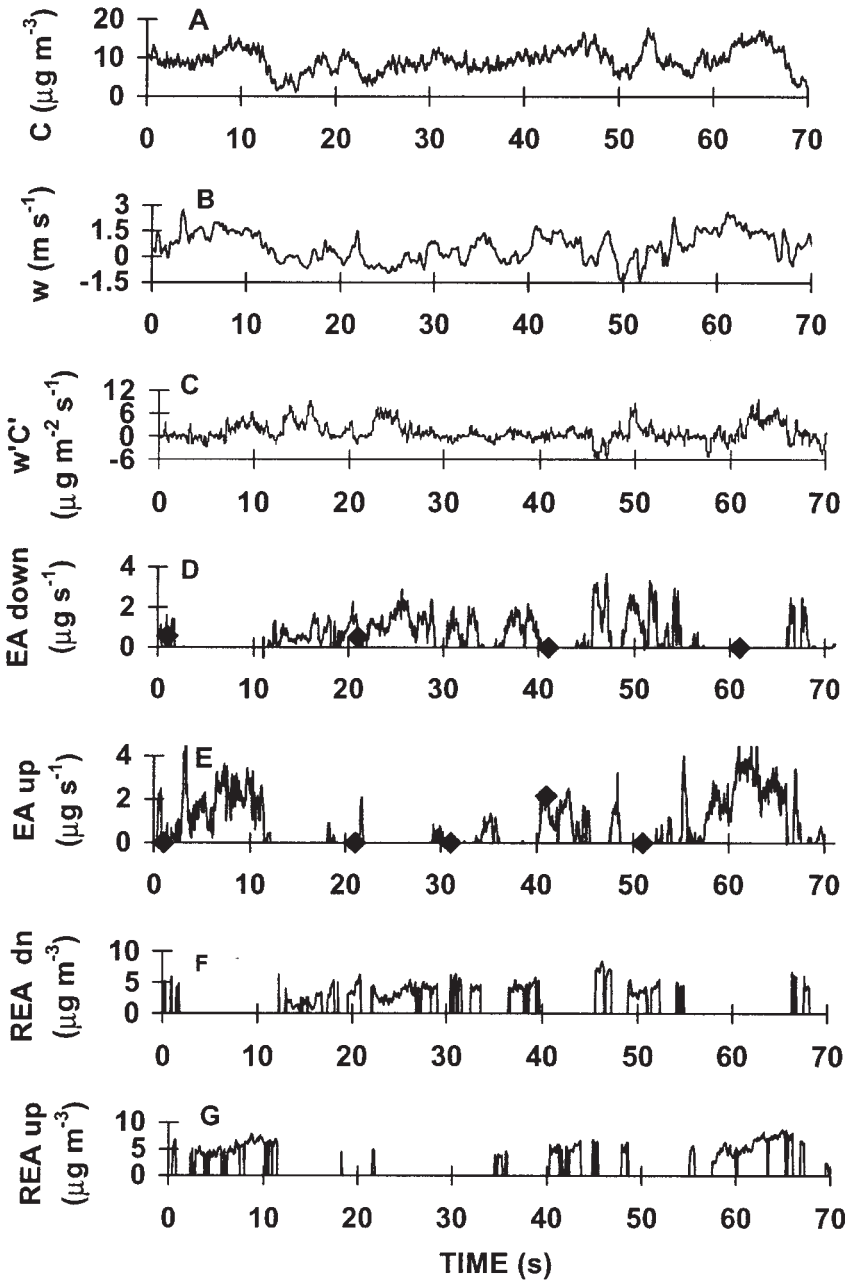

FIGURE 24.2 Fast-response measurements of trace gas concentration (*a*); vertical wind velocity (*b*); their application to eddy covariance (*c*); eddy accumulation (*d, e*); relaxed eddy accumulation (*f, g*); the points (filled diamonds) shown in *d* and *e* illustrate a periodic sampling strategy.

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With a cycling time of 20 s, a periodic sampler can provide 90 samples during a 30-minute period. This cycling time provides ample opportunity for accurately delivering a proportional sample into the appropriate eddy accumulator reservoir. Figure 24.2*d* and *e* gives an example of the sampling strategy used for eddy accumulation with periodic sampling. The solid line illustrates a nearly continuous measurement, whereas the points illustrate samples collected using the periodic sampling strategy. Rinne et al. (2000) have shown that periodic sampling can result in measurements that are nearly equivalent to continuous sampling.

Relaxed Eddy Accumulation (REA). Lenschow (1995) notes that we can express Eq. (24.2) in terms of concentration (mass per volume) as

$$\text{Flux} = (C_u - C_d)\,\frac{V}{\kappa t} \tag{24.4}$$

and Eq. (24.3) for the entire sampling period (so that the total volume collected, $2V$, is for both up and down reservoirs) as

$$2V/t = \kappa|\overline{w'}| \tag{24.5}$$

By combining Eqs. (24.4) and (24.5), we get

$$\text{Flux} = (C_u - C_d)\,0.5|\overline{w'}| \tag{24.6}$$

Businger and Oncley (1990) suggest that for a particular velocity distribution, |w′|bar can be estimated as

$$|\overline{w'}| = ß\sigma_w \tag{24.7}$$

where σ_w is the standard deviation of the vertical wind velocity and ß is a dimensionless proportionality constant. Their analysis of surface-layer field measurements indicates that ß is nearly constant, about 0.6, over a range of stability conditions. Combining Eqs. (24.6) and (24.7) allows us to calculate a flux as

$$\text{Flux} = ß\sigma_w\,(C_u - C_d) \tag{24.8}$$

Flux measurements based on Eq. (24.8) are referred to as *relaxed eddy accumulation* (REA, or *conditional sampling*). The major components of an REA system are (1) an instrument that measures vertical wind speed with a fast-response time, (2) a system that directs flow into the appropriate reservoir (separator), (3) a system to receive and store the wind data and control the separator (controller), (4) the storage reservoirs, and (5) a system for analyzing the trace gases collected in the reservoirs. A significant advantage of REA is that the flow is constant, which greatly simplifies the task of building a suitable separator and controller. One variant of the REA method is to only collect air during large updrafts and downdrafts. This has the advantage of increasing the concentration difference between the up and down samples. This generally decreases the analytical uncertainty associated with the resulting flux measurement. The disadvantage of this approach that it is then necessary to estimate a modified ß. This usually is accomplished by using fast response measurements of another scalar (e.g., temperature) for which the flux is known and then calculating the ß that is needed to generate that flux using Eq. (24.8). The threshold velocity, which determines whether the updraft/downdraft is sampled, can be selected to maximize the signal-to-noise ratio of $(C_u - C_d)$. Oncley et al. (1993) discuss the choice of this threshold velocity and conclude that a value of around $0.6\sigma_w$ is optimal.

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Gradient Flux. Trace gas fluxes in the turbulent boundary layer often are assumed to be proportional to the vertical concentration gradient (dC/dz). This relationship is expressed as

$$\text{Flux} = K\,(dC/dz) \tag{24.9}$$

and is considered analogous to molecular diffusion. This assumption appears to be reasonable in some, but not all, cases. It is less likely to result in accurate flux measurements at sites with complex terrain or when wind conditions are not steady.

The major components of a gradient flux system are (1) a system for collecting air samples, (2) a system for quantifying the trace gas(es) of interest, and (3) a method for estimating K. The analytical precision required for accurately characterizing dC is often a significant challenge, and it is frequently desirable to maximize dC by increasing the distance dz between sampling points, but the method becomes invalid if the distance is too large. There are a number of methods that have been used to estimate the eddy diffusivity coefficient K, including those described below.

Eddy Covariance Tracer. A straightforward approach to estimating K is to measure the gradient and flux using eddy covariance of a tracer and then assume that the compound of interest is transported in a similar manner. This is accomplished by rearranging Eq. (24.9) to

$$K = \text{flux}\,(dz/dC) \tag{24.10}$$

and using the measured tracer flux and gradient. It is often convenient to use temperature as the tracer because the flux and gradient can be measured relatively easily. The use of a gas for which fluxes can be measured directly, such as CO_2 or water vapor, is also possible. The best choice is to use a scalar that has a similar source distribution. It is generally assumed that K for the tracer is the same as that for the trace gas being investigated.

Profile Similarity. We can estimate the K in Eq. (24.9) using profile measurements of mean wind speed and temperature at two heights (Dyer and Hicks, 1970; Businger et al., 1971) and assuming that trace gases are transported in a manner similar to temperature. The thermal diffusivity is estimated as

$$K = [k^2 z^2 \Phi^{-2}]\, R_K\, (dU/dz) \tag{24.11}$$

where k is the von Karman's constant (approximately 0.4), z is height above ground level (or the zero-plane displacement for rough surfaces), dU/dz is the vertical gradient in mean wind speed, Φ is the stability function, and R_K is the ratio of the eddy diffusivities for temperature and momentum. R_K and Φ are estimated as a function of the Richardson number R_i:

$$R_i = \frac{g\,(dT/dz)}{T\,(dU/dz)} \tag{24.12}$$

where g is the acceleration due to gravity and $T(K)$ is virtual potential temperature. Dyer and Hicks (1970) empirically determined relationships for determining R_K and Φ that are dependent on stability conditions:
Unstable conditions ($R_i < 0$):

$$\Phi = (1 - 16R_i)^{0.25} \tag{24.13a}$$

$$\mathrm{R_K} = (1 - 16R_i)^{0.25} \tag{24.13b}$$

Stable conditions ($R_i > 0$):

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$$\Phi = (1 - 5.2R_i) \tag{24.13c}$$
$$R_K = 1 \tag{24.13d}$$

Neutral conditions ($R_i \simeq 0$):

$$\Phi = 1 \tag{24.13e}$$
$$R_K = 1 \tag{24.13f}$$

Surface Energy Balance. The surface energy balance equation (Stull, 1988) can be expressed as

$$R - G = L + H \tag{24.14}$$

where R is net radiation, G is soil heat flux, L is latent heat flux, and H is sensible heat flux. Combining Eqs. (24.9) and (24.14) results in

$$R - G = K\lambda\, dq/dz + KC_p\rho\, d\theta/dz \tag{24.15}$$

where dq is the difference in humidity and $d\theta$ is the difference in potential temperature at two heights and λ (= 2.44 J/kg at 300 K) is the latent heat of vaporization, C_p (= 1005.76 J/kg/K at 300 K) is the specific heat of dry air, and ρ (= 1.16 kg/m^3 at 300 K and 100 kPa) is the density of dry air. We can then rearrange Eq. (24.15) and solve for K as

$$K = \frac{R - G}{\lambda\, dq/dz + C_p\rho\, d\theta/dz}) \tag{24.16}$$

This method for estimating K requires measurements of net radiation, soil heat flux, and temperature and humidity at two heights. These measurements can be made with the meteorological sensors described in Chap. 19.

Convective Boundary Layer. Wyngaard and Brost (1984) proposed that the gradient flux method also could be used in the daytime convective boundary layer (CBL) that lies above the surface layer and can extend up to several kilometers. This method assumes that the mean vertical gradient of a scalar in the CBL is determined by the depth of the CBL z_i, the convective velocity scale w^*, and the fluxes at the bottom and the top of the CBL. If the flux at the top of the CBL is zero, then K can be defined as

$$K = \frac{z_i w^*}{g_b} \tag{24.17}$$

where g_b is a dimensionless variable that is a function of height within the CBL. The convective velocity scale is defined as

$$w^* = \left(\frac{gHz_i}{T}\right)^{1/3} \tag{24.18}$$

Methods for estimating z_i are given in Chap. 19. Concentration gradients in the CBL can be measured using tethered-balloon or aircraft sampling systems. Moeng and Wyngaard (1989) used the results of a large eddy simulation model to relate g_b to height z within the CBL as

$$g_b = 0.4\,(z/z_i)^{-3/2} \tag{24.19}$$

The CBL gradient-flux technique assumes that boundary layer mixing is dominated by convective turbulence and that boundary layer conditions evolve slowly compared with the convective turnover time of about 10 minutes. The results are not affected by vertically

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homogeneous horizontal advection or time dependence in the mean mixing ratio, and the method can account for entrainment. In principle, this technique has reasonable assumptions. In practice, it is often the case that the boundary layer that is not well mixed, usually due to cloud activity, and the assumptions are not valid (see Davis et al., 1994; Guenther et al., 1996a). The most likely violations of the mixed-layer assumptions are vertically varying horizontal advection caused by heterogeneity in surface fluxes on the scale of one to a few kilometers and irregular mixing caused by extensive convective cloud activity.

The footprint associated with this flux estimation method is on the order of 10 km^2, which is considerably larger than the footprint of tower-based surface layer measurement techniques. This enables integration over a larger sample size and often may be complementary to other measurement techniques.

Variance. Surface fluxes also can be estimated from the measured variance in trace gas concentration (Wesely, 1988). Lenschow (1995) derives the relationships used for this relationship in the surface layer as

$$Flux = \sigma_C u^* \Phi \tag{24.20}$$

and in the lower part of the CBL as

$$Flux = 0.77 \sigma_C w^* (z/z_i)^{1/3} \tag{24.21}$$

where σ_C is the square root of the variance. Since this is an indirect technique but has the same requirements for fast-response chemical sensors as does eddy covariance, it is an attractive option primarily for cases where a fast-response sensor is available but it would difficult to obtain corresponding vertical wind velocity measurements. This might be the case for measurements made on an aircraft or a tall mast.

Mass Balance Methods

Trace gas fluxes also can be characterized by quantifying all the processes that influence the concentration within a spatial domain. This can be expressed as

$$dC/dt + U + \text{flux} + S = 0 \tag{24.22}$$

where the four terms are

1. *dt,* the time rate of change within the system
2. U, the change due to transport into and out of the system
3. Flux, exchange between the air and other components of the system
4. S, chemical loss and production within the system

Fluxes are estimated by rearranging Eq. (24.22)

$$\text{Flux} = dC/dt + U + S \tag{24.23}$$

This technique is also called the *budget method.* Our domain of interest can be bounded by physical walls (the enclosure approach), by atmospheric features (the boundary layer approach), or may include the entire earth system (global budget approach). These methods are described below, and examples are given in Table 24.2.

Enclosure Approach. Enclosure techniques rely on the use of a physical barrier to separate the studied system from its surroundings. Enclosures can be existing structures, such

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TABLE 24.2 Mass Balance (MB) and Tracer Ratio (TR) Studies

Method	Compounds/source	Reference
Soil core MB	Pesticides from a field	Majewski et al. (1993)
Convective boundary layer MB	Isoprene from a forest	Guenther et al. (1996a,b,c)
Enclosure MB	Isoprene from a forest	Guenther et al. (1996a,b,c)
Global MB	Global acetone	Singh et al. (1994)
Global MB	Global ethane	Rudolph (1984)
Artificial TR	Fume hood exhaust	Lamb and Cronn (1986)
Artificial TR	Regional urban emissions	Lamb et al. (1978)
Artificial TR	Industrial site	Guenther et al. (1990)
Artificial TR	Natural gas production	Lamb et al. (1995)
Natural TR	Biomass burning	Greenberg et al. (1984)

as a building, or a device designed for the purpose of making the measurement. Enclosure shapes, sizes, and materials of construction can vary greatly depending on the focus of the investigation. The enclosure typically is sized such that it is only slightly larger than the emission source. It should be constructed of materials that will not react with the trace gas being investigated. It is also important that the materials are not a source (from outgassing) of the trace gas or of any compounds that might interfere with the analysis. A stainless steel frame covered with 5-mm Teflon film is a good choice for many applications. Additional details on enclosure methods are given by Livingston and Hutchinson (1995).

An important consideration in the design of an enclosure system is minimizing deviations from ambient conditions. For example, if solar radiation can influence the emission source, then the enclosure must be designed to allow a reasonable level of solar radiation to reach the source. An enclosure can be static (no air exchange) or dynamic (air is exchanged with the outside environment). Dynamic systems generally are favored because they minimize deviations from the ambient conditions (e.g., humidity, temperature, and trace gas concentrations) that influence the source.

If the lifetime of the measured trace gas is much longer than the residence time (for dynamic systems) or the measurement time (for static systems), then the term S in Eq. (24.23) can be neglected. A dynamic system with a sufficient flow rate has a very small concentration change with time. This allows us to eliminate the term dC/dt in Eq. (24.23). If there are no chemical sources or sinks within the enclosure, then the remaining term can be estimated as

$$U = \frac{C_o - C_I}{f} \tag{24.24}$$

where C_O and C_I are the concentrations at the outlet and inlet airstreams of the enclosure and f is the flow rate into the enclosure. With a static enclosure system, we eliminate the term U in Eq. (24.23). The resulting term needed to estimate emissions using Eq. (24.23) if there are no chemical sources or sinks is

$$dC/dt = \frac{C_2 - C_1}{t} \tag{24.25}$$

where C_2 and C_1 are the concentrations measured at the end and beginning of the measurement period and t is the length of the measurement period. It is often desirable to make measurements at several times and then determine dC/dt from a linear fit to concentration

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versus time. For both static and dynamic enclosures, the flux typically is normalized by the quantity (e.g., area or mass) of the source in the enclosure. Successful enclosure measurements depend on having analytical precision and accuracy that are sufficient for characterizing the concentration difference. A major advantage of the static enclosure method is that the concentration differences often are much larger.

It is important to ensure that trace gas concentrations are well mixed in the enclosure. This can be accomplished in a dynamic enclosure with a sufficiently high flow rate relative to the enclosure volume. In other cases, a fan or a paddle can be used to ensure mixing.

There are several potentially useful options to consider when developing an enclosure system. An environmental control system allows the manipulation of environmental conditions. Another consideration is the possibility of automating the system in order to characterize emission variations with time. Portability and cost are important considerations as well.

Boundary Layer Approach. The atmospheric boundary layer provides a convenient natural system that can be used to measure fluxes by the mass balance method. Both the daytime CBL and the nighttime nocturnal boundary layer (NBL) can be used. The importance of each of the four terms depends on the lifetime and the emission pattern of the trace gas being investigated. Guenther et al. (1996a,1996b) used CBL measurements to estimate regional emissions of isoprene, a trace gas with a midday lifetime of about an hour. They observed very little change in mean CBL concentration with time [that is, dC/dt in Eq. (24.23) was negligible], and they assumed that their measurement site was reasonably homogeneous [so that U in Eq. (24.23) is also negligible]. The remaining term in Eq. (24.23), the chemical loss rate of isoprene in CBL, was strongly dependent on the concentration of OH, which is commonly the most important trace gas remover in the CBL. Models can be used to estimate OH to within a factor of 2 or 3, but it is difficult to measure OH directly. The footprint of this flux estimate is about equal to the lifetime of the trace gas and the mean horizontal wind speed. With a wind speed of 5 m/s, the footprint for a gas with a lifetime of 1 hour is about 18 km. The boundary layer approach also can be used for long-lived gases. In this case, the term S in Eq. (24.23) is usually negligible, and the flux will be determined by measurements of dC/dt and U.

Global Budget Approach. For most gases, the entire earth system can be considered a closed system, and we can neglect the term U in Eq. (24.23). Global average fluxes are estimated from the global average time rate of change dC/dt and the global average chemical production and loss S. This method can be applied to long-lived gases because these compounds are relatively well mixed, which makes it easier to estimate the global average from a limited data set. The application of this method usually is limited to compounds for which chemical production and loss are relatively easy to characterize.

Tracer Ratio Methods. The tracer ratio technique uses a tracer gas for which a flux and concentration are reasonably well known to estimate the flux of a target gas for which the concentration is known. This is expressed as

$$\text{Flux} = F_t\,(\Delta C/\Delta C_t) \tag{24.26}$$

where F_t is the flux of the tracer compound and ΔC_t and ΔC are the difference between the downwind and background concentration of the tracer and target gases, respectively. The tracer and target gases must have similar source distributions and be transported through the atmosphere in a similar manner. When multiple gases are emitted from a single source, we often can use our knowledge of the emissions of one gas to characterize the emissions of another. In other cases, the emission source is simulated with an artificial tracer. The major advantage of this method is that no meteorological measurements or dispersion modeling is required. Examples of studies applying these methods are given in Table 24.2.

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TRACE GAS EMISSION MEASUREMENTS

CASE STUDIES

Isoprene from a Forest Canopy: Micrometeorological and Mass Balance Methods

Isoprene (C_5H_8) is a reactive trace gas that is produced by vegetation in large quantities and emitted into the atmosphere. Isoprene emissions have received considerable attention due to the important role of isoprene in determining the chemical composition of the atmosphere. The factors controlling isoprene operate on a variety of spatial and time scales and are further complicated by the large variability in emissions observed for different plant species. Thus accurate isoprene emission estimates require studies that employ a variety of emission measurement techniques.

Eight different flux measurement techniques were used by Guenther et al. (1996b) to investigate isoprene emissions from a forest near Oak Ridge, Tennessee, in the summer of 1992. This included four different enclosure systems that provided emission estimates for individual leaves and branches that, combined with regional forest distribution data, were used to estimate fluxes over scales ranging from 30 m^2 to over 6000 km^2. Two surface-layer flux systems (a relaxed eddy accumulator and a flux-gradient technique) were deployed above the forest canopy, with a mean height of about 26 m, on a 44-m walkup tower to measure fluxes over a region of about 1 km^2. A tethered-balloon sampling system was used to obtain the concentration measurements needed for the CBL gradient and CBL mass balance flux estimation methods that characterize emissions over regions of about 30 and 700 km^2, respectively. All eight techniques used concentration measurements that were determined by gas chromatography using either a flame ionization detector or a reduction gas detector.

The enclosure systems were used to investigate fluxes from individual leaves and branches. The four types included (1) a portable leaf enclosure with environmental control, (2) a portable leaf enclosure with no environmental control, (3) a tower-mounted branch enclosure for investigating branches at different canopy depths, and (4) a tripod-mounted branch enclosure for investigating lower branches of various tree species throughout the region. The leaf enclosure with environmental control system consisted of a commercial open-path gas exchange system (MPH 1000, Campbell Scientific, Logan, UT) that provided control of temperature, light intensity, water vapor, and CO_2 concentration within the enclosure. The other enclosures were relatively simple systems manufactured out of machined Teflon for the leaf enclosure and a Teflon-film-covered stainless steel support frame for the branch enclosure.

Samples of air exiting the enclosures were collected into glass syringes or evacuated Suma-deactivated stainless steel canisters and analyzed with a gas chromatograph. Isoprene emission rates $E(\mu g\ C\ g^{-1}\ h^{-1})$ for individual leaves and branches were calculated using Eq. (24.23). All the enclosure systems were tested prior to the study to demonstrate that there was no loss or production of isoprene in the enclosure, which meant that the term S in Eq. (24.23) was negligible. Since these were dynamic (flow-through) systems, the term dC/dT in Eq. (24.23) also was negligible. Fluxes were calculated by estimating the remaining term in Eq. (24.23) as

$$U = f(C_o - C_i)\, b^{-1} \tag{24.27}$$

where f is the flow rate (m^3/h) into the enclosure, C_o is the isoprene concentration ($\mu g/m^3$) of the outlet airstream, C_i is the isoprene concentration ($\mu g/m^3$) of the inlet airstream, and b is the foliar mass (g dry weight) within the enclosure.

Isoprene fluxes in the surface layer above the forest canopy were measured by relaxed eddy accumulation and gradient profile methods. Thirty-minute average isoprene fluxes were estimated using Eq. (24.9) with the concentration gradients and eddy diffusivity estimates obtained with the gradient profile system. Whole-air samples were collected on the

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walkup tower at heights of 28.8, 32.3, and 38 m above ground level (AGL). Concentration gradients were estimated by a least-squares best fit. In some cases, concentrations were determined only at heights of 28.8 and 38 m. Samples were collected by pushing air with a Teflon diaphragm pump (KNF Neuberger, Princeton, NJ) through 40-m Teflon lines and into evacuated 15-liter Teflon bags located at the bottom of the tower. No significant difference in isoprene concentration was observed when air samples were pulled directly into Teflon bags placed on the tower at the 28.8- and 38-m heights instead of sampling through the Teflon lines. The gradient-flux estimates were calculated using Eq. (24.10) and assuming similarity between water vapor fluxes and isoprene fluxes. A lagrangian micrometeorological model was used to demonstrate that eddy diffusivities based on water vapor provide better results for isoprene flux estimates than eddy diffusivities based on CO_2, wind speed, or temperature. Water vapor was expected to be more representative of isoprene fluxes because both are unidirectional gas fluxes, whereas the CO_2 flux contains both a strong emission (from soils) and deposition (into the canopy) component.

The relaxed eddy accumulation system consisted of a three-dimensional (3D) sonic anemometer (Applied Technology, Inc., SWS/3K, Boulder, CO), a separator that included a Teflon diaphragm pump (KNF Neuberger, Princeton, NJ) and three-port Teflon isolatch valves (General Valve Co., Fairfield, NJ), and a controller that included a computer and control program and a custom-designed pump control and valve control board. The pump control system provided a constant airflow through the REA system. Air was pulled into the pump through Teflon tubing (3 m in length, 0.318 cm in diameter) and immediately directed through valves into either a vent line or one of two Teflon lines (40 m in length, 0.635 cm in diameter) leading to two 15-liter evacuated Teflon bags located at the base of the tower. The three-port valves were switched at a maximum rate of 10 Hz to direct samples into the appropriate Teflon bag. The time required for input air to reach the three-port valves was matched to the processing time of the sonic anemometer, computer, and valve control board. After an approximately half-hour sampling period, air samples in the Teflon bags were analyzed with the gas chromatography system. The REA system was deployed at a height of 30.5 m AGL on the walkup tower. A 4-minute running mean for vertical wind speed w_0 (m/s) and standard deviation of vertical wind velocity σ_w (m/s) were calculated in real time and used to calculate the vertical wind speed threshold w_T, which was set equal to 0.5 $\sigma_w \pm w_0$. Estimates of ß were calculated by assuming similarity between isoprene and sensible heat fluxes (i.e., eddy covariance estimates of sensible heat flux and the mean temperatures associated with updrafts and downdrafts were used to estimate ß.)

Isoprene fluxes estimated by the CBL mass balance approach were calculated using Eq. (24.23). The terms dC/dT and U were negligible, and the remaining term was calculated as

$$S = z_i C_m \tau^{-1} \tag{24.28}$$

where z_i is the mixed-layer height (m AGL) τ is the estimated lifetime of isoprene(s), and C_m (mg carbon per cubic meter) is the mean mixed-layer isoprene concentration. Estimates of z_i were obtained using airsondes (AIR, Boulder, CO) that measured temperature and humidity profiles up to heights of 5 km AGL. The mixed-layer height was identified by an inversion layer that appears as a region of increasing potential temperature with height. The lifetime of isoprene τ was estimated using the OH and ozone reaction rate coefficients reported by Atkinson (1990), the measured O_3 concentration, the OH diurnal variation described by Lu and Khalil (1991), and a maximum OH concentration of 4×10^6 molecules per cubic centimeter (Guenther et al., 1996a).

Fluxes estimated by the CBL gradient-flux technique were based on Eqs. (24.9) and (24.17). A major advantage of this technique is that it does not depend directly on estimates of OH concentrations.

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Pesticide Emissions from Fallow Soil: Micrometeorological and Mass Balance Methods

Measurements of pesticide volatilization rates are needed to characterize the impact of this activity on air quality and to investigate potential methods of controlling these emissions. Majewski et al. (1993) used a mass balance method and two micrometeorological methods to characterize the emission of volatilizing pesticides (triallate and trifluralin) that had been applied recently to soil in a fallow field. The same analytical method, gas chromatography with an electron capture detector (GC-ECD), was used for all flux methods. A summary of the experiment is given here, and the reader is referred to Majewski et al. (1993) for additional details.

The mass balance flux estimate was made by measuring the decrease in the mass of pesticide in the soil at 12-hour intervals. The loss of pesticide was assumed to be equal to the decreased mass. This assumption is valid only if there is no chemical transformation in the soil and there is no transport out of the soil through groundwater. Soil samples were placed in clean glass jars with Teflon-lined lids and stored at −20°C. Samples were then thawed under low light and room temperature for at least 2 hours. The moisture content was brought to about 10 percent by adding distilled water and mixing. A 100-ml aliquot of a hexane-2-propanol (3:1) mixture was used to extract the pesticides from the soil.

The two micrometeorological methods were relaxed eddy accumulation and gradient flux with profile similarity. The REA flux measurements were based on the GC-ECD analysis of pesticide concentrations in the up and down reservoirs collected by the REA system. Analysis of fast-response wind, water vapor, and temperature data indicated that ß, needed to calculate the REA fluxes using Eq. (24.8), was nearly constant and equal to 0.59. However, since the REA used for this study had a relatively slow response, a modified ß was calculated using measured latent heat fluxes and the assumption of similar behavior of the pesticides and water. The gradient-flux estimates were determined using Eq. (24.9) with K determined from measurements of mean wind speed and temperature at two heights using a modified form of Eq. (24.11). The REA was positioned at a height of 1.75 m, whereas the gradient-flux measurements were made at heights of 0.5 and 1 m. The three flux measurement methods agreed within about 13 to 27 percent. Because the gradients could be measured very near the source (within 1 m), the concentration differences of the vertical gradient tended to be greater (and therefore with less analytical uncertainty) than for the REA system.

Global Ethane Emissions: Mass Balance

Rudolph (1995) combined estimates of the global loss rate and average concentration of ethane to estimate global annual emissions of this compound. About 1500 measurements of ethane in the remote troposphere were compiled into a database and used to derive a global annual average mixing ratio of 860 ppt. There were large differences between the mean southern (384 ppt) and northern (1330 ppt) hemisphere mixing ratios and considerable variability in the northern hemisphere (near to sources). The global average flux was calculated using a form of Eq. (24.23) where the dC/dT term was considered negligible. The term U in Eq. (24.23) was calculated from an estimate of the troposphere to stratosphere exchange rate (0.8 per year) and the mean ethane concentrations in the troposphere and stratosphere. The only known significant removal process for tropospheric ethane is reaction with OH radicals, so the term S was estimated from global and seasonal databases of ethane and OH concentrations and reported rate constants (see Atkinson, 1990).

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Methane Emissions from Natural Gas Facilities and Urban Areas: Tracer-Ratio Methods

The characterization of methane emissions from natural gas facilities is of interest because of the role of methane as an atmospheric greenhouse gas and because these emissions can be a significant financial loss for gas producers. Lamb et al. (1995) used three tracer-ratio methods to locate leaks and quantify methane emission rates from (1) isolated sources, (2) enclosed sources, and (3) area sources. Each method involved the use of an artificial tracer gas, sulfur hexaflouride (SF_6). The SF_6 tracer was released from gas cylinders through a regulator, and the emission rate was measured using a calibrated mass flowmeter. Methane and SF_6 was analyzed both by collecting samples in stainless steel canisters, for later GC analysis, and by using real-time nearly continuous analyzers. The real-time analyzers provided an excellent means of determining if there were interfering sources in the area and for ensuring that the methane and SF_6 plumes were collocated.

Carbon Monoxide Emissions from Biomass Burning: Tracer Ratio

Regional and global trace gas emissions from biomass burning have been estimated using the reported estimates of CO_2 emissions from this source as a natural tracer. For example, Greenberg et al. (1984) measured concentrations of CO_2, CO, and hydrocarbons upwind and downwind of biomass burning regions in Brazil. They combined these measurements with reported global estimates of CO_2 emissions from biomass burning and used Eq. (24.26) to estimate fluxes of CO and hydrocarbons.

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P • A • R • T • 4

DATA ANALYSIS

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CHAPTER 25
INTRODUCTION TO DATA ANALYSIS

Frank R. Burden

VISUALIZATION

The preceding chapters have discussed a wide range of environmental measurements and have presented the data in a variety of ways. The following two chapters describe some methods for reducing the dimensionality of the data, extracting maximum information, and dealing with time series. This chapter discusses the very first stages of evaluating the data by means of graphical techniques. This is the most important part of any data analysis, for it gives the initial guide as to the form and direction for the interpretation of the data, so it is worth the time spent on it even if the tools to be used in the final analysis are already determined.

There is no correct manner by which the data should be presented, although the primary goal must be to extract the maximum amount of useful knowledge from the data and to make them readily available to any interested party. This is commonly done by way of formulas, tables, graphs, and maps. A formula usually implies that there is a known fundamental relationship underlying the data, and this is often deduced from primary physical laws, although it also may be the result of result an empirical model. A formula represents an end result, whereas the initial task is often to collate a large amount of primary data into digestible chunks prior to analysis.

The routine, and often automatic, unattended collection of environmental data can result in a very large amount of information that needs to be analyzed. If the structure of the data is already well known, then a proceed-as-before is the obvious step. However, where the data are from a new source or pursuant to a new problem and are to be analyzed for the first time, then the first step should be to chart or graph the data. This step is often the most important because the human eye is (at least within the radius of 4 light years) the most sophisticated pattern matching and recognition device known. Furthermore, when attached to a brain already trained to analyze the problem at hand, it is largely unbeatable. Number crunching is another matter, and for that, computers have been invented to *assist.* This can be easier said than done for multivariate data, where there may be a large number of variables to be considered. So where to start?

If the data have been collected into a spreadsheet, such as Microsoft Excel, well and good; otherwise, it is a good idea to import the data into such a spreadsheet. Spreadsheets usually provide a few simple routines that can be used to try to get an immediate look and feel for the data. It may be that there are reasons for suspecting some relationships between the variables a priori (e.g., if the $[Na^+]$ increases, then the $[Cl^-]$ is expected to do likewise); however, it should be checked.

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INTRODUCTION TO DATA ANALYSIS

PRELIMINARY GRAPHIC ANALYSIS

One of the first steps in analyzing new data is to examine the mean and variance. This can be done by way of tables, and most statistical software packages provide an abundance of measures. Figure 25.1 shows the basic statistical choices from WinStat.

Many of the these measures can be displayed visually using box and whisker plots, as in Fig. 25.2, where the mean, standard deviation, and standard error are shown in a compact manner for a six-variable data set. This can be a good start in showing whether the data are generally skewed or evenly distributed. This is a useful exercise because the variables may need to be scaled before further analysis, and the box and whisker plot helps to put the variables in a magnitude-based relationship with one another. Of course, if some variables are on widely differing scales, e.g., temperature and hydrogen ion concentration, then scaling, e.g., by using the pH, may have to be carried out before graphing.

Spreadsheets usually have a limited number and type of graphing functions, and these are mainly two-dimensional with some three-dimensional functionality. The main types are linear, scatter, pie, bar plots, and histograms, the main differences between linear and scatter plots being that the linear plot relies on a monotonically increasing independent (x) variable. Time-series analysis is covered in Chap. 27, and it will be assumed here that scatter plots are the immediate choice because they will work whether or not the data are monotonic in x. It would be prudent, then, to plot each variable against every other variable, although recourse to the spreadsheet correlation will show up any highly correlated variables that might prove fruitful to plot first in the expectation of finding a linear relationship.

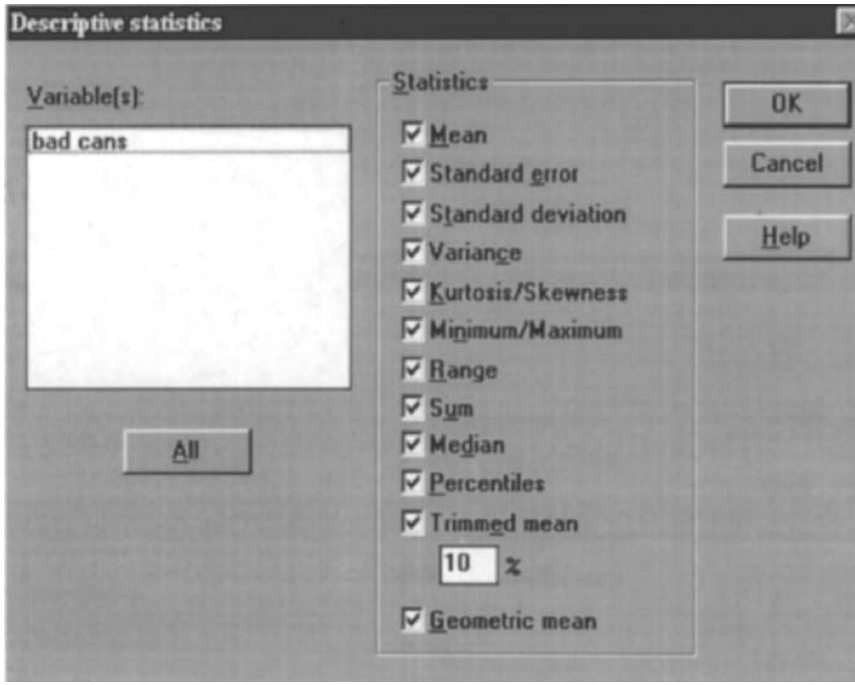

FIGURE 25.1 Winstat menu for descriptive statistics.

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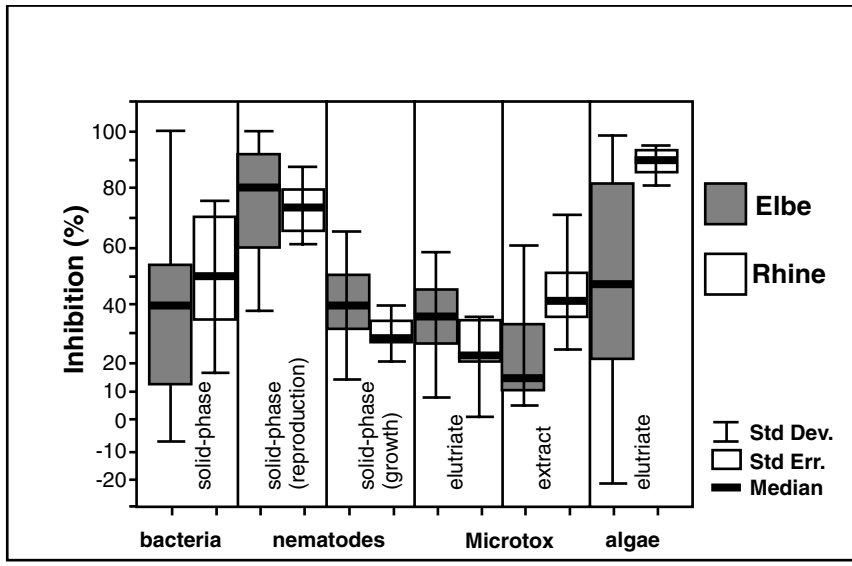

FIGURE 25.2 Box and whisker plot.

This is getting ahead of ourselves because there are many other relationships between data besides the linear, and the human eye often will discern them far more quickly than any computer algorithm. Figure 25.3 illustrates this.

What are not shown in this figure are any outliers, and these need to be identified early on so that time is not wasted in carrying out an analysis that is heavily biased. The actual decision to eliminate outliers is not straightforward and needs to be done on strictly statistical grounds. On the other hand, a graph often will show up outliers that have been caused by simple error of transcription or taken at a time when the experimental conditions are known to be imperfect or the equipment malfunctioned. The identification of such outliers still leaves a problem to be solved, but at least it can be accounted for early on in the analysis.

The eye can pick up more complex patterns than those illustrated, and often these can help in deciding the relevant direction of future analysis. These may include linear or nonlinear regression and cluster analysis, and such analyses are addressed in Chap. 26. Since the graphs here are for illustrative purposes only, the units, scales, and legends have been omitted for clarity of presentation, although these are essential when graphs are presented for real purposes.

It is sometimes useful to present as many variables as possible within the one diagram to allow the eye to use its full potential. For multiway data plots such as the four-way plot illustrated in Fig. 25.4, it can become immediately obvious that there are relationships (and/or correlations) between the variables 1, 2 and 1, 4. The matrix of plots is symmetric, so that the plot of variable 1 versus variable 2 gives a slightly different perspective to variable 2 versus variable 1. A further illustration is given in Fig. 26.1 in the next chapter.

The importance of a data point can be related to its distance from the origin and may give rise to leverage effects. Compass plots, as in Fig. 25.5, show this in a clear manner, and they are used often to determine the importance of the primary variables after reducing the data via principal components analysis (PCA; see Chap. 26).

All graphs that are presented in previous and future figures are on a two-dimensional surface (paper), but with the aid of perspective and/or coloring, (gray shaded here), the

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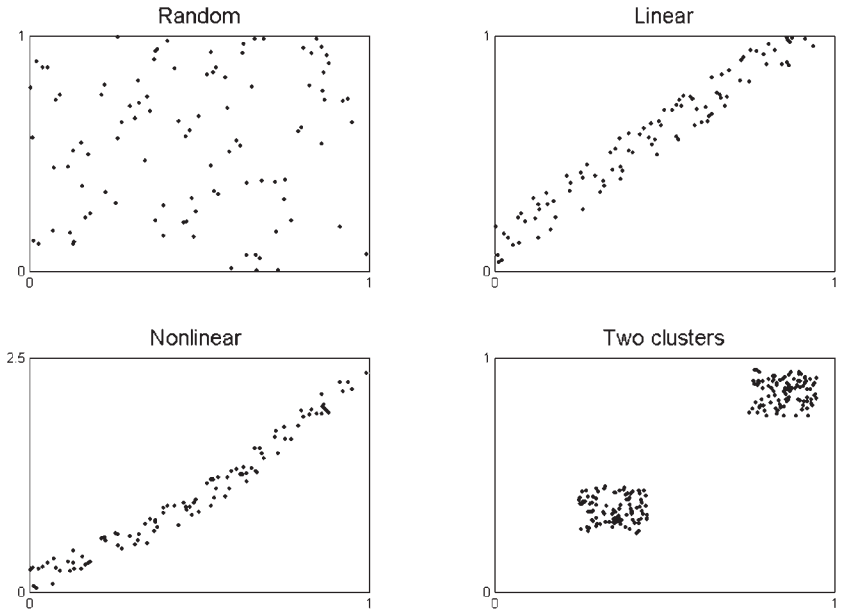

FIGURE 25.3 Scatter plots.

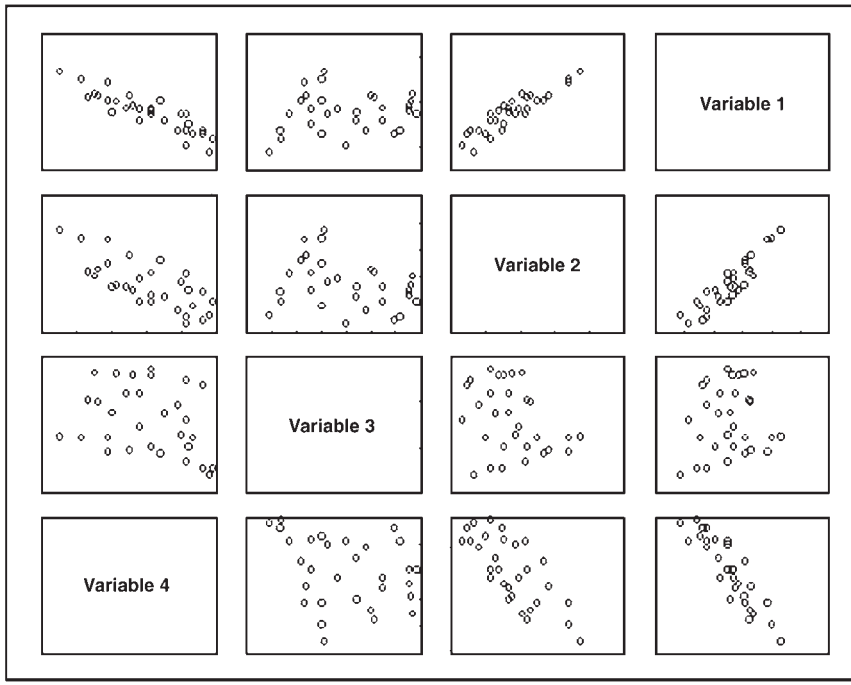

FIGURE 25.4 Multiway plots.

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eye can be persuaded to accept three- and four-dimensional objects, as shown in Fig. 25.6. These diagrams give the immediate impression of four centers with data distributed about them in a normal manner.

Three-dimensional data can be viewed from an infinite number of perspectives, and what may appear obvious in one perspective may not in another. Spreadsheets are useful tools for much of the preliminary data handling and graphing, but they have their limitations. There are many other more specialized packages available that are directed at scientific data analysis and which provide a range of graphing formats as well as data analyses. Rather than suggest one software package to cover the multitude of data presented in preceding chapters, it is suggested that demonstration versions be obtained or that the package in action be observed in another laboratory before purchase. The packages have their strengths and weaknesses, and it is important to obtain one that is well suited to the job at hand. Figures 25.7 through 25.9 show some data viewed from various perspectives and thus show different features of the data. A circle becomes a spiral or even several clusters of data; finding the best perspective gives deeper meaning to the data structure. Some packages allow for dynamic rotation of data about the three cartesian axes. This facility can be most useful in quickly showing any features of the data that need to be considered in analysis and should be investigated prior to purchasing software.

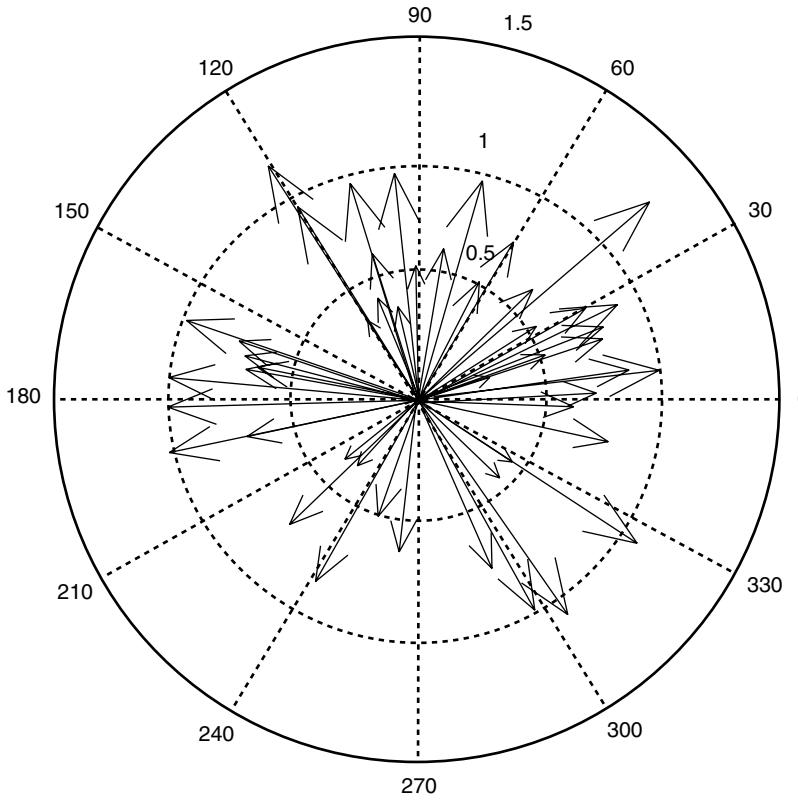

FIGURE 25.5 Compass plot.

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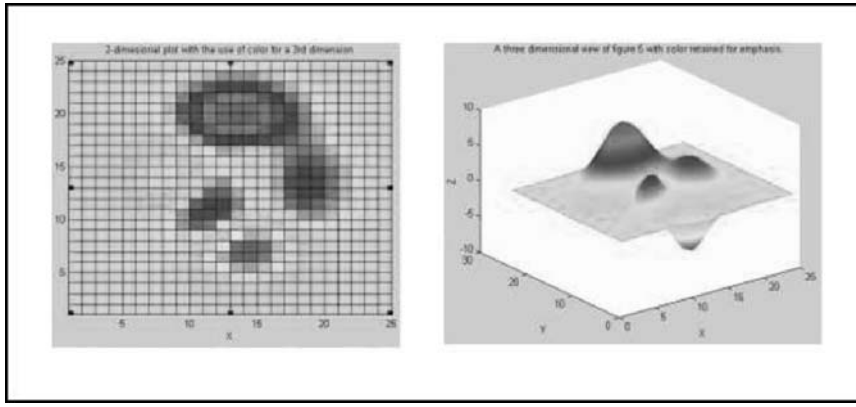

FIGURE 25.6 Three-dimensional representations.

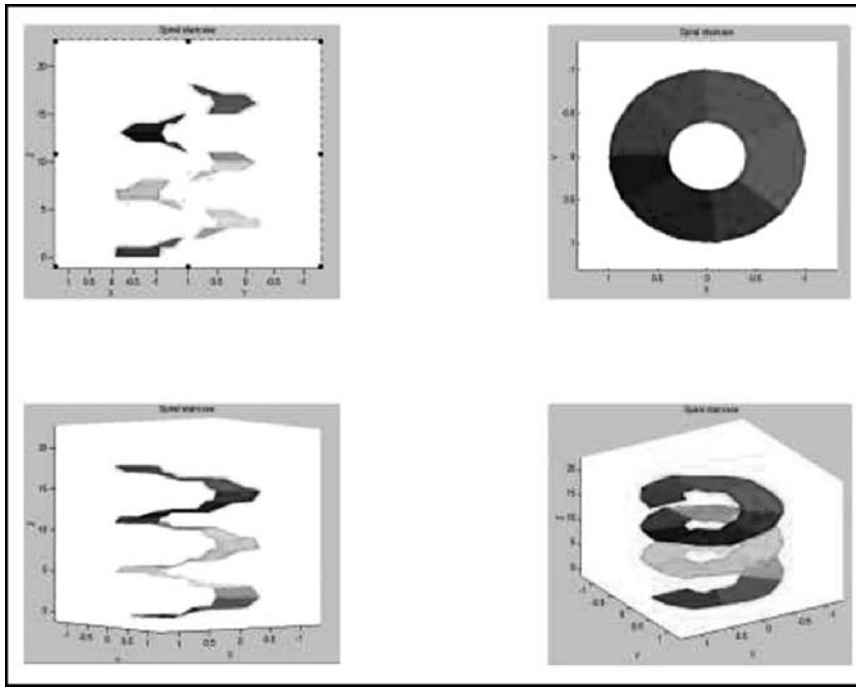

FIGURE 25.7 Three-dimensional perspectives.

DATA PROCESSING

Raw data are not always the most suitable form for graphing, especially if the recording instrument has incorporated some data transforms. This often can be the case, such as measuring pH rather than the molar concentration (or activity) of the hydrogen ion or making

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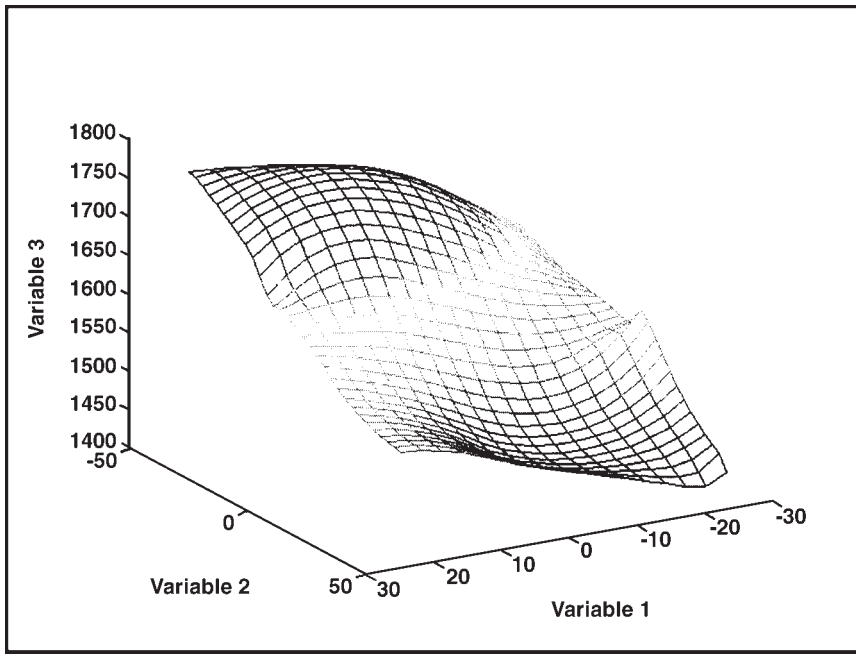

FIGURE 25.8 Surface plot.

the assumption of the applicability of Beer's law that concentrations are proportional to absorbances in spectroscopic measurements. These hidden transforms need to be made explicit before engaging in detailed data analysis. Figure 25.10 shows a plot from some environment of $[Cl^-]$ versus $[H^+]$ and versus $\log_{10}[H^+]$ (i.e., $-$pH). The difference is clear but can be missed without a data plot.

Whether or not hidden transforms have been made, it is necessary to consider if it is sensible to transform the data before engaging in data analysis. Such transforms may arise from knowledge of the process under investigation, a common one being where the process is exponential in a variable such as a reaction or equilibration processes. Of course, this can be partly verified by making some initial plots of the raw data and of the transformed data. These topics are discussed in Chap. 26 but may need to be considered when making preliminary plots of the data. Environmental data are often noisy, and this noise can obscure trends both in time and in other variables, and the topic of smoothing data prior to analysis is treated in Chaps. 26 and 27.

CONCLUSION

Data need to be subjected to as much visual scrutiny as possible before numerical data analysis is carried out. Quantification of the relationships between data should follow a qualitative assessment of possible relationships and the removal of outliers, especially those caused by incorrect data input or erroneous experimental procedures.

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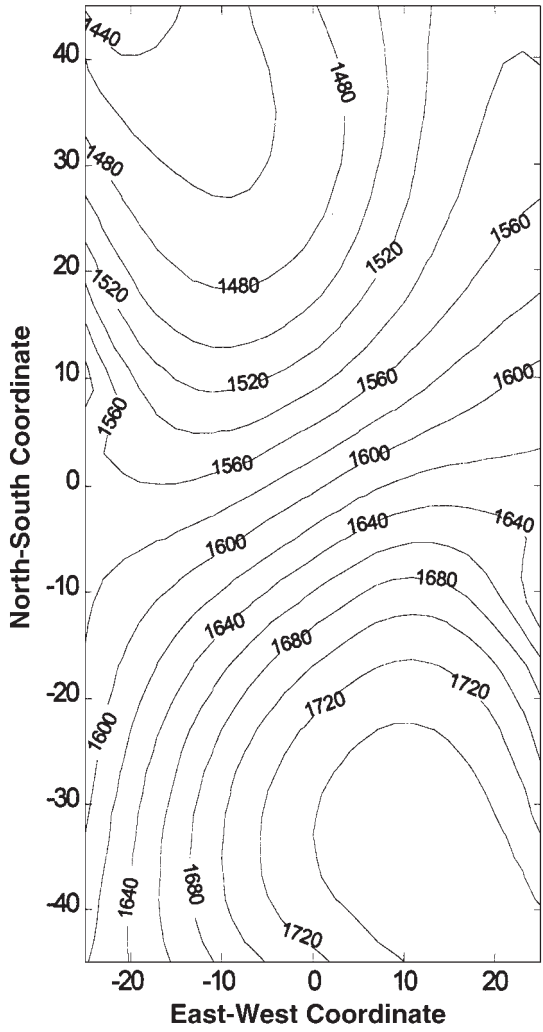

FIGURE 25.9 Contour plot.

SOFTWARE FOR ENVIRONMENTAL DATA ANALYSIS

Since there is an enormous variety of data that can be produced under the heading of environmental monitoring, it is impossible to recommend software that can satisfy all needs. However, there are some very powerful general-purpose packages that should be considered when contemplating environmental data analysis. The software mentioned here is for the Intel/Windows platform, although many are replicated on the Macintosh platform and some are available for Linux.

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INTRODUCTION TO DATA ANALYSIS

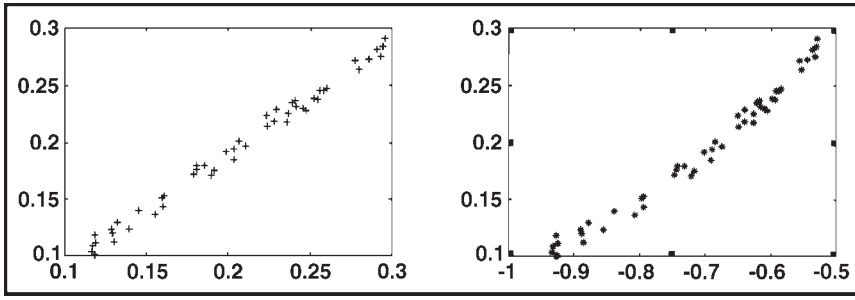

FIGURE 25.10 Hidden transformation effect.

TABLE 25.1 A Selection of General-Purpose Plotting Software Packages

Systat	*http://www.spssscience.com/systat*
SPSS and SigmaPlot	*http://www.spssscience.com/sigmaplot*
PLOTCHEM	*http://www.scisoftware.com*
Axum	*http://www.mathsoft.com*
Origin	*http://www.microcal.com*
DeltaGraph	*http://www.deltapoint.com*

The primary tool for collating and undertaking primary analysis is usually a spreadsheet. The most common spreadsheet is perhaps Microsoft Excel, although many graphing programs have their own embedded, though less powerful, spreadsheets. Beyond Excel, a number of readily available graphing/analysis packages are included in Table 25.1.

Reviews of these and other packages can be found at *http://www.umass.edu/microbio/sciplot/#packages.* Typing *plotting software* into a Web search engine such as Google will produce a wide variety of responses, and an advanced search can narrow this down for particular purposes.

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Source: ENVIRONMENTAL MONITORING HANDBOOK

CHAPTER 26
CHEMOMETRIC TOOLS AND TECHNIQUES IN ENVIRONMENTAL MONITORING

Mike J. Adams

INTRODUCTION

Recent times have witnessed a dramatic increase in public interest and concern regarding environmental issues. This trend has been accompanied by an expansion in environmental monitoring and the accompanying acquisition of large amounts of data covering a wide range of environmental parameters. Except in the most simple studies, these raw data often convey very little immediate information. In order to extract relevant information from data, the latter must be analyzed with the level of care and thought that went into their collection. Indeed, some serious consideration of subsequent data analysis and the statistical basis of the intended study should be made before the study commences.

Nothing can replace a well-planned and well-designed experiment, and no amount of mathematical manipulation of data can compensate for a badly designed study. The field of experimental design and optimization is the theme of many excellent texts, and all scientists should be encouraged to become familiar with at least the basic principles of this subject. For the environmental sciences, several books can be recommended (Einax et al., 1997; Hewitt, 1992).

With this caveat, and assuming the data recorded in the field or laboratory are sound, then we can begin to consider the wide variety of mathematical techniques and transformations available that will allow us to extract maximum useful information. We can assume that the data are *multivariate.* This is to say that the data are obtained from measurements of several or many features (variables) on many objects (samples). The application of multivariate analysis methods to chemical data is referred to as *chemometrics,* and this chapter is devoted to introducing some of the techniques and methods commonly employed to interpret environmental data.

From simple graphic and pictorial displays of data to the more sophisticated techniques involving factor analysis, the aim is to extract useful information from raw recorded measurements and interpret the data in terms of their chemical content. No matter how complex the original data or how sophisticated our subsequent analysis, a starting point usually is calculation of the simple, univariate statistical summaries and a visual examination of the data. Excellent texts covering the basic elements of statistics for analysts are available and should be consulted for a more detailed treatment (Miller and Miller, 1993).

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Summary Statistics

The data presented in Table 26.1 represent what may be considered a small but typical set of results from an environmental study. River water was sampled at three locations on five occasions and analyzed for some important anions (i.e., nitrate, chloride, sulfate, phosphate, and silicate), as well as conductivity and dissolved oxygen. The results of such studies are often published in the scientific literature (e.g., Marengo et al., 1995). Table 26.1 is a small data set, and patterns in these data are evident. Along with the measured data, Table 26.1 presents the familiar univariate statistics referred to as the *mean,* the *variance,* and the *standard deviation* for each of the variables monitored. The set of raw measurement data can be considered as a *data matrix* **X** comprising i rows ($i = 1,\ldots,n,$ where n is the number of samples) and j columns ($j = 1,\ldots,m,$ where m is the number of variables or features). A single value, or element, in **X** can be denoted $x_{i,j}$. Using this notation, the mean value of each variable is given by

$$\bar{x}_j = \frac{\sum_{i=1}^{n} x_{ij}}{n} \tag{26.1}$$

the variance is given by

$$s_{x_j}^2 = \frac{\sum_{i=1}^{n} (x_{ij} - \bar{x}_j)^2}{n-1} \tag{26.2}$$

and the standard deviation is given by

$$s_{x_j} = \sqrt{s_{x_j}^2} = \sqrt{\frac{\sum_{i=1}^{n} (x_{ij} - \bar{x}_j)^2}{n-1}} \tag{26.3}$$

These so-called summary statistics assume that the sample values are taken from a parent population having a normal distribution, and each is a *least-squares* estimated value. Given a normal population distribution, then these statistics provide an effective summary of our data. Their least-squares derivation implies that these statistics are disturbed easily by outliers; they are not *robust.* A more detailed discussion of these and alternative robust statistical metrics is given by Bajpai, Calus, and Fairley (Hewitt, 1992).

Although these simple statistics may summarize the data adequately, they provide no information regarding structure or patterns within the results. In order to search for such patterns, we must turn to bivariate or multivariate data analysis techniques and examine *interactions* between variables or *similarities* between samples. In the first instance, this can be done using graphic or pictorial representations, but before proceeding along this path, this is an appropriate point to consider the role of some simple *transformation* operations.

Transformations

It is often the case in multivariate data analysis that variables covering widely different ranges of, say, analyte concentration are encountered. In order to prevent a small group of features from dominating the subsequent analysis, some sort of scaling frequently is performed.

One range-transformation technique is the *min-max transformation.* The original data matrix **X** is converted to a new matrix **Z** in which each transformed variable has a minimum value of zero and a maximum value of unity; that is,

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CHEMOMETRIC TOOLS AND TECHNIQUES IN ENVIRONMENTAL MONITORING

TABLE 26.1 Results of River Water Analysis

Code	Nitrate, mg/liter	Chloride, mg/liter	Sulfate, mg/liter	Phosphate, mg/liter	Silicate, mg/liter	Conductivity, mS/cm	Dissolved O_2, mg/liter
11	5.49	5.12	4.00	0.24	9.71	15.40	7.65
21	11.28	10.29	11.20	1.37	7.41	47.69	4.75
31	10.16	30.47	23.50	0.78	4.57	56.24	6.30
12	2.14	4.21	9.00	0.20	11.57	19.08	7.39
22	12.10	12.43	21.00	1.26	2.43	48.65	5.23
32	9.30	32.92	24.79	0.72	2.48	55.15	5.80
13	1.82	4.13	11.26	0.22	10.30	26.70	5.72
23	12.20	13.46	18.00	1.38	2.80	51.40	4.55
33	7.10	29.58	22.84	0.72	2.07	57.40	5.80
14	3.18	6.07	6.18	0.11	11.60	13.09	5.80
24	13.70	14.42	28.00	1.34	3.13	46.06	3.59
34	9.72	31.56	38.64	0.68	2.63	51.08	6.10
15	8.12	6.10	5.34	0.10	9.98	15.70	6.91
25	13.80	12.30	21.00	1.28	5.73	45.37	4.22
35	8.90	28.50	27.17	0.70	6.50	52.22	7.00
Mean	8.60	16.10	18.13	0.74	6.19	40.08	5.79
Variance	15.633	124.372	99.746	0.240	13.194	280.847	1.384
Standard deviation	3.954	11.152	9.987	0.490	3.632	16.758	1.176

Note: The two-digit sample code refers to the location and time, respectively, of the sampling. Samples coded 1X were taken from near source, 2X from an agricultural area, and 3X from a near-estuarine location.

$$z_{ij} = \frac{x_{ij} - \min(x_j)}{\max(x_j) - \min(x_j)} \tag{26.4}$$

With z_{ij} representing a single element in the transformed matrix **Z.** The min-max transformation often is employed for scaling spectral data in order to aid comparison and database searching.

If the variances of the variables are similar, then *mean centring* is useful, and the transformed variables have mean values of zero, that is,

$$z_{ij} = x_{ij} - \bar{x}_j \tag{26.5}$$

By far the most common transformation is *standardization* or *autoscaling* of the raw data. Standardization is usually always necessary when the variables monitored are recorded in different units, e.g., concentration, pH, particle size, conductivity, etc. The treated elements in the standardized data matrix have no units, the mean of each variable is zero, and the standard deviation of each is unity. This transformation is achieved by both mean centring and variance scaling the original data, that is,

$$z_{ij} = \frac{x_{ij} - \bar{x}_j}{s_{xj}} \tag{26.6}$$

Having no units allows standardized data to be used for comparing the distribution of, say, conductivity data with anion concentrations. The standardized data from the river water samples are given in Table 26.2.

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TABLE 26.2 The Standardized Data Matrix

Code	Nitrate, mg/liter	Chloride, mol/liter	Sulfate, g/liter	Phosphate, mg/liter	Silicate, mg/liter	Conductivity, mS/cm	Dissolved O_2, mg/liter
11	−0.786	−0.985	−1.415	−1.016	0.967	−1.473	1.586
21	0.677	−0.521	−0.694	1.281	0.336	0.454	−0.882
31	0.393	1.288	0.538	0.077	−0.448	0.964	0.437
12	−1.635	−1.067	−0.914	−1.105	1.481	−1.253	1.365
22	0.885	−0.329	0.288	1.065	−1.036	0.511	−0.477
32	0.177	1.508	0.667	−0.035	−1.022	0.899	0.012
13	−1.714	−1.073	−0.688	−1.054	1.130	−0.799	−0.059
23	0.910	−0.237	−0.013	1.306	−0.934	0.675	−1.051
33	−0.380	1.208	0.472	−0.042	−1.136	1.033	0.012
14	−1.370	−0.900	−1.197	−1.293	1.488	−1.611	0.008
24	1.290	−0.151	0.988	1.228	−0.843	0.357	−1.869
34	0.284	1.386	2.054	−0.127	−0.980	0.656	0.267
15	−0.120	−0.897	−1.280	−1.312	1.042	−1.455	0.954
25	1.315	−0.341	0.288	1.106	−0.129	0.316	−1.333
35	0.076	1.112	0.905	−0.079	0.084	0.724	1.032

Graphic Exploratory Data Analysis

The simple pictorial representation of complex multivariate data can have more power of persuasion for confirming patterns and structure than relying solely on sophisticated mathematical methods. Properly selected and constructed graphic images offer the advantage of clear and usually simple presentation of essential facts. In addition, the wide range of computer software available for graphic display of data makes graph production simple. Even the most common spreadsheet programs incorporate quite sophisticated graphing and charting capabilities.

The most widely used chart type is the simple *bivariate scatter plot*; the values for one variable for each object are plotted agains the values of a second variable. For our river water data with 7 recorded variables, this requires 21 plots to display all combinations. Each image can represent an element of a graphic matrix object (Fig. 26.1). The scatter-plot matrix is symmetric about a diagonal (not shown) of each variable plotted against itself. Relationships and interactions between pairs of variables are discerned much more easily in these pictures than by visual examination of the numerical data matrix. However, as the number of variables m increases, so the number of possible bivariate combinations also increases, and this display technique becomes less effective and loses its impact (e.g., with 20 variables, 190 bivariate plots are required).

The efficient and effective display of multivariate data has exercised many minds, and many ingenious techniques have been proposed in the literature. A summary and discussion are presented by Thompson (Hewitt, 1992). For example, the use of a Fourier function to describe and display multivariate data has been proposed. The function for each object, or sample i, is given by

$$f(t)_i = (x_{i,1}/\sqrt{2}) + x_{i,2} \sin(t) + x_{i,3} \cos(t) + x_{i,4} \sin(2t) + x_{i,5} \cos(2t) + \cdots \quad (26.7)$$

The argument t varies in the interval $-\pi$ to $+\pi$, and the parameters $x_{i,1}, x_{i2}, \ldots, x_{i,m}$ are the values of the features describing each object. It is anticipated that curves close to each other represent similar objects. For the case of a large number of objects (greater than six

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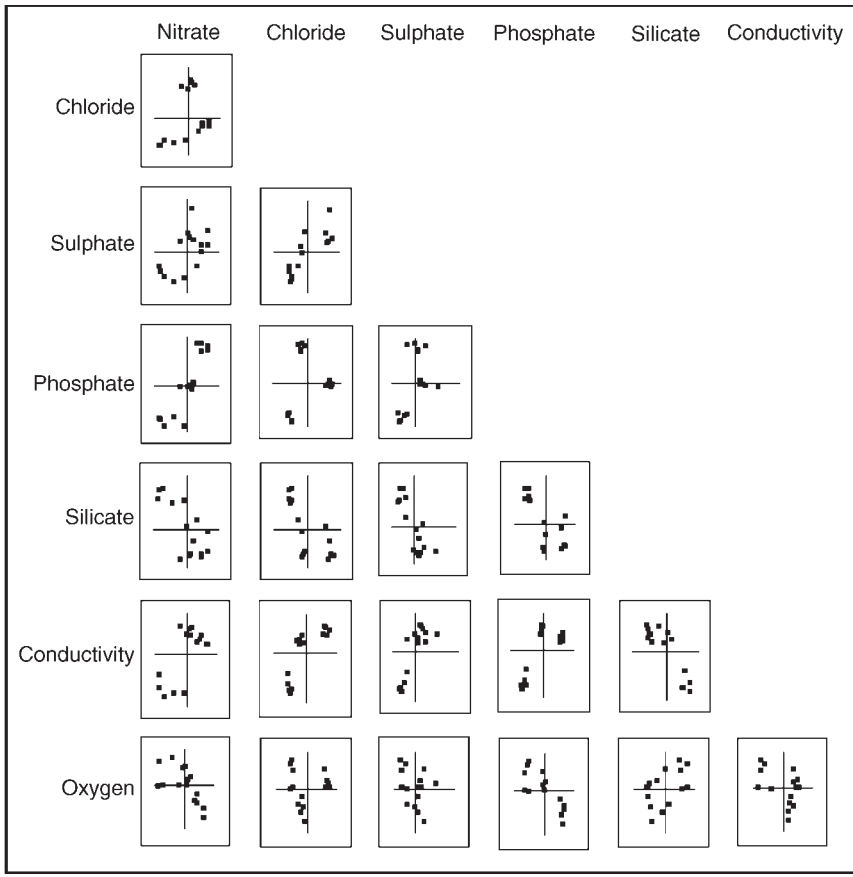

FIGURE 26.1 A matrix of bivariate scatter plots illustrating the interactions between all pairs of variables (data from Table 26.1).

or seven), such plots can be untidy. For small data sets, the technique is effective and useful because it is easily programmed into a computer spreadsheet.

A more common display tool is the *star* or *radar-plot.* This method allows simultaneous treatment and visualization of multivariate data of up to about 10 variables. Each feature is represented by a vector radiating out from a center point, and each object is represented by a star of m vectors (Fig. 26.2). The value of this technique, as with all graphic methods, lies in the ability of the eye to identify similar shapes and visual features.

Preliminary graphic or pictorial methods can be valuable in discerning patterns in data and can provide good visual support of subsequent statistical and mathematical analyses. The methods are limited, however, to generally less than 10 variables, and they are heavily influenced by outliers. In general, graphic methods are more appropriate when used in conjunction with pattern-recognition algorithms, and our introduction to this subject begins by examining some bivariate statistics.

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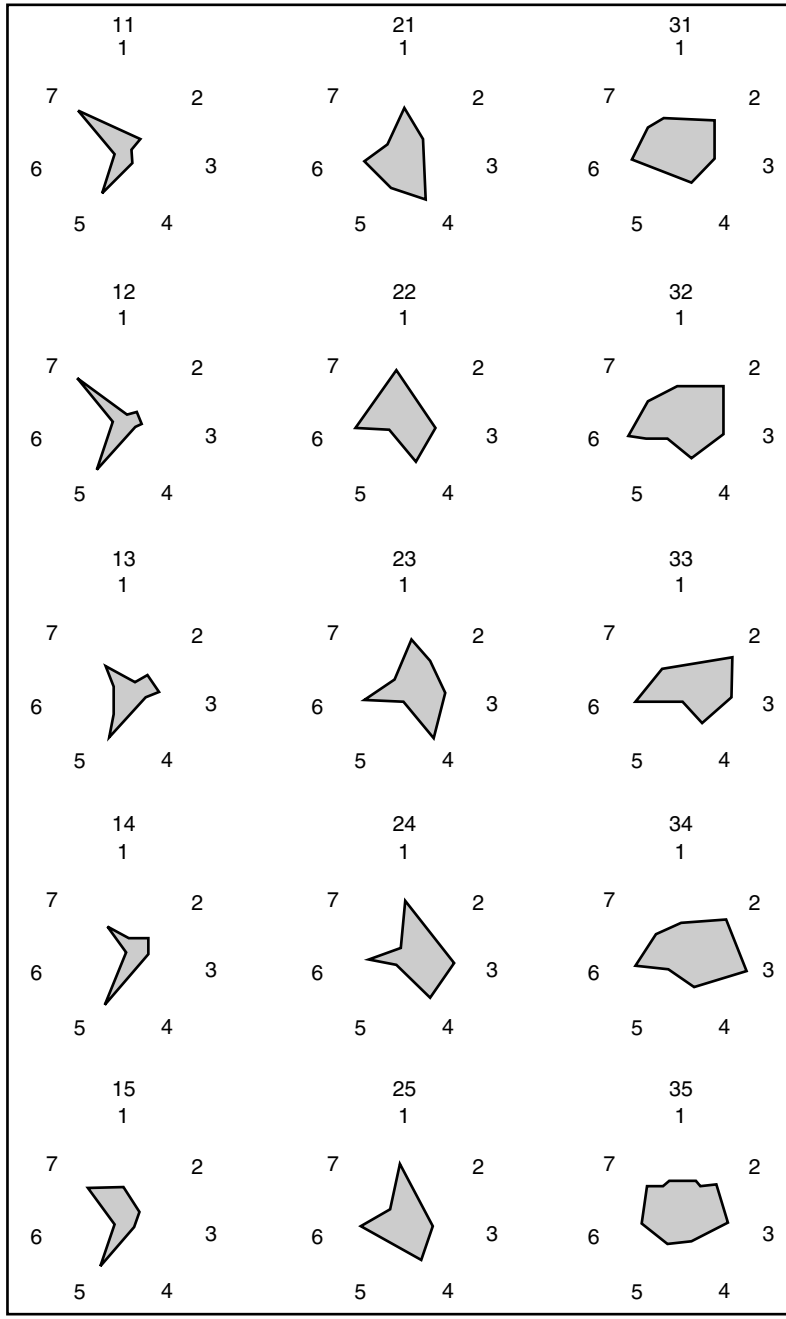

FIGURE 26.2 A star plot of the seven variable values associated with each water sample from Table 26.1.

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Bivariate Data Analysis

The bivariate scatter plots in Fig. 26.1 graphically illustrate relationships and interactions between pairs of variables. In order to quantify the extent of such relationships, we need to introduce another statistic, the *covariance*. Just as variance describes the spread of observed data values about a mean value, so covariance provides a measure of the spread of two variables about their means. This is illustrated in Fig. 26.3 for two standardized variables. The shape of the projected contour plot indicates the degree of interaction, the covariance, between the variables.

The value of the covariance $c_{1,2}$ between variables denoted by the matrix columns $x_{i,1}$ and $x_{i,2}$ is given by

$$c_{1,2} = \frac{\sum_{i=1}^{n} (x_{i,1} - \bar{x}_1)(x_{i,2} - \bar{x}_2)}{n - 1} \tag{26.8}$$

Obviously, variables $x_{i,1}$ and $x_{i,2}$ should be measured in the same units or have no units.

For the nitrate and chloride concentration values from Table 26.1, the covariance is 14.66 $(\text{mg/liter})^2$, and for chloride and sulfate it is 91.30 $(\text{mg/liter})^2$. A high covariance value indicates a strong dependence between variables, and a covariance of zero is indicative of statistically independent variables; thus chloride and sulfate are related (e.g., they may have a common source or be interacting).

Because covariance is recorded in $(\text{units})^2$ and can take any value (positive or negative) from zero, it is not intuitively obvious just what the degree of dependence is between two variables. A better, and easier to visualize, statistic is the *correlation coefficient r.* For two variables $x_{i,1}$ and $x_{i,2}$ with standard deviations of s_1 and s_2, respectively, the correlation coefficient is defined by

$$r_{1,2} = \frac{c_{1,2}}{s_1 \cdot s_2} \qquad -1 \le r \le 1 \tag{26.9}$$

that is, the covariance divided by the product of the standard deviations. Using Eq. (26.9), the correlation coefficient for nitrate and chloride concentrations is 0.36, and for chloride and sulfate it is 0.82. The high correlation (dependence) between the concentration of chloride and sulfate compared with that between chloride and nitrate is now obvious.

The correlation coefficient is a standardized value (mean centered and variance scaled) and so has no units and is independent of the units used for the original measurements. It is worth noting that if the original data are standardized, then $s_1 = s_2 = 1$, and calculation of covariance gives correlation.

Using the standardized data matrix (Table 26.2), we can calculate the correlation coefficient between each pair of variables recorded, and the correlation matrix is given in Table 26.3. This matrix, and similarly for the covariance matrix, is square and symmetric about the leading diagonal.

The ease of calculating correlation coefficients and the apparent simplicity in interpreting r values make it a much misused statistic. It always should be remembered that it is a measure only of *linear* dependence between variables and that by itself it does not imply a *causal relationship* between those variables.

Examination of Table 26.3 shows that several variables in our data are highly correlated, and this indicates that the dimensionality of the original data can be reduced to make for easier and perhaps more profitable interpretation. However, before we move on to more sophisticated data-reduction techniques, we can extend our current discussion of correlation to include the concept of object *similarity* and so examine the use of *cluster analysis.*

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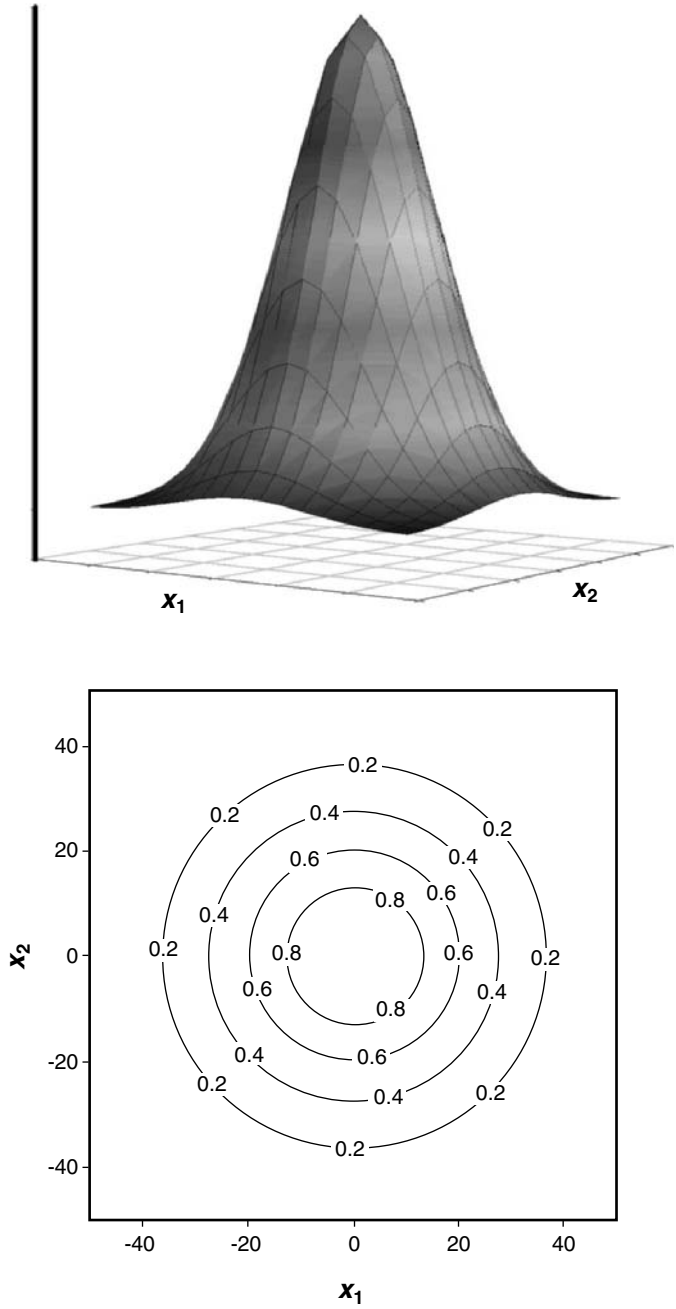

FIGURE 26.3 A bivariate normal distribution and its projected contour plot. The covariance between variable x_1 and x_2 illustrated is zero.

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TABLE 26.3 The Between-Variables Correlation Matrix from the Data in Table 26.1

	Nitrate	Chloride	Sulfate	Phosphate	Silicate	Conductivity	Dissolved O_2
Nitrate	1						
Chloride	0.36	1					
Sulfate	0.56	0.82	1				
Phosphate	0.88	0.25	0.50	1			
Silicate	−0.73	−0.73	−0.81	−0.71	1		
Conductivity	0.69	0.80	0.82	0.74	−0.90	1	
Dissolved O_2	−0.67	−0.01	−0.34	−0.80	0.50	−0.46	1

Cluster Analysis

Cluster analysis is the name given to a large class of data-analysis techniques, the purpose of which is to identify groups, or clusters, of similar objects characterized by a multivariate feature set. Application of these methods requires no a priori information about groups present, and for this reason, such methods belong to the class of data-analysis tools employed for *unsupervised pattern recognition.* Hierarchical cluster analysis methods are the most commonly encountered of these tools, and the steps required to perform such an analysis are stated easily. Using the original data matrix, a suitable matrix of similarity measures between objects is constructed first. From this similarity matrix, the most similar pair of objects is combined to produce a new "grouped" object, and the process is repeated until all objects have been included in a single cluster. The combination of choice of an appropriate similarity metric and the manner in which objects are grouped (or clustered) gives rise to many potential methods. Several reviews and discussions are available that provide examples of the range of techniques (Adams, 1995; Einax et al., 1997; Everitt, 1980).

In the preceding section, the notion of similarity was implicit in discussing correlation. Variable pairs with a high correlation obviously exhibit similar trends in their behavior, and if we were to *transpose* the data matrix and examine correlation between objects, then pairs of objects with high correlation could be considered similar. This measure of similarity would be indicative of trends in the distribution or patterns of the variables describing each object. Thus objects with, say, similar infrared (IR) spectra can be assumed to have similar structural features.

A more widely used similarity measure for cluster analysis is the *euclidean distance metric.* It is generally accepted without proof that similarity and distance are complementary; objects close together in multidimensional space are more alike than those farther apart. For two objects described by two variables $x_{i,j}$ ($i = 1, 2$ and $j = 1, 2$), the distance d between objects is given by the Pythagoras equation

$$d = \sqrt{(x_{1,1} - x_{2,1})^2 + (x_{1,2} - x_{2,2})^2} \tag{26.10}$$

This can be extended easily to multidimensional space, and the euclidean distance between two objects can be calculated from

$$d = \sqrt{\sum_{j=1}^{m} (x_{1,j} - x_{2,j})^2} \tag{26.11}$$

where m is the number of variables and $x_{i,j}$ is the number of elements of the data matrix.

The euclidean distance can be calculated for all pairs of objects defined by the standardized variables. The between-objects *distance matrix* for the river water data is presented in Table 26.4.

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TABLE 26.4 The Between-Objects Euclidean Distance Matrix Derived from the Standardized Data Matrix Presented in Table 26.2

	11	21	31	12	22	32	13	23	33	14	24	34	15	25	35
11	0.00	4.34	4.61	1.15	4.78	4.98	2.19	5.15	4.77	1.82	5.91	5.47	0.96	5.01	4.17
21	4.34	0.00	2.98	4.61	1.77	3.28	3.80	1.51	3.23	4.22	2.39	4.06	4.00	1.36	3.34
31	4.61	2.98	0.00	4.81	2.30	0.79	4.33	2.65	1.12	4.84	3.20	1.65	4.37	2.85	1.01
12	1.15	4.61	4.81	0.00	5.12	5.16	1.64	5.46	4.89	1.51	6.13	5.54	1.70	5.29	4.26
22	4.78	1.77	2.30	5.12	0.00	2.37	4.39	0.75	2.39	4.92	1.65	2.92	4.47	1.30	2.82
32	4.98	3.28	0.79	5.16	2.37	0.00	4.54	2.67	**0.68**	5.08	3.09	1.44	4.73	3.00	1.58
13	2.19	3.80	4.33	1.64	4.39	4.54	0.00	4.59	4.21	1.11	5.14	5.02	2.16	4.42	4.00
23	5.15	1.51	2.65	5.46	0.75	2.67	4.59	0.00	2.67	5.12	1.38	3.36	4.81	1.07	3.27
33	4.77	3.23	1.12	4.89	2.39	**0.68**	4.21	2.67	0.00	4.84	3.25	1.78	4.60	3.13	1.73
14	1.82	4.22	4.84	1.51	4.92	5.08	1.11	5.12	4.84	0.00	5.64	5.60	1.67	4.84	4.51
24	5.91	2.39	3.20	6.13	1.65	3.09	5.14	1.38	3.25	5.64	0.00	3.36	5.45	1.19	3.76
34	5.47	4.06	1.65	5.54	2.92	1.44	5.02	3.36	1.78	5.60	3.36	0.00	5.23	3.48	1.74
15	0.96	4.00	4.37	1.70	4.47	4.73	2.16	4.81	4.60	1.67	5.45	5.23	0.00	4.54	4.02
25	5.01	1.36	2.85	5.29	1.30	3.00	4.42	1.07	3.13	4.84	1.19	3.48	4.54	0.00	3.30
35	4.17	3.34	1.01	4.26	2.82	1.58	4.00	3.27	1.73	4.51	3.76	1.74	4.02	3.30	0.00

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To proceed with the cluster analysis, we now need to decide on a means by which similar objects are clustered and substituted by new representative "group" objects. Popular methods include nearest neighbor, furthest neighbor, and averaging (Fig. 26.4). Use of the averaging method is illustrated here.

Visual examination of Table 26.4 shows samples 32 and 33 to be most similar (having the smallest separating distance), so these objects are combined to form a new object 3233. The distance between this object and all others is calculated as being the average of the distances for 32 and 33. The size of the distance matrix is thus reduced by one column and one row, and the process of combining the next most similar pair of objects continues until only one grouped object containing all samples remains. At each stage in this process, the identity of objects combined is recorded along with their new distance value. This information can then be displayed as a two-dimensional linkage diagram referred to as a *dendrogram* (Fig. 26.5). The dendrogram has reduced the original data matrix to a two-dimensional graph that clearly illustrates, in this case, the presence of three district groups of samples, with each group containing five objects, a result in agreement with our knowledge concerning the source and distribution of the river water samples.

Cluster analysis is not a statistical-based process and should not be employed to prove the existence of groups. Rather, cluster analysis is best employed as part of the tool kit for *exploratory* data analysis. The evidence for certain groups and clusters and the cause of structure found should be investigated by other techniques. Nevertheless, the power of hierarchical clustering methods to reduce systematically, and often convincingly, complex multidimensional data to a two-dimensional representation has made these techniques popular, and they are employed widely.

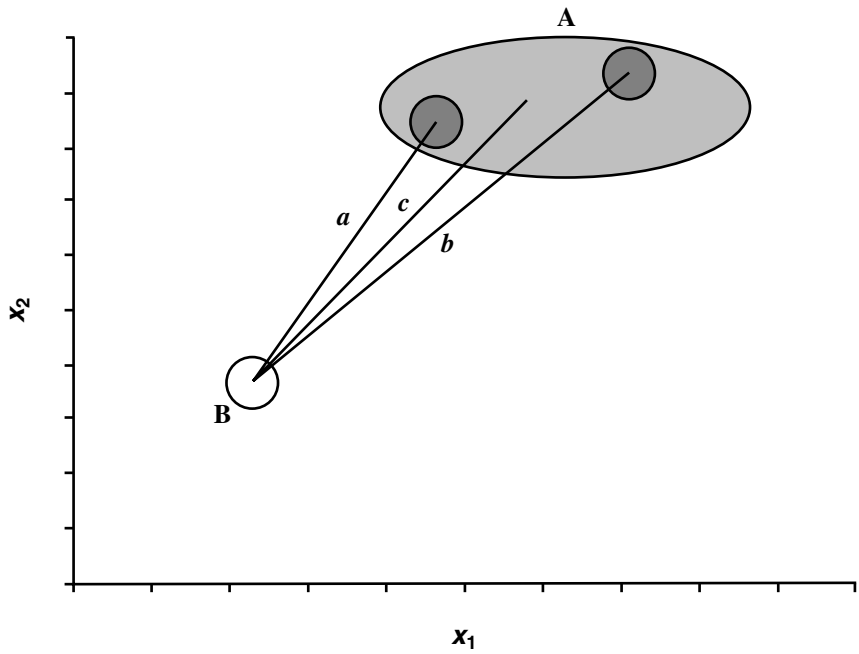

FIGURE 26.4 Objects can be combined (clustered) according to a variety of distance measures; group A is at a distance from group B given by (*a*) nearest neighbors, (*b*) furthest neighbors, and (*c*) average distance.

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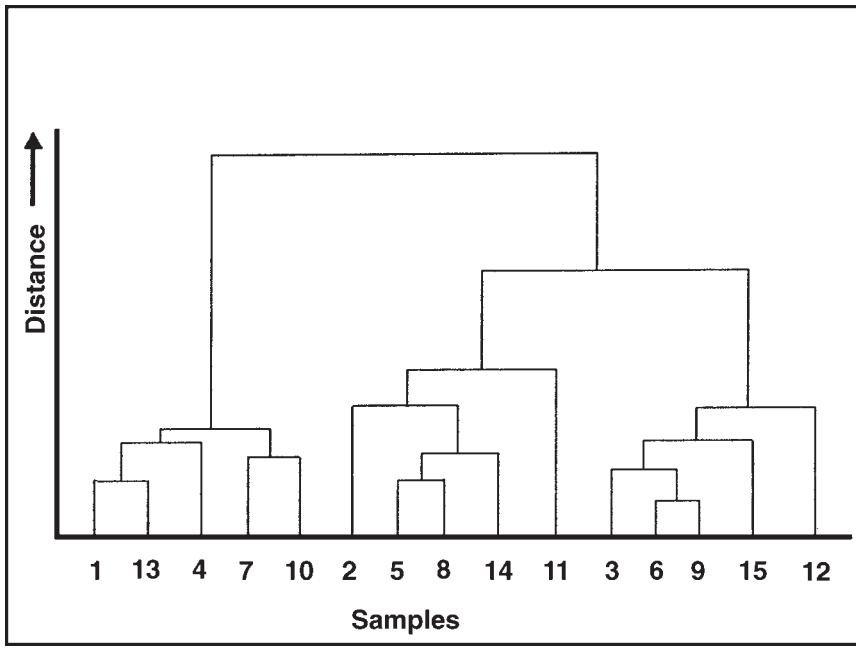

FIGURE 26.5 A dendrogram illustrating the similarity between samples, resulting from hierarchical cluster analysis using an average-distance linkage scheme (see text).

Discriminant Analysis

Whereas cluster analysis neither needs nor assumes a priori information about sample objects, discriminant analysis uses knowledge of groups or clusters to describe their differences. Relationships between groups can be identified and quantified, and subsequent unknown objects can be assigned to one of the groups.

Discriminant analysis belongs to the field of *supervised pattern recognition.* Our aim is to develop objective rules for the classification of objects into previously identified classes. To illustrate the procedures and processes involved, a small, artificial data set will be employed (Table 26.5). The data could relate, for example, to a study on classifying land as contaminated or not. As shown in Table 26.5, the data matrix is partitioned into two known classes of land (each containing nine samples) and a third group of two samples (*test objects*) that are assumed to belong to one of the identified classes. Each object is characterized here by two variables only for the sake of simplicity. In practice, multivariate application of the techniques to be discussed is straightforward.

In order to get a visual impression of the separability of the two classes of objects and where the test objects lie, scatter plots are always valuable. Figure 26.6 shows all 20 objects represented in the *pattern space* defined by variables $x_{i,2}$ versus $x_{i,1}$. It is evident that the two groups of objects do form identifiable clusters, but neither variable can by itself provide sufficient information for complete differentiation of the classes.

A wide range of modeling algorithms is available to perform classification, and here we will concentrate on two *deterministic* models, the *k-nearest neighbor method* (*k*-NN) and *linear discriminant analysis* (LDA).

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TABLE 26.5 A Simple Bivariate Data Set Comprising Two Groups of Known Samples and Two Unclassified Samples

	Group 1			Group 2				
Sample i	$x_{i,1}$	$x_{i,2}$	Sample i	$x_{i,1}$	$x_{i,2}$	Sample i	Test objects	
1	2.09	8.13	10	2.00	5.11	19	2.50	4.52
2	4.16	7.03	11	1.04	4.10	20	5.55	4.05
3	2.55	6.74	12	3.06	4.00			
4	3.06	6.14	13	5.16	4.06			
5	5.16	6.27	14	2.08	3.08			
6	6.07	6.05	15	5.04	3.01			
7	7.12	6.19	16	6.27	2.59			
8	4.19	5.17	17	3.02	2.04			
9	7.03	4.04	18	5.02	1.51			
Mean	4.60	6.19		3.63	3.28			

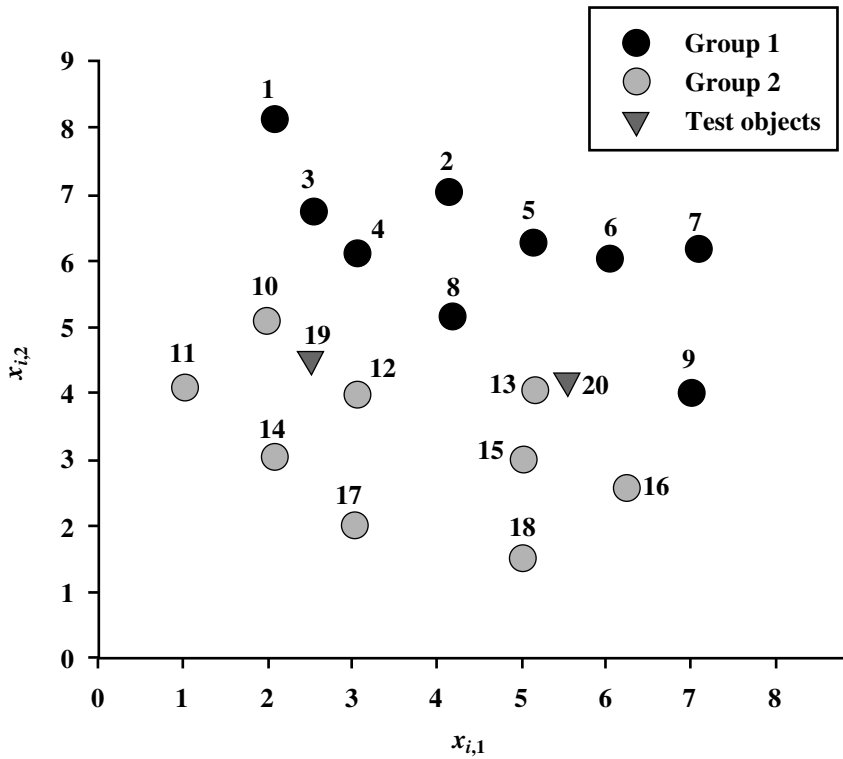

FIGURE 26.6 A bivariate plot of samples from group 1, contaminated land, and group 2, uncontaminated land, and the location of the two test samples.

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Classification Using the k-NN Method. The simplest case for this algorithm is the 1-NN model. A test object is assigned to the class containing its nearest neighbor, as measured by some distance metric. Using only two variables ($x_{i,1}$ and $x_{i,2}$) and with reference to Fig. 26.6, the nearest neighbor of test object 20 is object 13, of group 2, so test object 20 would be assigned to group 2, i.e., the class of an uncontaminated site. Using and including more variables precludes the use of simple diagrams, but between-object euclidean distances are calculated easily, as we saw in our discussion of cluster analysis. Table 26.6 gives the distances calculated for test objects 19 and 20 with respect to all training objects. From these results, test objects 19 and 20 are both assigned to group 2, uncontaminated land.

The 1-NN method can be extended to more (k) neighbors, with final group assignment decided according to a majority vote procedure, i.e., to the group with the greatest representation in the set of the k nearest training objects.

Since the k-NN method is based on similarity measured by distance, it is obviously affected by the original units used to characterize the data. The variable with the largest amount of scatter (the largest variation) will contribute the greatest to determination of the euclidean distance. In practice, it may be advisable to perform standardization of variables before calculating distances.

The question of which classification scheme performs best cannot be addressed by using unknown test objects. Instead, the efficiency of a procedure can be assessed by examining its performance on the training set. Each training object, in turn, is treated as a test object and classified by the algorithm under study. This procedure is known as the *leave-one-out method,* and the degree of agreement between application of the classification method and the known, assumed-correct result can be used as a measure of the method's efficacy. This method of assessment can be reported as the number of correctly classified training objects (NCC) or the percentage correct classification rate (% CCR).

TABLE 26.6 The Between-Object Euclidean Distances for Objects 19 and 20 to Each of the Samples in the Training Sets of Groups 1 and 2

Sample i	$x_{i,1}$	$x_{i,2}$	Test object 19	Test object 20
1	2.09	8.13	3.633	5.350
2	4.16	7.03	3.009	3.288
3	2.55	6.74	2.221	4.029
4	3.06	6.14	1.714	3.251
5	5.16	6.27	3.184	2.254
6	6.07	6.05	3.884	2.066
7	7.12	6.19	4.913	2.654
8	4.19	5.17	1.811	1.762
9	7.03	4.04	4.555	1.480
10	2.00	5.11	0.773	3.705
11	1.04	4.10	1.519	4.510
12	3.06	4.00	**0.764**	2.491
13	5.16	4.06	2.699	**0.390**
14	2.08	3.08	1.500	3.603
15	5.04	3.01	2.955	1.158
16	6.27	2.59	4.235	1.628
17	3.02	2.04	2.534	3.231
18	5.02	1.51	3.926	2.595

Note: The smallest distance for each test object is shown in boldface.

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Table 26.7 summarizes the predictive ability of the 1-NN and 3-NN methods applied to the unscaled data.

Linear Discriminant Analysis. The underlying theory of linear discriminant analysis (LDA) and its application are fundamentally different from that of the simple *k*-NN method. In LDA, or *discriminant function analysis,* we are seeking to create new synthetic features (variables) that are *linear combinations* of the original variables and that best indicate the differences between the known groups in contrast to the variances within the groups. Thus LDA is a statistical technique that assumes that the original or transformed data are sampled from multivariate normal populations.

The process of performing LDA aims to derive and construct a boundary between the known classes of the training objects using statistical parameters. This boundary is developed using a *discriminant function* that provides a value or *score* when applied to a test object (Davis, 1973).

If $f(x_i, c_p)$ is some measure of likelihood of object x_i belonging to group or class c_p, then the discriminant score D_i, for assigning x_i to one of two groups is given by

$$D_i = f(x_i,c_1) - f(x_i, c_2) \tag{26.12}$$

which may be interpreted as saying that we classify test object x_i into class 1 if D_i is positive; otherwise, x_i is considered to belong to group 2.

The value of the discriminant score is calculated from a *linear combination* of the values of the variables describing the objects, each suitably *weighted* to provide optimal discriminatory power. Thus Eq. (26.12) for two variables can be written as

$$D_i = w_1 x_{i,1} + w_2 x_{i,2} \tag{26.13}$$

or, in matrix notation,

$$D_i = \boldsymbol{w} \cdot \boldsymbol{x_i} \tag{26.14}$$

The weights or variable coefficients used in Eq. (26.13) are determined by

$$\mathbf{w} = [\bar{\mathbf{x}}_\mathbf{j}(1) - \bar{\mathbf{x}}_\mathbf{j}(2)]\, \mathbf{S}^{-1} \tag{26.15}$$

where $\bar{\mathbf{x}}_\mathbf{j}(1)$ and $\bar{\mathbf{x}}_\mathbf{j}(2)$ are the vectors of the mean values for variables *j* for groups 1 and 2, respectively. Equation (26.15) thus represents the ratio of the separation of the means of the two groups to the within-group variance for the groups, the *pooled* covariance matrix **S,** based on the two training groups.

The separation between the variable means expresses the degree of separation between the groups, whereas the covariance matrix describes the within-group spread or variation. The latter can be considered the *noise* in the discriminating function.

TABLE 26.7 Summary of Classification Results Using the 1-NN ($k = 1$), 3-NN ($k = 3$), and Linear Discriminant Analysis (LDA) Algorithms

	$k = 1$		$k = 3$		LDA	
	NCC	%CCR	NCC	%CCR	NCC	%CCR
Group 1	8	88.9	8	88.9	9	100.0
Group 2	9	100.0	9	100.0	9	100.0
Total	17	94.4	17	94.4	18	100.0

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The group mean differences are determined easily, that is,

$$\bar{x}_j(1) - \bar{x}_j(2) = \frac{\sum_{i=1}^{n(1)} x_{ij}(1)}{n(1)} - \frac{\sum_{i=1}^{n(2)} x_{ij}(2)}{n(2)} \tag{26.16}$$

where $n(1)$ and $n(2)$ are the number of objects in group 1 and group 2, respectively, and $x_{i,j}(c_p)$ is the ith value of variable j in group c_p). Using the two-dimensional data

$$\bar{\mathbf{x}}_\mathbf{j}(1) - \bar{\mathbf{x}}_\mathbf{j}(2) = \begin{bmatrix} 0.97 \\ 2.92 \end{bmatrix} \tag{26.17}$$

the sum of variable products for group 1 is calculated by

$$\boldsymbol{S}_{(1)} = \sum_{i=1}^{n(1)} [x_{i,1}(1) - \bar{x}_1(1)]\,[x_{i,2}(1) - \bar{x}_2(1)] \tag{26.18}$$

Similarly for group 2,

$$\boldsymbol{S}_{(2)} = \sum_{i=1}^{n(2)} [x_{i,1}(2) - \bar{x}_1(2)]\,[x_{i,2}(2) - \bar{x}_2(2)] \tag{26.19}$$

The pooled covariance **S** is given by

$$\boldsymbol{S} = \frac{\boldsymbol{S}_{(1)} + \boldsymbol{S}_{(2)}}{n(1) + n(2) - 2} \tag{26.20}$$

For our example,

$$\mathbf{S}_{(1)} = \begin{bmatrix} 27.96 & 11.26 \\ -11.26 & 10.49 \end{bmatrix} \quad \mathbf{S}_{(2)} = \begin{bmatrix} 25.73 & -7.93 \\ -7.93 & 10.41 \end{bmatrix} \quad \mathbf{S} = \begin{bmatrix} 3.36 & -1.20 \\ -1.20 & 1.31 \end{bmatrix} \tag{26.21}$$

and

$$\mathbf{S}^{-1} = \begin{bmatrix} 0.44 & 0.41 \\ 0.41 & 0.14 \end{bmatrix} \tag{26.22}$$

The vector of coefficients **w** can now be calculated, that is,

$$\mathbf{w} = \begin{bmatrix} 0.44 & 0.41 \\ 0.41 & 1.14 \end{bmatrix} \cdot \begin{bmatrix} 0.97 \\ 2.92 \end{bmatrix} = \begin{bmatrix} 1.62 \\ 3.72 \end{bmatrix} \tag{26.23}$$

and substituted into Eq. (26.13):

$$D_i = 1.62x_{i,1} + 3.72x_{i,2} \tag{26.24}$$

The discriminant function is linear; all the terms are added together to give a single number, the discriminant score. In two dimensions, the function is a line of slope α; that is,

$$\alpha = \frac{w_2}{w_1} = \frac{3.72}{1.62} = 2.30 \tag{26.25}$$

This is plotted in Fig. 26.7.

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We can select values for $x_{i,j}$ and substitute these in Eq. (26.24). For example, using the midpoint between the two group means,

$$D_{(0)} = w_1\left(\frac{\bar{x}_1(1) + \bar{x}_2(2)}{2}\right) + w_2\left(\frac{\bar{x}_2(1) + \bar{x}_2(2)}{2}\right) = 24.26 \qquad (26.26)$$

$D_{(0)}$ defines the *discriminant index,* the point along the discriminant function halfway between the center of group 1 and the center of group 2.

We may substitute the multivariate mean of group 1 to obtain $D_{(1)}$ and the multivariate mean of group 2 to yield $D_{(2)}$:

$$D_{(1)} = w_1\,\bar{x}_1(1) + w_2\,\bar{x}_2(1) = 30.46 \qquad (26.27)$$

$$D_{(2)} = w_1\,\bar{x}_1(2) + w_2\,\bar{x}_2(2) = 18.06 \qquad (26.28)$$

These points define the centers of the two original groups along the discriminant function.

The location of these specific points can be plotted directly on the discriminant function displayed as a one-dimensional axis (Fig 26.7). This is referred to as the *discriminant plot,* and the position of every object can be projected onto the discriminant function (Fig. 26.8). The concept of a linear discriminant axis reduces the multidimen-

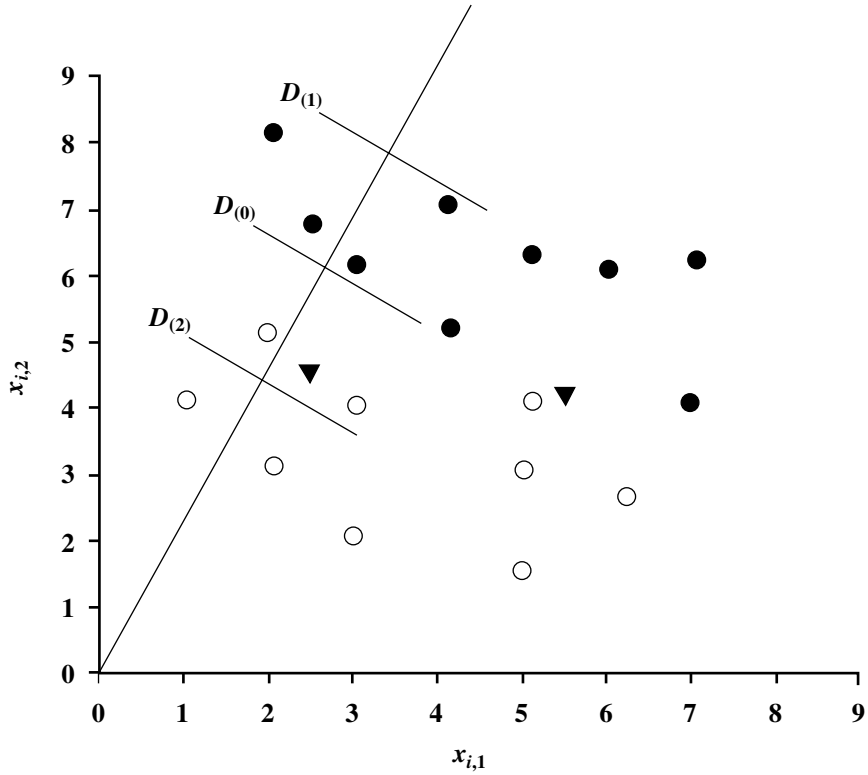

FIGURE 26.7 The bivariate data of Table 26.5 and the discriminant function. The locations of the discriminant index, $D_{(0)}$ and group means $D_{(1)}$ and $D_{(2)}$ are illustrated.

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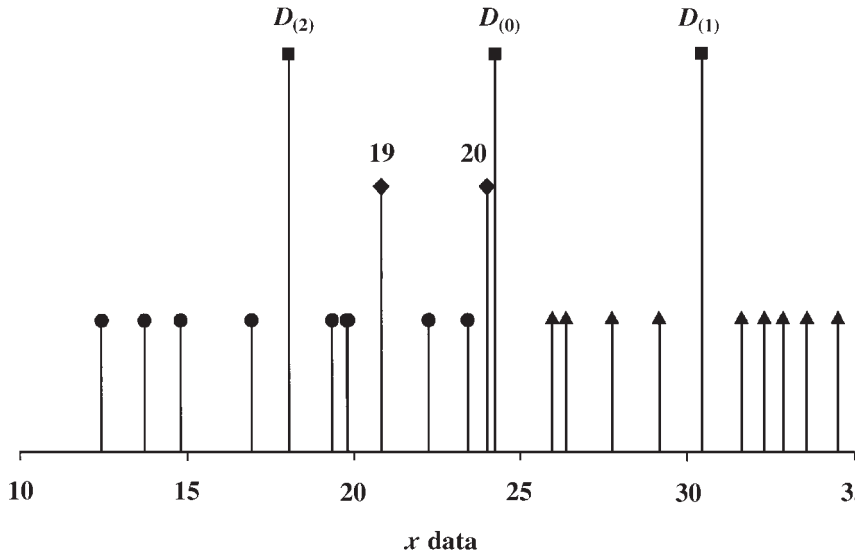

FIGURE 26.8 A discriminant plot illustrating the projection of each object onto the discriminant function.

sional classification problem to one dimension, with the projection achieved so that discrimination between classes is preserved as well as possible. The results of applying LDA to the data of Table 26.5 are summarized using the leave-one-out technique in Table 26.7.

Application of the LDA algorithm, therefore, proceeds by calculating the weight coefficients using training objects (the *training phase*) and employment of these weights in assigning test objects to groups (the *classification phase*). Coomans and Massart (Brereton, 1992) provide extensions to the use of LDA and further discussion of its application,

DATA REDUCTION

The potential to reduce the amount of data used to describe and characterize a series of objects is very appealing. Two principal features of all real data provide us with the opportunity to achieve data reduction with minimal loss of relevant information. First, all real data contain errors or noise, and second, the variables we measure are rarely independent (in a statistical sense) but can be highly correlated. For example, suppose that we are studying a group of circular objects and measure and record the diameter and circumference of each object. The second variable is redundant because it is derived from (and hence highly correlated with) the first variable. We could remove the second variable without losing any information. In this section data reduction and information extraction are considered using *principal components analysis.*

Principal Components Analysis (PCA)

Principal components are derived from the eigenvectors of a covariance matrix, and with the abundance of statistical and mathematical software available today, they are computed

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easily. It is important, however, to appreciate their structure and characteristics so that efficient and effective application of PCA is achieved.

Table 26.3 shows the between-variable correlation matrix for the river water data, and some high-correlation values are evident. It should not be surprising that conductivity is highly correlated with chloride concentration, that nitrate and phosphate are highly correlated, and that there is a strong relationship between chloride and sulfate. Our recorded variables are not statistically independent. By suitable transformation and combination, we would expect to be able to describe our 15 samples by far fewer uncorrelated and hopefully physically significant new variables—*principal components.* As with linear discriminant analysis, we seek to derive new, synthetic features or variables from a linear combination of original variables. On this occasion, however, our aim is to determine the combinations yielding maximum variance.

Purely for the sake of simplicity and to allow geometric interpretation of the operations involved, we will consider initially the two variables chloride and sulfate concentrations from the river water data. The 15 water samples can be displayed in this two-dimensional pattern space using a simple bivariate scatter plot (Fig. 26.9). The variance associated with chloride concentration is 124.37 $(\text{mg/liter})^2$, with sulfate concentration it is 99.75 $(\text{mg/liter})^2$, and the covariance between these two variables is 91.30 $(\text{mg/liter})^2$. The covariance matrix **C** is therefore given by

$$\mathbf{C} = \begin{bmatrix} 124.37 & 91.30 \\ 91.30 & 99.75 \end{bmatrix} \tag{26.29}$$

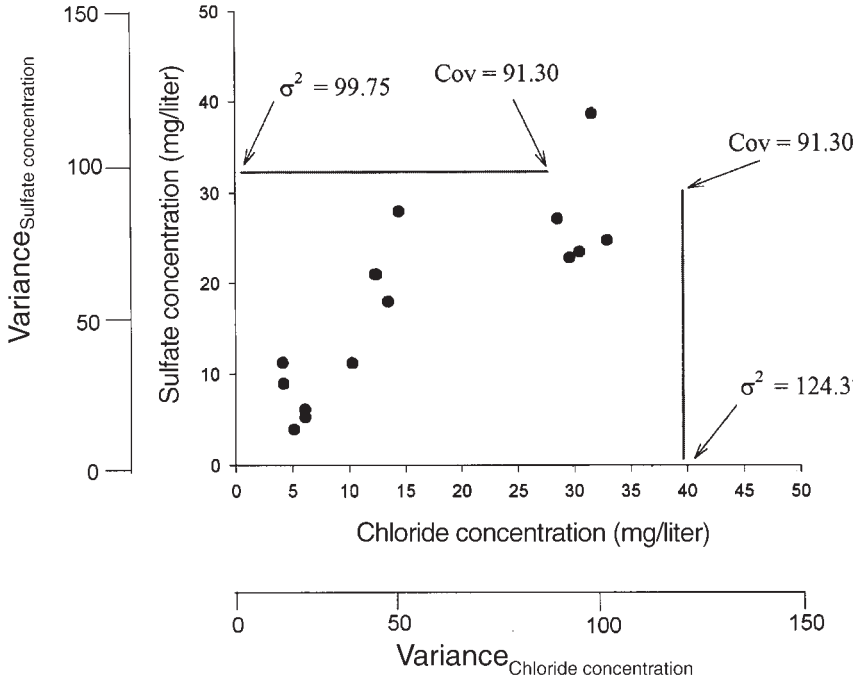

FIGURE 26.9 Scatter plot of chloride and sulfate concentrations from Table 26.1 and the variance and covariance values associated with these analytes.

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and this structure can be illustrated as in Fig. 26.9. The variance of the chloride values is denoted by a line of length equal to the variance along a chloride-value axis, and similarly for sulfate variance on a sulfate-value axis. Because the chloride concentration varies with changes in sulfate concentration, we may plot a line from the end of the chloride variance line parallel to the sulfate variance line. The length of this line is equal to the covariance between the two variables. In a similar manner, the same covariance value modifies the sulfate variance line. The result is two points defining the two column vectors of the matrix **C.**

In order to assist in interpreting the structure inherent in these data, we can impose a pictorial image. The elements of an $m \times m$ matrix can be regarded as defining points lying on an m-dimensional ellipsoid. For the covariance matrix **C** as defined by Eq. (26.29), the ellipse is illustrated in Fig. 26.10; the principal axes of this ellipse are given by the *eigenvectors* of **C,** and the *eigenvalues* represent the lengths of these axes. PCA is concerned with determining these axes and calculating their magnitudes. If we measure m variables on a set of objects, we can calculate an $m \times m$ matrix of variances and covariances and from this extract m eigenvectors and m eigenvalues. The m eigenvectors will be *orthogonal,* i.e., orientated at right angles to each other, and will be uncorrelated (Davis, 1973).

The two eigenvectors $\mathbf{V}_1$ and $\mathbf{V}_2$ extracted from the matrix **C** are

$$\mathbf{V_1} = \begin{bmatrix} 0.753 \\ 0.658 \end{bmatrix} \qquad \mathbf{V2} = \begin{bmatrix} -0.658 \\ 0.753 \end{bmatrix} \tag{26.30}$$

and the corresponding eigenvalues λ_1 and λ_2 are

$$\lambda_1 = 204.18 \qquad \lambda_2 = 19.94 \tag{26.31}$$

The significance of these values is illustrated in Fig. 26.10.

The total variance of the chloride and sulfate is the *trace* of their covariance matrix, i.e., the sum of the individual variances [124.37 + 99.75 = 224.12 $(\text{mg/liter})^2$] Of this sum, chloride concentration contributes 55.5 percent and sulfate concentration 44.5 percent. The sum of eigenvalues derived from a matrix is also equal to its trace, 204.18 + 19.94 = 224.12. The first eigenvalue represents about 91 percent of this total, and the remaining 9 percent is provided by the second principal axis.

The elements of the eigenvectors are sometimes referred to as *loadings,* and the original data can be transformed into new variables, called *scores,* by projecting the data onto the principal axes defined by the loadings. These scores are the *principal components.* Thus

$$\text{PC}(1)_i = 0.753x_{i,1} + 0.658x_{i,2} \tag{26.32a}$$

and

$$\text{PC}(2)_i = -0.658x_{i,1} + 0.753x_{i,2} \tag{26.32b}$$

that is, the loadings are the coefficients used to transform the original variables. The results for chloride and sulfate concentration data are presented in Table 26.8.

A scatter plot of the mean-centered principal components is presented in Fig. 26.11. The variance associated with PC(1) is 204.18 and with PC(2) is 19.94, and the correlation between PC(1) and PC(2) is zero.

From this basic introduction to PCA we can go on to analyze the full multivariate river water data. The eigenvectors and eigenvalues calculated from the covariance matrix of standardized variables (i.e., the correlation matrix) are given in Table 26.9. Our original seven variables can be transformed into seven new variables using the calculated seven

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TABLE 26.8 Principal Components Derived from the Original Chloride and Sulfate Concentrations Provide New Variables That Are Not Correlated and That Are Linear Combinations of the Original Data [$PC(1)_i = 0.753\ x_{i,1} + 0.658\ x_{i,2}$; $PC(2)_i = -0.658\ x_{i,1} + 0.753\ x_{i,2}$

Sample	PC(1)	PC(2)
1	−17.57	−3.41
2	−8.94	−1.39
3	14.35	−5.41
4	−14.96	0.96
5	−0.88	4.58
6	17.05	−6.05
7	−13.54	2.71
8	−2.07	1.64
9	13.25	−5.32
10	−15.42	−2.39
11	5.23	8.54
12	25.14	5.27
13	−15.95	−3.04
14	−0.97	4.67
15	15.28	−1.35

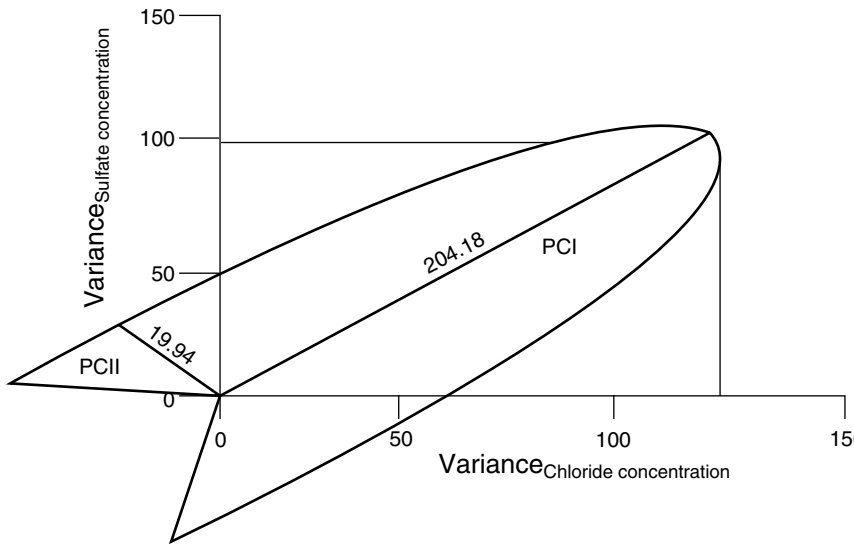

FIGURE 26.10 Pictorial representation of the eigenvectors and eigenvalues associated with the covariance matrix **C.**

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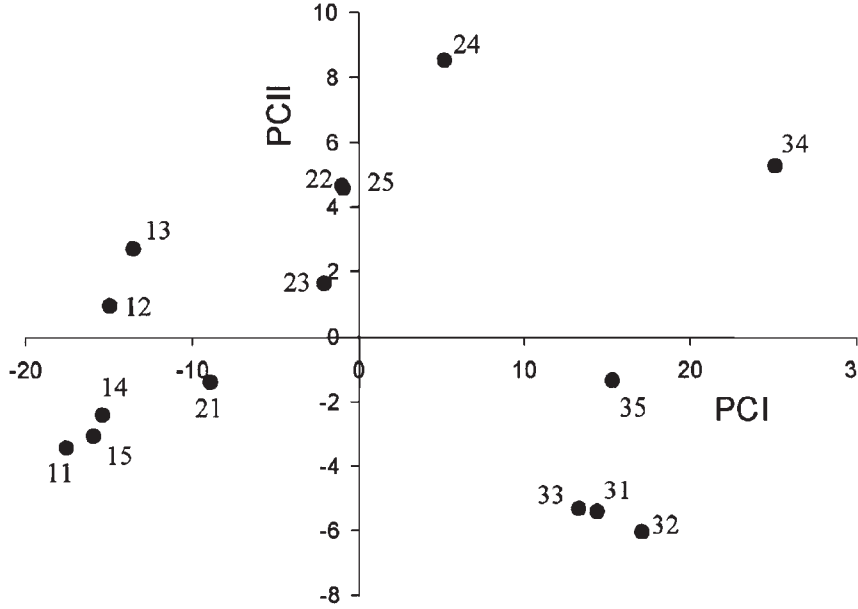

FIGURE 26.11 Scatter plot of mean-centered principal components of chloride and sulfate concentration data.

TABLE 26.9 Eigenvectors and Eigenvalues Derived from the Standardized River Water Data of Table 26.2

	Eigenvector						
Variable	I	II	III	IV	V	VI	VII
Nitrate	−0.386	−0.286	0.595	0.483	−0.018	−0.356	−0.231
Chloride	−0.317	0.568	0.001	−0.126	0.081	−0.586	0.459
Sulfate	−0.385	0.319	−0.375	0.623	0.262	0.389	−0.037
Phosphate	−0.386	−0.393	0.222	−0.243	0.325	0.381	0.581
Silicate	0.429	−0.114	−0.024	0.123	0.844	−0.273	−0.026
Conductivity	−0.430	0.163	0.034	−0.536	0.319	0.058	−0.629
Dissolved O_2	0.291	0.547	0.673	0.032	0.068	0.395	0.023
Eigenvalue	4.812	1.477	0.294	0.190	0.119	0.096	0.011
% Variance	68.75	21.10	4.20	2.71	1.70	1.37	0.16
Cumulative % variance	68.75	89.86	94.06	96.77	98.47	99.84	100.00

Note: The seven original variables are transposed to seven new linear combinations according to the weights prescribed by their seven eigenvectors. The information content of each eigenvector is related to its variance (the magnitude of its eigenvalue).

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CHEMOMETRIC TOOLS AND TECHNIQUES IN ENVIRONMENTAL MONITORING

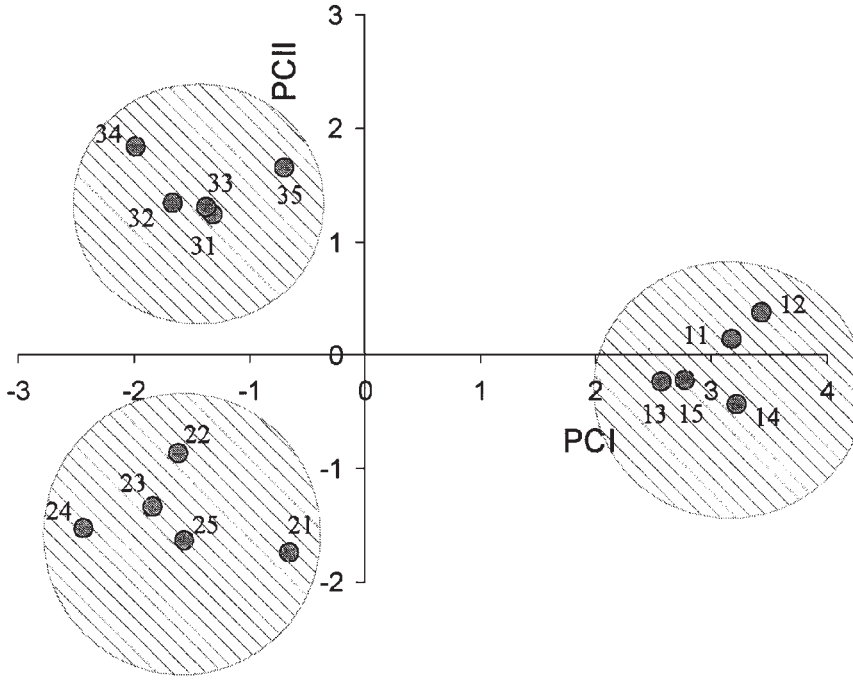

FIGURE 26.12 Scatter plot of the river water samples described by the first two principal components, PCI and PCII, calculated from the analytical data.

eigenvectors. The new variables are uncorrelated and are ranked according to the magnitude of the corresponding eigenvalue, i.e., according to their contribution to the total variance contained in the data. This interpretation of eigenvalues and eigenvectors leads to several useful generalizations (Reyment and Joreskog, 1993):

- The locations of eigenvectors along the principal axes of hyperellipsoids position the eigenvectors to coincide with the directions of maximum variance.
- The eigenvector associated with the largest eigenvalue determines the direction of maximum variance of the data points; the eigenvector associated with the second largest eigenvalue locates the direction of maximum variance orthogonal to the first.
- Eigenvectors are linearly independent vectors that are linear combinations of the original variables. They can be considered as new variables that are uncorrelated and account for the variance of the data in decreasing order of importance.
- The sum of the squared projections of data points onto the eigenvectors is proportional to the variance along the eigenvector. This variance is equal to the associated eigenvalue.

Inspection of Table 26.9 shows that almost 90 percent of the total variance in the original data can be accounted for in the first two factors derived from eigenvectors I and II. Using these two eigenvectors as the loadings or coefficients applied to the standardized data produces the principal components PCI and PCII. These are displayed as a bivariate scatter plot in Fig. 26.12. The three groups of samples, each containing five objects, are easily

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distinguished. This result is in agreement with our previous cluster analysis, but now we are able to see which features are providing the discriminatory power. The loadings plot of Fig. 26.13 displays the weight associated with each variable according to its contribution to PCI and PCII. It is clear that PCI separates the samples according to the simple ionic species and conductivity against silicate concentration and dissolved oxygen. PCII, on the other hand, provides a separation by chloride, sulfate, and dissolved oxygen (estuarine parameters).

The ability to perform such a chemical interpretation of eigenvectors is a major reason for the success of PCA in chemometrics. The process can be extended further to factor analysis (including both orthogonal and nonorthogonal rotation of the principal axes), but space prevents further discussion. The interested reader is encouraged to consult the many texts now available on this subject (e.g., Rayment and Joreskog, 1993; Brereton, 1992; Adams, 1995; Malinowski, 1991).

REGRESSION ANALYSIS

Identifying a relationship between variables and properties of objects leads us naturally to *regression analysis,* and the question of whether we can go on to predict some characteristic or property from measured variables. In the laboratory, regression analysis is used widely in the process of *calibration.* In analytical chemistry, for example, calibration is the procedure that relates instrumental measurements to the concentration of an analyte of interest. Calibration is one of the key steps associated with the analysis of many industrial, environmental, and biological materials. Calibration belongs to the field of study referred to as *modeling,* and many texts and articles are available describing its

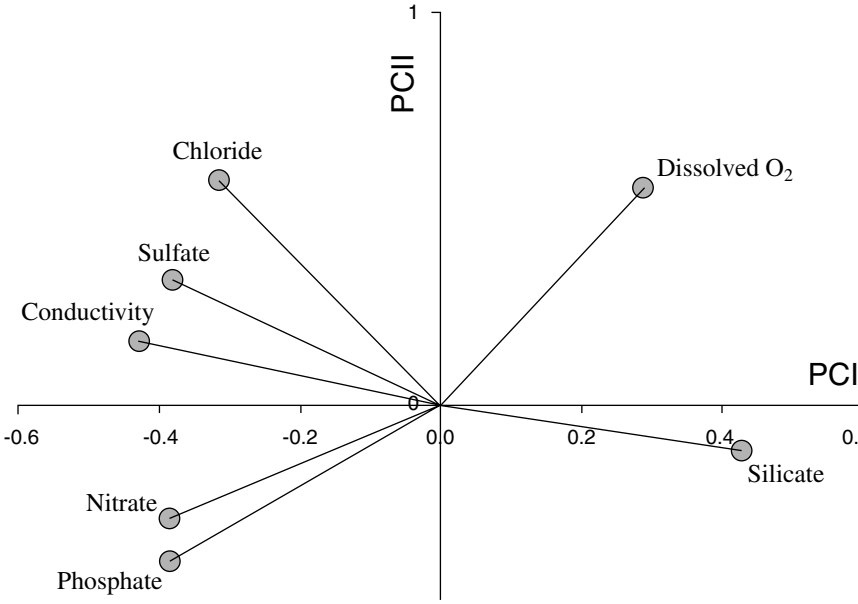

FIGURE 26.13 The weight associated with each original variable in forming PCI and PCII can be illustrated by this loadings plot.

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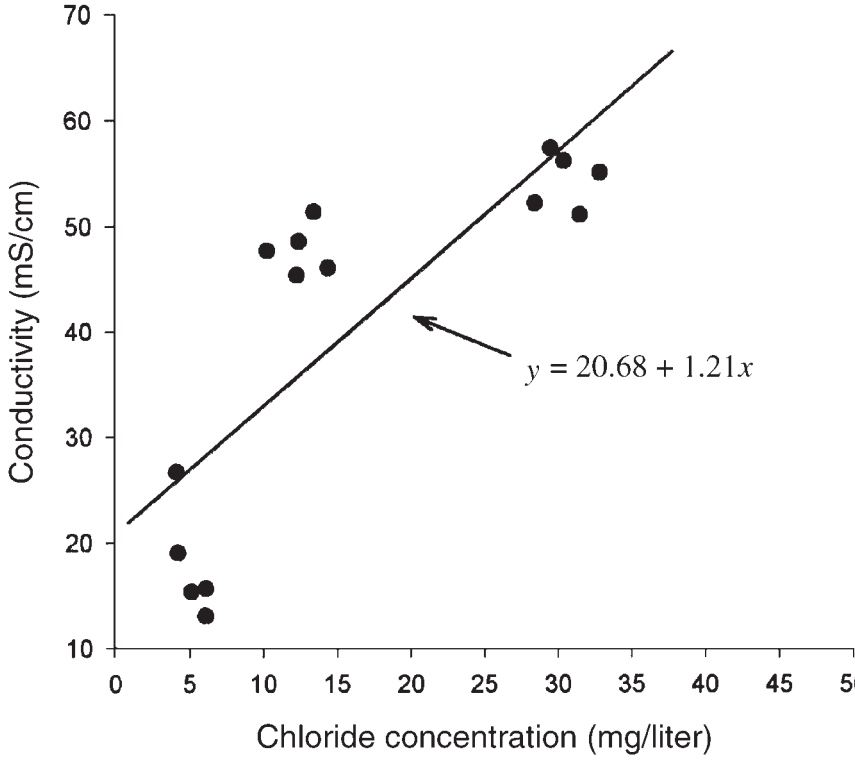

FIGURE 26.14 Scatter plot of water conductivity versus chloride concentration data (from Table 26.1) and the least-squares best-fit line.

theory, use, and application (e.g., Thomas, 1994). In this section we will concentrate on some of the important and basic features of modeling that have arisen in chemometrics and which may be considered as standard tools and techniques in modern chemical data analysis.

As an example and solely in order to illustrate the techniques discussed, we will refer to the relationship between water conductivity and the chemical species measured and presented in Table 26.1. It is not surprising that conductivity is proportional to ion concentration, and this is borne out by inspection of the correlation coefficients between conductivity and the levels of anions as presented in Table 26.3. For the sake of argument, let us assume that we have measured conductivity and chloride concentration only on our river water samples. The scatter plots in Figs. 26.1 and 26.14 illustrate the relationship between these variables. Our task is to determine the quantitative nature of this relationship and so be able to predict conductivity from chloride concentration. In this example, the conductivity is the *dependent* or *regressed variable,* denoted as *y,* and the other variable (chloride) is the *independent variable,* denoted *x.* Assuming a linear relationship between *y* and *x,* the fitted line will cross the *y* axis at point a_0 (the *intercept*) and will have a slope of a_1. The equation of the line is given by

$$\hat{y}_i = a_0 + a_1 x_i \tag{26.33}$$

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where $\hat{y}_i$ are estimated, modeled, values of y_i at specified values of x_i. We define the best-fitting line as that which minimizes the *deviations* between estimated and known, measured values of y, i.e.,

$$\Sigma(\hat{y}_i - y_i)^2 = minimum \tag{26.34}$$

Substitution of Eq. (26.33) into Eq. (26.34) and differentiating with respect to a_0 and a_1 to determine these unknown constants leads to the *normal equations*

$$a_0 n + a_1 \Sigma x_i = \Sigma y_i \tag{26.35}$$

$$a_0 \Sigma x_i + a_1 \Sigma x_i^2 = \Sigma (y_i x_i)$$

where n is the number of pairs of x and y values used.

This pair of simultaneous equations can be solved using the data from Table 26.1 to provide the *least-squares* best line:

$$\hat{y} = 20.68 + 1.21x \tag{26.36}$$

This line is illustrated in Fig. 26.14, and Fig. 26.15 presents a plot of predicted ($\hat{y}$) conductivity values versus actual (y) values.

The *goodness of fit* r^2 of the model line is given by

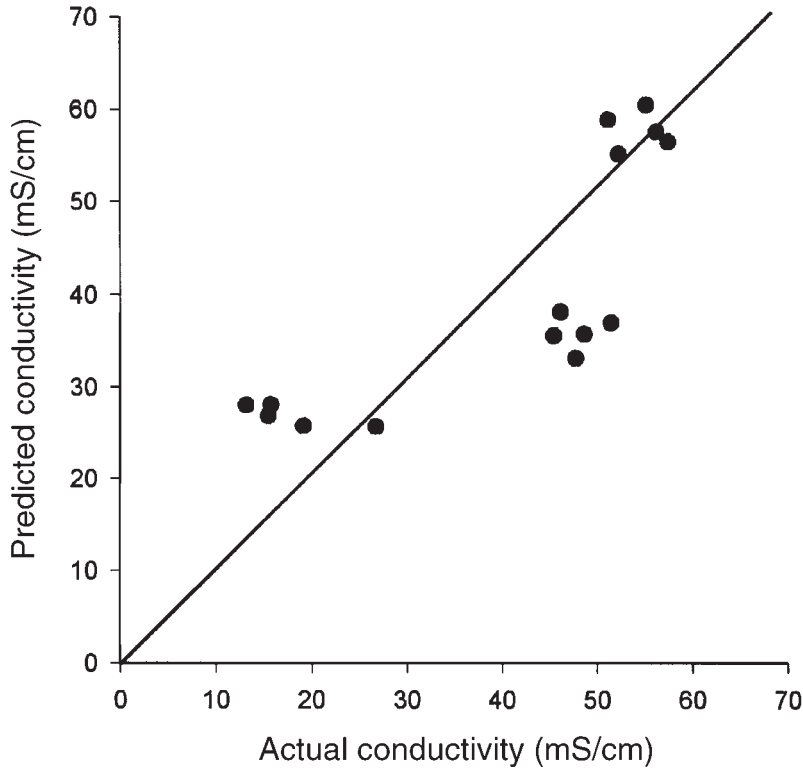

FIGURE 26.15 Predicted values of conductivity versus recorded conductivity values for the river water samples using a simple single-analyte least-squares model.

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$$r^2 = \frac{SS_R}{SS_T} \tag{26.37}$$

where SS_R is the sum of squares due to regression, that is,

$$SS_R = \Sigma(\hat{y}_i - \bar{y})^2 \tag{26.38}$$

And SS_T is the total sum of squares, that is,

$$SS_T = \Sigma(y_i - \bar{y})^2$$

r^2 is the square of the correlation coefficient discussed in preceding sections. The deviations between predicted values and known values $\hat{y}_i$ are referred to as *residuals,* and visual inspection is generally of value (Fig. 26.16).

This simple univariate linear model is obviously inadequate for accurately predicting conductivity values. Factors other than simple chloride concentration will influence the solutions' conductivity, and new terms can be added to the model to improve its performance. This is the subject of *multivariate calibration and modeling,* and such techniques are used extensively. Predicted values of the dependent variable for a new sample are obtained by evaluating a particular linear combination of dependent variable values. That is,

$$\hat{y}_i = a_0 + a_1 x_{1,i} + a_2 x_{2,i} + \cdots + a_m x_{m,i} \tag{26.39}$$

Multiple linear regression (MLR) is usually applied when no explicit causal model between dependent and independent variables is known. Instead, its application is driven by observed correlations between the variables. Strong correlation between the so-called independent variables can introduce mathematical instability into the model, and MLR is usually restricted to cases involving fewer than 10 independent variables. Computer software for performing MLR is widely available and an important component of all statistical

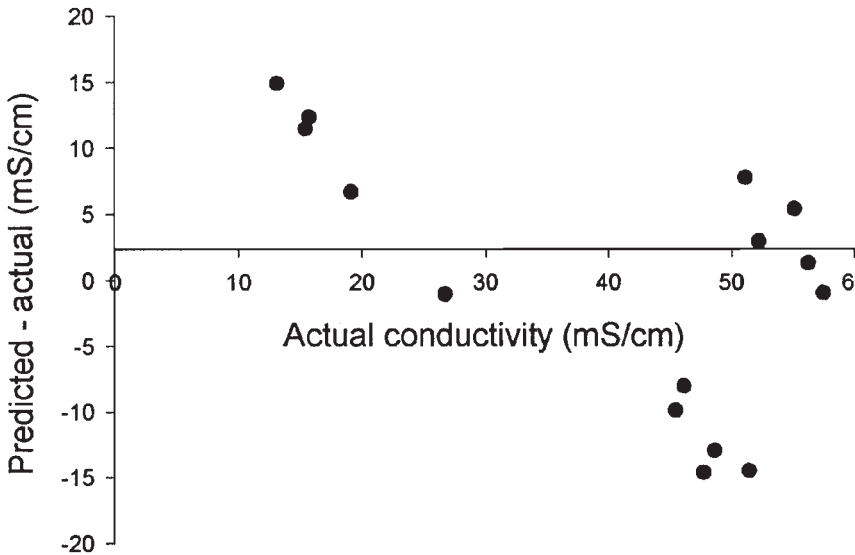

FIGURE 26.16 Residuals plot for conductivity values using the single-analyte least-squares model.

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packages. The user generally is allowed to select the independent variables to enter into the model, or this can be achieved automatically using stepwise forward regression or backward elimination regression. In both cases, statistical metrics are used to decide on the efficiency of the model should a variable be added or removed.

In recent years, regression techniques termed *soft-model-based methods* have become popular and have been applied successfully in many branches of analytical science. The two most common methods are principal components regression (PCR) and partial least-squares regression (PLSR). They are closely related techniques based on regressing eigenvectors from the data matrix onto the dependent variable. It is beyond the scope of this chapter to go into the detailed mathematical derivation of these models, but detailed information is available (Martens and Naes, 1991). Application of PCR to our river water data will serve to illustrate the use and application of the method.

Table 26.10 provides the eigenvectors from the variance-covariance matrix of the standardized independent variables (the correlation matrix). The correlation between each of the six principal components and conductivity is also given. It can be seen that the first principal component is by far the factor with the highest correlation, and a single univariate model can be postulated, that is,

$$\hat{y} = a_0 + a_1 PC(1) \tag{26.40}$$

Using the least-squares technique, then

$$\hat{y} = 40.08 + 7.655 PC(1) \tag{26.41}$$

A plot of $\hat{y}$ versus y is shown in Fig. 26.17. This simple univariate model is far superior to that of Eq. (26.36) but contains information from all six independent variables. Since it is a univariate model, Eq. (26.41) does not suffer from the mathematical instabilities associated with MLR (Eq. 26.39).

Following the procedure adopted with MLR, other principal components could be added to the model, with each containing different weights of all variables.

PCR and PLSR are now widely accepted and applied tools for multivariate modeling in the chemical sciences. Their use has extended the field for quantitative analysis and modeling, and many computer software packages are available for their application.

TABLE 26.10 Eigenvectors of the Six Independent Regression Variables and the Correlation Coefficient of Each Principal Component with Recorded Solution Conductivity

	Eigenvector					
Variable	I	II	III	IV	V	VI
Nitrate	0.4403	−0.2284	−0.6212	0.3277	0.2544	−0.4427
Chloride	0.3211	0.6147	0.0131	−0.2173	0.6569	0.2006
Sulfate	0.4136	0.3825	0.3334	0.6656	−0.3569	0.0337
Phosphate	0.4364	−0.3532	−0.2165	−0.0757	−0.1424	0.7822
Silicate	−0.4670	−0.1741	0.0240	0.6260	0.4942	0.3391
Dissolved O_2	−0.3514	0.5183	−0.6747	0.0696	−0.3346	0.1892
Correlation of PC with conductivity	0.912	0.240	0.005	−0.140	0.073	0.250

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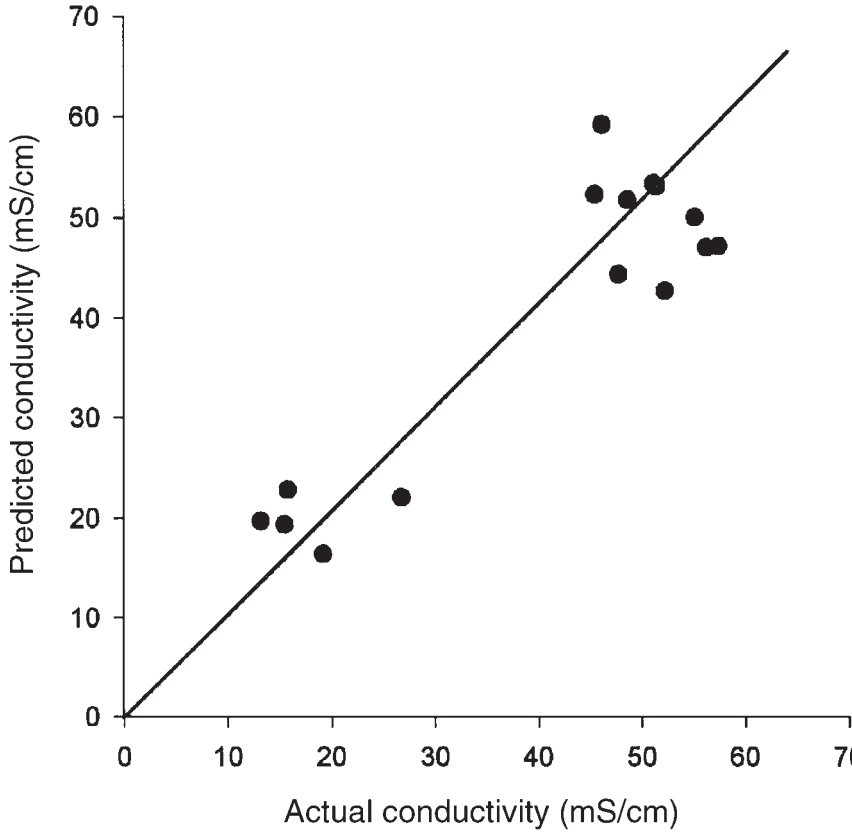

FIGURE 26.17 Predicted values of conductivity versus recorded conductivity values for the river water samples using a univariate model with the first principal component as the independent variable.

CONCLUSIONS

The field of chemometrics represents a broad and diverse discipline of chemical science, and in this chapter it has been possible to only briefly cover some of the more common techniques and methods in widespread use. Integrating aspects of mathematics, statistics, and computational science with chemistry provides a powerful set of tools with which chemists can view their measurements and data.

Specialist computer software for chemometricians is available from several reputable companies, but for exploratory analysis and a quick view of data structure, the ubiquitous spreadsheet can provide many useful functions. For more detailed analysis and data manipulation, one of the common mathematical programming packages is useful.

The interested reader is encouraged to experiment with data analysis and study the literature. The relatively small time involved in becoming familiar with chemometric methods will more than pay for itself in terms of interpreting and understanding the data.

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CHAPTER 27
TIME-SERIES ANALYSIS

Richard G. Brereton*

INTRODUCTION

Time series occur widely in environmental chemistry because many processes can be monitored over time. The formal aim of time-series analysis is to determine cyclic trends. Annual trends are common, a well-known example being the CO_2 concentration in Manua Lou (Keeling et al., 1995), which is most in the winter when fossil fuels are burned and least in the summer. This is imposed on a separate upward and noncyclic trend indicating a general increase in pollution with time. Very long-term trends such as occur in paleoclimatology (Berner, 1990) are well known. The earth's orbit around the sun changes over the millennia by a mathematically well-understood model, which results in climate changes that, for example, have caused the ice ages, consequently influencing the chemical fossil record. Systematic changes due to the tides have been observed, as well as more obvious diurnal rhythms.

In all cases, one or more cyclic trends can be described by a trigonometric function such that

$$f(t) = g(t)\cos(\theta t) + h(t) \tag{27.1}$$

An aim is to find the value of θ.

Time-series analysis has its origins in a variety of disciplines, especially economics, where statistics such as consumer preferences, economic growth, or unemployment often follow cyclic trends. For example, employment in a holiday resort may be most in the summer and so follows an annual cycle, but economic boom-bust often has a cycle of 5 to 10 years that also will influence employment. Normally, several trends are superimposed such that, for example,

$$f(t) = g(t)\left[\alpha\cos(\theta t) + ß\cos(\phi t) + \gamma\cos(\psi t)\right] + h(t) \tag{27.2}$$

could be a simple model of turn-over in the hotel trade, one factor being weekly (business trade being most in weekdays, holiday trade on weekends), the other being annual (holiday trade being most in the summer), and the final being long term according to how much money is in people's pockets. The values of the coefficients α to γ represent the strength or importance of these factors. Engineers also use time-series analysis, for example, in the analysis of circuits.

There are numerous texts in this area, a classic being that by Chatfield (1996), but others are recommended (Box and Jenkins, 1970; Anderson, 1971; Janacek and Swift, 1993). In geology, the book entitled, *Statistics and Data Analysis in Geology,* by Davis, contains much valuable information (Davis, 1986).

*This chapter is based in part on material published in R. G. Brereton, '*Introduction to chenometrics: Data Analysis for the Laboratory and Chemical Plant*', Wiley, Chichester, (2002).

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SAMPLING AND DATA PREPARATION

The first step is to observe a parameter, e.g., the concentration of CO_2 at various intervals in time. It is important to recognize that the sampling rate must relate to the maximum expected cyclic frequency, as discussed below.

Frequencies

There are various units for frequency, the most common are

- Cycles per unit time (often called hertz if time is measured in s)
- Radians per unit time

One cycle equals 2π radians. Ideally, a time series is sampled at regular intervals. Figure 27.1 shows two such series.

Of course the samples in Fig. 27.1 do not provide a very detailed picture of the sinewave, and the underlying data form a smoother pattern. The time series is said to be sampled *sparsely,* the underlying data being illustrated in Fig. 27.2. There may be entirely legitimate reasons for sampling at this rate; e.g., it may be expensive and time-consuming. In addition, the analytical technique may not be very accurate and may require a sample that uses a lot of material; e.g., in a geological core there would be a maximum rate at which the core could be sampled, limiting the feasible frequency.

Nyquist Frequency

Consider the time series of Fig. 27.2, each sampling point being indicated. If the time series were sampled at half the rate, it will appear that there is no oscillation because every alternative data point will be eliminated (Fig. 27.3). Therefore, there is no way to distinguish

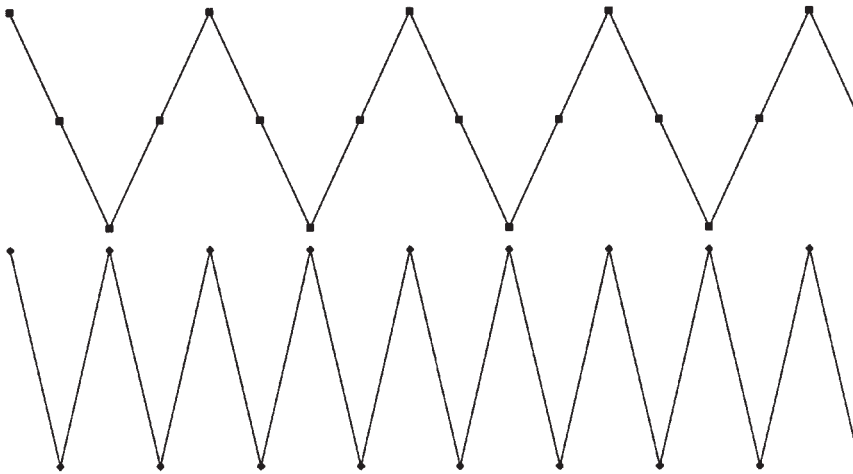

FIGURE 27.1 Two time series sampled once per unit time at a frequency of (*top*) 0.25 cycles or 0.5π radians per unit time and (*bottom*) 0.5 cycles or π radians per unit time.

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TIME-SERIES ANALYSIS

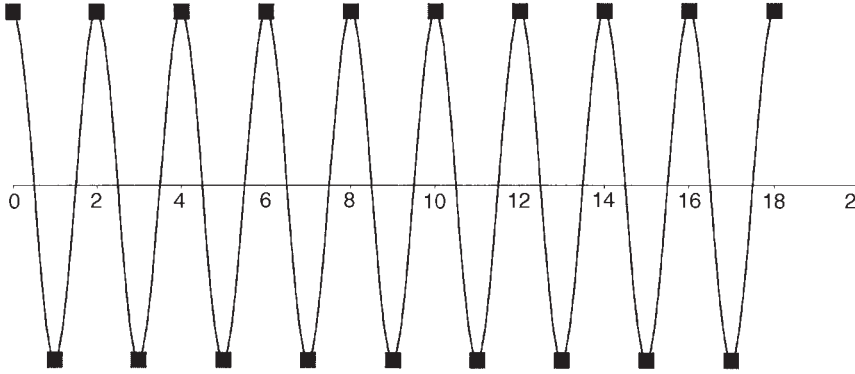

FIGURE 27.2 Sampling a time series.

such a series from a zero-frequency series. The oscillation frequency in Fig. 27.2 is called the *Nyquist frequency* or ν_{Nyq}. Anything that oscillates faster than this frequency will appear to be at a lower frequency, so a frequency of $\nu_{Nyq} + \delta$ will be indistinguishable from one of $\nu_{Nyq} - \delta$. A frequency of $2\nu_{Nyq}$ will appear to be indistinguishable from one of 0, and a frequency of $2\nu_{Nyq} + \delta$ will appear to oscillate at the rate of δ, and so on. Hence the sampling rate establishes the range of observable frequencies. The higher the rate, the greater is the range. In order to increase the frequency band, a higher sampling rate is required, and so more data points must be collected per unit time.

The equation

$$N = 2ST \tag{27.3}$$

links the number of samples obtained (e.g., $N = 100$), the range of observable frequencies (e.g., $S = 10$ cycles per year), and total sampling time (e.g., $T = 5$ years). In other words, in order to reliably observe a process that oscillates at the rate of 10 cycles per year, it is necessary to take at least 100 samples over a 5-year period. Higher frequencies are *folded over* or *aliased.* There are also a number of other factors that distort the apparent rate of oscillation close to the Nyquist frequency, especially in environmental samples that cannot always be obtained evenly in time, so a good rule of thumb is to have a sampling rate at least twice the minimum frequency required to observe a cyclic process. Therefore, to monitor a process that is suspected to be of a frequency of 5 cycles per hour, it is advisable to sample 20 times an hour or every 3 minutes, although it is still possible to obtain some information by sampling at a lower rate.

Interpolation

Most mathematical techniques for time-series analysis assume data that are equally spaced in time. In many applications, such as electronic circuits or spectroscopy, it is easy to obtain data of this nature. However, it is rare to be able to obtain regularly spaced samples in environmental monitoring. If the aim is to sample once a month, it is not necessarily possible to sample on exactly the same date each month, and in fact, since months have different lengths, even if this is achieved, the samples will still be unequally spaced in time.

In order to obtain an evenly spaced data set, it is normal to *interpolate* the raw data. There are a number of methods, but a simple one is as follows.

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TIME-SERIES ANALYSIS

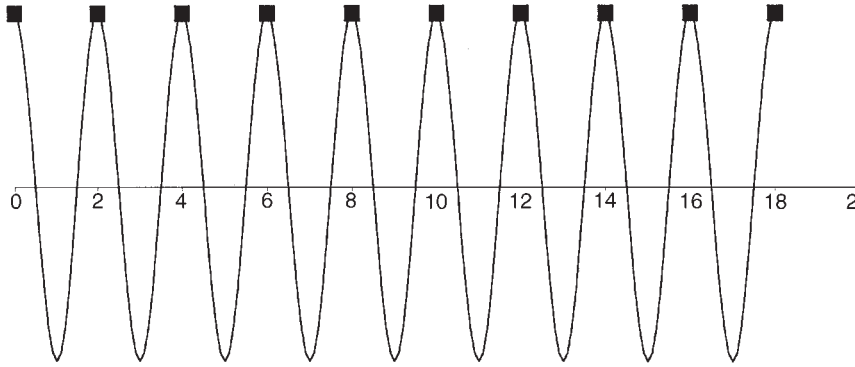

FIGURE 27.3 Sampling at twice the Nyquist frequency.

1. Establish a desired sampling interval, which normally should be slightly smaller than the average sampling interval for the overall data set. If this interval is given by δt, then the nth interpolated sample will be at time $t = n(\delta t - 1)$.
2. For each interpolated sampling time, see if a real sample is obtained at exactly that time, and if so, keep it.
3. If not, take the real samples immediately before and after the desired interpolated sampling time. If these occur at times t_1 and t_2, then the interpolated measurement is given by

$$\text{Interpolated } f(t) = \frac{(t - t_1) f(t_2) + (t_2 - t) f(t_1)}{t_2 - t_1} \tag{27.4}$$

A simple numerical example is presented in Table 27.1. For example, the interpolated measurement at $t = 2$ is $(0.3 \times 2.112 + 0.5 \times 1.854)/0.8 = 1.950$. Notice that some measurements will be ignored using this method of interpolation, such as the measurement at $t = 5.6$. More elaborate approaches that use all the initial information are possible but can distort the underlying time series substantially.

Preprocessing

In environmental chemistry it is quite common to scale the data prior to time-series analysis. Instead of raw measurements (e.g., the concentration of a heavy metal), a function of this is used in time-series analysis. A common form of scaling is logarithmic, an example being pH, which is the logarithm of $[H^+]$. If we want to study the change in acidity of seawater with time, it is usual to use a pH scale. This protects against very large values dominating the analysis.

A problem with logarithmic scaling is that in some circumstances an analyte may be undetected or at a very low concentration. Using unscaled data, a value of 0 is entirely acceptable, but the logarithm of 0 is undefined. One way around this is to replace all 0s by a number that is slightly less than the smallest positive number in the data set (e.g., half this) and then take the logarithm of this new value. For example, if the lowest detected concentration of a compound is 1 mg/ml, replace a 0 value (which often occurs because the real concentration is below detection limits) by 0.5 mg/ml prior to logarithmic scaling.

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TABLE 27.1 Interpolation

Time	Measurement	Interpolated time	Interpolated measurement
1	2.261	1	2.261
1.7	1.854	2	1.950
2.5	2.112	3	1.884
3.2	1.793	4	1.401
4	1.401	5	1.532
5.1	1.5456	6	0.784
5.6	0.771		
6	0.784		

NOISE

Imposed on the cyclic processes is noise. In fact, sometimes processes modeled by noise can be quite interesting in their own right, but time-series analysis is restricted to determining cyclic trends, and therefore, the techniques usually employed aim to reduce the influence of any noncyclic phenomena, which could be treated as a form of noise.

In many traditional areas of statistics, although the nature and origin of noise often are unknown, they frequently obey a normal distribution. Indeed, many statistical tests such as the *t* test and *F* test assume this and are only approximations in the absence of experimental study of such noise distributions.

In environmental sampling and analysis, there are three fundamental sources of noise or error (all error is noise, but not all noise is error):

1. The first involves sample preparation, e.g., dilution, weighing, and extraction efficiency. We will not discuss these errors further in this chapter, but it is important to recognize experimentally that this can distort measurements, especially if different investigators are employed during different phases in a project.
2. The second is inherent to a measurement technique. No instrument is perfect, so the signal is imposed on noise. The observed signal is given by

$$x = \tilde{x} + e \tag{27.5}$$

   where $\tilde{x}$ is the perfect or true signal, and e is a noise function. The aim of most signal-processing techniques is to obtain information on the true underlying signal in the absence of noise, i.e., to separate the signal from the noise.

3. The final relates to the underlying process within the environment. For example, there may be a seasonal variation in CO_2 levels in the air, but other factors affect this, some of which may occur more or less randomly. This nondeterministic element of the time series can seriously distort the apparent cyclic patterns.

In addition, there are two main types of noise.

Stationary Noise

The noise at each successive point in time does not depend on the noise at the previous point. The magnitude of the noise at sampling time *t* is independent of that at the previous sampling time. This noise is sometimes also called *white noise.*

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In turn, there are two major forms of stationary noise:

1. *Homoskedastic noise.* This is the simplest to envision. The features of the noise, normally the mean and standard deviation, remain constant over the entire data series. The most common type is modeled by a *normal distribution* with mean 0 and standard deviation dependent on the particular application. In most real-world situations, there are several sources of noise, but a combination of different distributions often tends toward a normal distribution (this is called the *central limit theorem*). Hence this is a good approximation in the absence of more detailed knowledge of a system.
2. *Heteroskedastic noise.* This type of noise is dependent on the size of the measurement, often proportional to intensity. The noise may still be represented by a normal distribution, but the standard deviation of that distribution is proportional to intensity. A form of heteroskedastic noise often appears to arise if the data are transformed prior to processing, a common method being a logarithmic transform used in many types of spectroscopy, such as electronic absorption spectroscopy, or infrared spectroscopy. The true noise distribution is imposed on the raw data, but the transformed information distorts this.

Figure 27.4 illustrates the effect of both types of noise on a time series. It is important to recognize that quite detailed models of noise are possible, but in practice, it is not easy to perform sufficient experiments to determine such distributions. Indeed, it may be necessary to obtain several hundred or thousand samples to obtain an adequate noise model, which is rarely feasible in environmental science. It is not possible to rely too heavily on published studies of noise distribution because each application is different, and the experimental noise distribution is a balance between several sources, which differ in relative importance for any sampling experiment.

In the absence of certain experimental knowledge, it is best to stick to a fairly straightforward distribution such as a normal distribution.

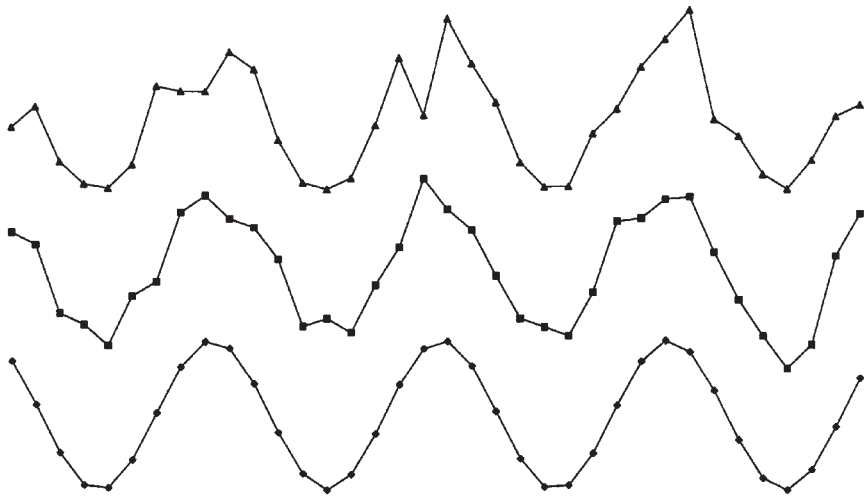

FIGURE 27.4 A time series (*bottom*) plus homoskedastic (*middle*) and heteroskedastic (*top*) noise.

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Correlated Noise

Sometimes the level of noise in each sample of a time series depends on that of the preceding one. Consider, for example, a parameter that depends on a cyclic change in temperature. Although there will be well-defined cycles over a year, there will be random local variations in temperature that are unlikely to be in the form of sudden blips. This type of noise is sometimes also called *nonstationary noise.*

Many such sources cannot be understood in great detail, but a generalized approach is that of *autoregressive moving average* (ARMA) noise.

1. The moving average component relates the noise at time i to the values of the noise at previous times. A model of order p is given by

$$e_i = \sum_{t=0}^{t=p} c_{i-t} e_{i-t} \tag{27.6}$$

where e_{i-t} is the noise at time $i - t$ and c_{i-t} is a coefficient. A simple approach for obtaining this type of noise is to put $p = 1$ and set the coefficient to 1. Under such circumstances,

$$e_i = g_i + e_{i-1} \tag{27.7}$$

where g_i may be generated using a normal distribution. Table 27.2 illustrates a stationary noise distribution and a moving average (MA) distribution generated simply by adding successive values of the noise so that, for example, the noise at time = 4 is given by $0.112 = -0.009 + 0.062$.

TABLE 27.2 Stationary and Moving Average Noise

Time	Stationary	MA
1	−0.128	
2	0.142	0.015
3	−0.060	0.082
4	0.051	−0.009
5	0.062	0.112
6	−0.144	−0.083
7	−0.106	−0.250
8	0.065	−0.041
9	0.055	0.120
10	−0.001	0.054
11	0.044	0.043
12	−0.084	−0.040
13	0.215	0.131
14	−0.011	0.204
15	−0.084	−0.095
16	−0.145	−0.229
17	0.115	−0.030
18	0.008	0.123
19	0.131	0.139
20	0.037	0.168

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2. The *autoregressive* component relates the noise to the observed value of the response at one or more previous times. A model of order p is given by

$$x_i = \sum_{t=0}^{t=P} c_{i-t} x_{i-t} + e_i \tag{27.8}$$

Note that in a full ARMA model, e_i itself is dependent on past values of noise.

There is a huge literature on ARMA processes, which are particularly important in the analysis of long-term trends such as in economics. It is quite likely that an underlying factor causing errors in estimates changes with time rather than fluctuating completely randomly. There have been developed a battery of specialized techniques to cope with such situations. The environmental chemist must be aware of these noise distributions, but there is rarely sufficient experimental evidence to establish highly sophisticated noise models. It is well advised, though, when studying a process to determine whether a stationary noise distribution is adequate, especially if the results of simulations are to be relied on, so an appreciation of basic models is important.

CORRELOGRAMS

After obtaining the samples and interpolating and preprocessing the data as required, it is necessary to use statistical techniques to examine the main cyclic trends in the data.

Autocorrelograms

A common approach is to calculate an autocorrelogram. Consider the information depicted in Fig. 27.3, which represents a process changing with time. It appears that there is some cyclicity, but this is buried within the noise. The data are presented in Table 27.15.

A correlogram involves calculating the correlation coefficient between a time series and itself shifted by a given number of data points called a *lag*. Correlation coefficients have values between $+1$ and -1 and are a method of determining the similarity between two series. They often are defined as

$$r_{xy} = \frac{cov_{xy}}{s_x s_y} \tag{27.9}$$

where cov_{xy} is the *covariance* between x and y and s_x is the standard deviation of x. The higher the magnitude, the more similar the two series are. Hence an autocorrelogram compares how similar a time series is with itself shifted by a certain number of points in time. If there is cyclicity, high correlation coefficients will be obtained for lags corresponding to cyclic frequencies.

If there are I datapoints in the original time series, then a correlation coefficient for a lag of l points will consist of $I - l$ data points. Hence, in Table 27.3, there are 30 points in the original time series but only 25 points in the data set for which $l = 5$. For a lag of 5, point number 1 in the shifted time series is the same as point number 6 in the original one. The correlation coefficient for lag l is given by

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TABLE 27.3 Data for Auto-Correlogram

i	data, /=0	data, /=5
1	2.768	0.262
2	4.431	1.744
3	−0.811	5.740
4	0.538	4.832
5	−0.577	5.308
6	0.262	3.166
7	1.744	−0.812
8	5.740	−0.776
9	4.832	0.379
10	5.308	0.987
11	3.166	2.747
12	−0.812	5.480
13	−0.776	3.911
14	0.379	10.200
15	0.987	3.601
16	2.747	2.718
17	5.480	2.413
18	3.911	3.008
19	10.200	3.231
20	3.601	4.190
21	2.718	3.167
22	2.413	3.066
23	3.008	0.825
24	3.231	1.338
25	4.190	3.276
26	3.167	
27	3.066	
28	0.825	
29	1.338	
30	3.276	

$$r_l = \frac{\sum_{i=1}^{I-l} x_i x_{i+p} - \frac{1}{I-l}\sum_{i=1}^{I-l} x_i \sum_{i=l}^{I} x_i}{\sqrt{\sum_{i=1}^{I-l} x_i^2 - \frac{1}{I-l}\sum_{i=1}^{I-l} x_i}\ \sqrt{\sum_{i=1}^{l} x_i^2 - \frac{1}{I-l}\sum_{i=l}^{I} x_i}} \tag{27.10}$$

Sometimes a simplified equation is employed:

$$r_l = \frac{\left(\sum_{i=1}^{I-l} x_i x_{i+p} - \frac{1}{I-l}\sum_{i=1}^{I-l} x_i \sum_{i=l}^{I} x_i\right)/(I-l)}{\left(\sum_{i=1}^{I} x_i^2 - \frac{1}{I}\sum_{i=1}^{I} x_i\right)/I} \tag{27.11}$$

The latter equation is easier for repetitive computations because the term at the bottom needs only to be calculated once, and such shortcuts were helpful prior to the computer age.

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However, using modern packages, it is not difficult to use the first equation, which will be used in this chapter. Notice that the two calculations will provide slightly different answers.

There are a number of properties of the autocorrelogram:

1. For a lag of 0, the correlation coefficient is 1.
2. It is possible to have negative lags as well as positive lags, but for an autocorrelogram, $r_l = r_{-l}$, and sometimes only half the correlogram is displayed.
3. The closer the correlation coefficient is to 1, the more similar the two series are. If a high correlation is observed for a large lag, this indicates cyclicity.
4. As the lag increases, the number of data points used to calculate the correlation coefficient (the *window*) decreases, and so r_l becomes less informative and more dependent on noise. Large values of l are not advisable; a good compromise is to calculate the correlogram for values of l up to $I/2$, or half the points in the original series.

The autocorrelogram for the time series of Fig. 27.5 is presented in Fig. 27.6. The cyclic pattern is now much clearer than in the original data. Note that the graph is symmetric about the origin, as expected, and the maximum lag used is 14.

A correlogram emphasizes cyclic features. Sometimes noncyclic trends are superimposed over the time series. Such situations occur regularly in economics. Consider trying to determine the factors relating to expenditures in a seaside resort. A cyclic factor undoubtedly will be seasonal, there being more business in the summer. However, other factors such as interest rates and exchange rates also will come into play, and the information will be mixed up in the resulting statistics. Expenditure also can be divided into food, accommodation, clothes, and so on. Each will be influenced to a different extent by seasonality. In environmental chemistry, correlograms are most valuable when time-dependent noise interferes with stationary noise, e.g., in a river where there may be specific types of pollutants or changes in chemicals that occur spasmodically but once discharged take time to dissipate.

A correlogram also can be represented in the form of probabilities, e.g., the chance that there really is a genuine underlying cyclic trend of a given frequency. Such calculations, though, make certain definitive assumptions about the underlying noise distributions and experimental error and are not always applicable to a given system.

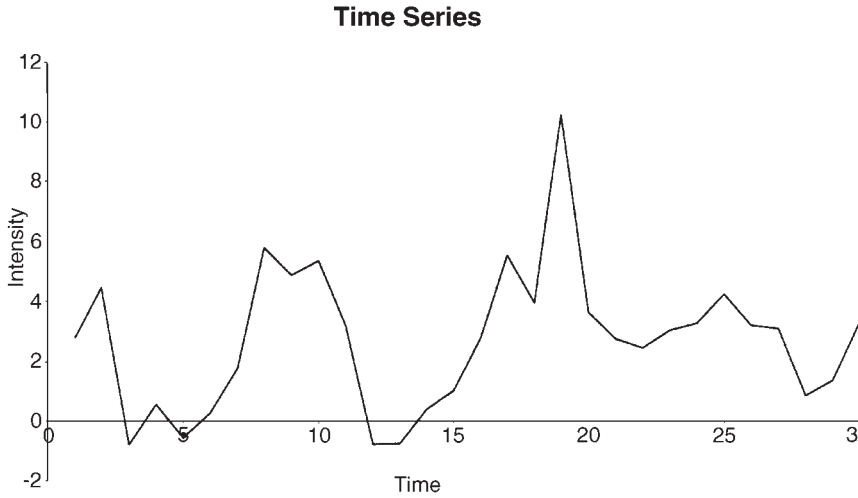

FIGURE 27.5 Time series used for calculation of an autocorrelogram.

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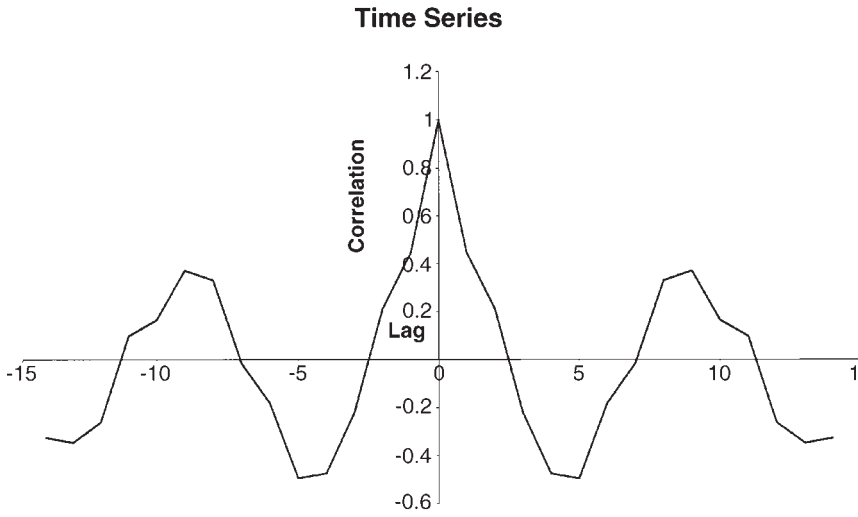

FIGURE 27.6 Auto-correlogram for data of Fig. 27.5.

Cross-Correlograms

It is possible to extend these principles to the comparison of two independent time series. Consider measuring the levels of Ag and Ni in a river over time. Although each may show a cyclic trend, are there trends common to both metals? The cross-correlation function between x and y can be calculated for a lag of l, that is,

$$r_l = \frac{c_{xy,l}}{s_x s_y} \tag{27.12}$$

where $c_{xy,l}$ is the covariance between the functions at lag l, given by

$$c_{xy,l} = \sum_{i=1}^{I-l} (x_i - \bar{x})\,(y_{i+1} - \bar{y})/(I - l) \qquad \text{for } l \geq 0$$

$$c_{xy,l} = \sum_{i=1-1}^{I} (x_i - \bar{x})\,(y_{i+1} - \bar{y})/(I - l) \qquad \text{for } l < 0$$

and s corresponds to the appropriate standard deviations. Note that the average of x and y strictly should be recalculated according to the number of data points in the window, but in practice, provided that the number of data points is not too small, using the overall average is acceptable. Notice that it is not necessary that the two time series are of equal length, but regions of equal size must be found for each correlation function. It is, of course, essential that the two time series are sampled or interpolated to be equally spaced in time.

The cross-correlogram is no longer symmetric about 0, a negative lag not giving the same result as a positive lag. Table 27.4 presents two time series. The raw time series and the corresponding cross-correlogram are illustrated in Fig. 27.7. The correlogram suggests that both contain a cyclic trend at around 8 data points, since the correlograms exhibit a strong minimum at $l = \pm 8$.

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TABLE 27.4 Two Time Series for Calculation of Cross-Correlogram

Series 1	Series 2
2.768	1.061
2.583	1.876
0.116	0.824
−0.110	1.598
0.278	1.985
2.089	2.796
1.306	0.599
2.743	1.036
4.197	2.490
5.154	4.447
3.015	3.722
1.747	3.454
0.254	1.961
1.196	1.903
3.298	2.591
3.739	2.032
4.192	2.485
1.256	0.549
2.656	3.363
1.564	3.271
3.698	5.405
2.922	3.629
4.136	3.429
4.488	2.780
5.731	4.024
4.559	3.852
4.103	4.810
2.488	4.195
2.588	4.295
3.625	4.332

Multivariate Correlograms

In the real world, there may be a large number of variables that change with time, e.g., the concentration of several polyaromatic hydrocarbons in industrial waste. Rather than calculating correlograms for each individual parameter, it is often valuable to calculate the principal compound or similar multivariate function of the raw data and then look at the cyclic trends with time.

FURTHER METHODS

Smoothing Functions

Sometimes it is desirable to smooth the data either before or after a correlogram has been calculated. A variety of methods can be applied.

The simplest are linear filters whereby the resulting smoothed data are approximated by a linear function of the raw data. Normally, this involves using the surrounding data points in time to recalculate a value for point *i.* Algebraically, such functions are expressed by

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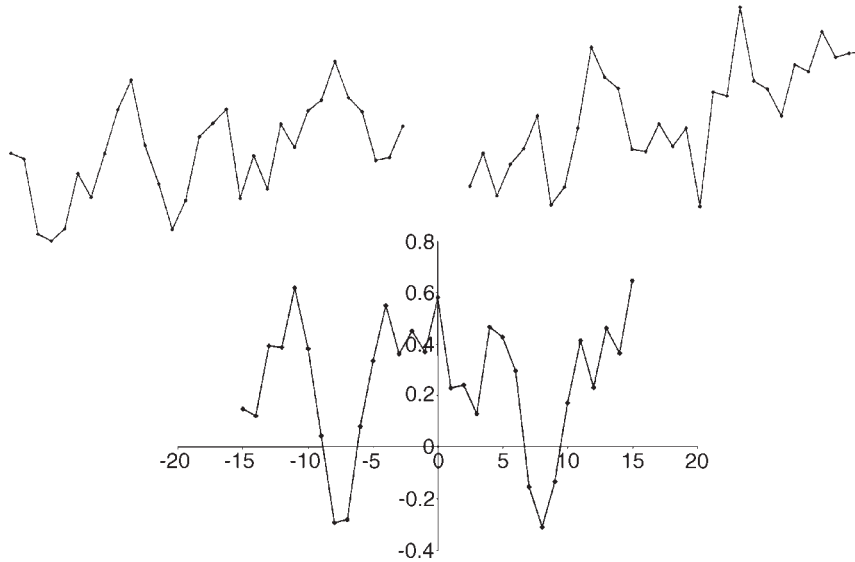

FIGURE 27.7 Example of two time series and their cross-correlogram.

$$x_{i,\text{new}} = \sum_{j=-p}^{p} c_j x_{i+j} \tag{27.13}$$

where c_j is often called a *weight.*

One of the simplest is a three-point moving average (MA). Each point is replaced by the average of itself and the points before and after, so in the preceding equation,

- $p = 1$
- $c_j = 1/3$ for all 3 points

The filter can be extended to a five-, seven-, etc.-point MA, the weights being equal to $1/(2p + 1)$. The effect of a five-point moving average filter is presented in Fig. 27.8. The number of points used in the calculation depends on the nature of the data:

- The more the points in the filter, the greater is the reduction in noise, but the higher is the chance of blurring the signal. This can have a significant effect for oscillations close to the Nyquist frequency.
- The number of points $(2p + 1)$ in the filter is the *window.*

Several other MA methods have been proposed in the literature, two of the best known being three-point windows, namely, the Hanning window (named after Julius Von Hann) (weights 0.25, 0.5, and 0.25) and the Hamming window (named after R. W. Hamming) (weights 0.23, 0.54, and 0.23)—not to be confused but with very similar effects.

Fourier Analysis

A final technique sometimes used is to Fourier transform (FT) a time series. There are several excellent texts on Fourier transform techniques, and we will use the discrete Fourier

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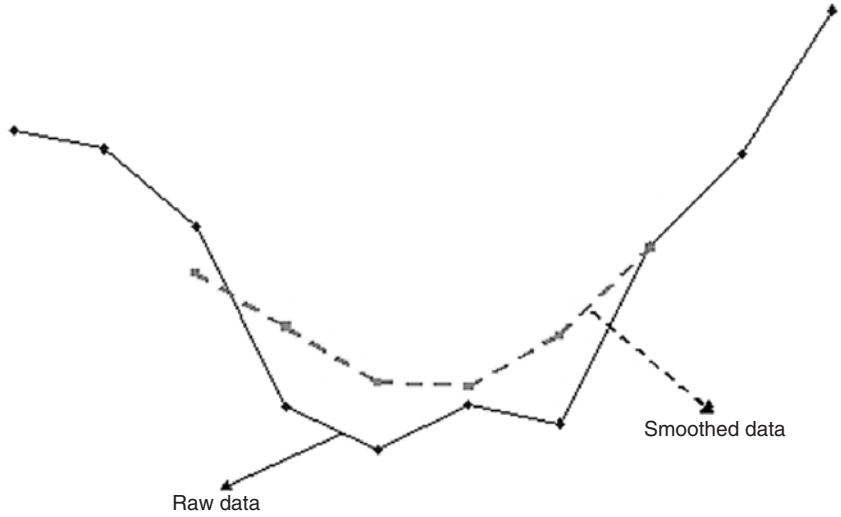

FIGURE 27.8 Smoothing using a five-point moving average.

transform (DFT). The method can be applied to time series of any size and is not limited to data sets whose length equals a power of 2. We will not discuss the theory of FTs in this chapter.

However, by Fourier transforming a correlogram, cyclically repeating features are transformed into peaks, so the frequencies can be presented along the horizontal axis (Fig. 27.9). This transform is sometimes called a *spectrum,* and the procedure of calculating a correlogram followed by Fourier transformation is often called *spectral analysis* in statistical texts, which must be distinguished from the chemist's terminology, which has a particular physical connotation.

It is important to recognize that although it is also possible to FT a raw time series, the clarity of the transform is normally quite poor because it will be dominated by noise, sampling errors, etc., and the procedure for computing a correlogram prior to Fourier transformation improves the quality of the spectrum greatly. It is possible to FT a cross-correlogram, in which case the frequencies will be those which are common to two time series. The vertical axis relates to the *strength* or importance of an oscillation. Finally, there are a number of methods for smoothing and enhancing the quality of these transforms.

CONCLUSION

Time series are very common in environmental monitoring, and there are a number of well-established statistical techniques for handling these types of data. There are many potential steps in a full spectral analysis, such as interpolation, preprocessing, smoothing, calculation of correlograms, and Fourier transformation. The resulting data are normally presented graphically, usually as a correlogram. If a good idea of noise distributions is available, it is sometimes possible to produce a numeric value of the probability of underlying cyclic processes.

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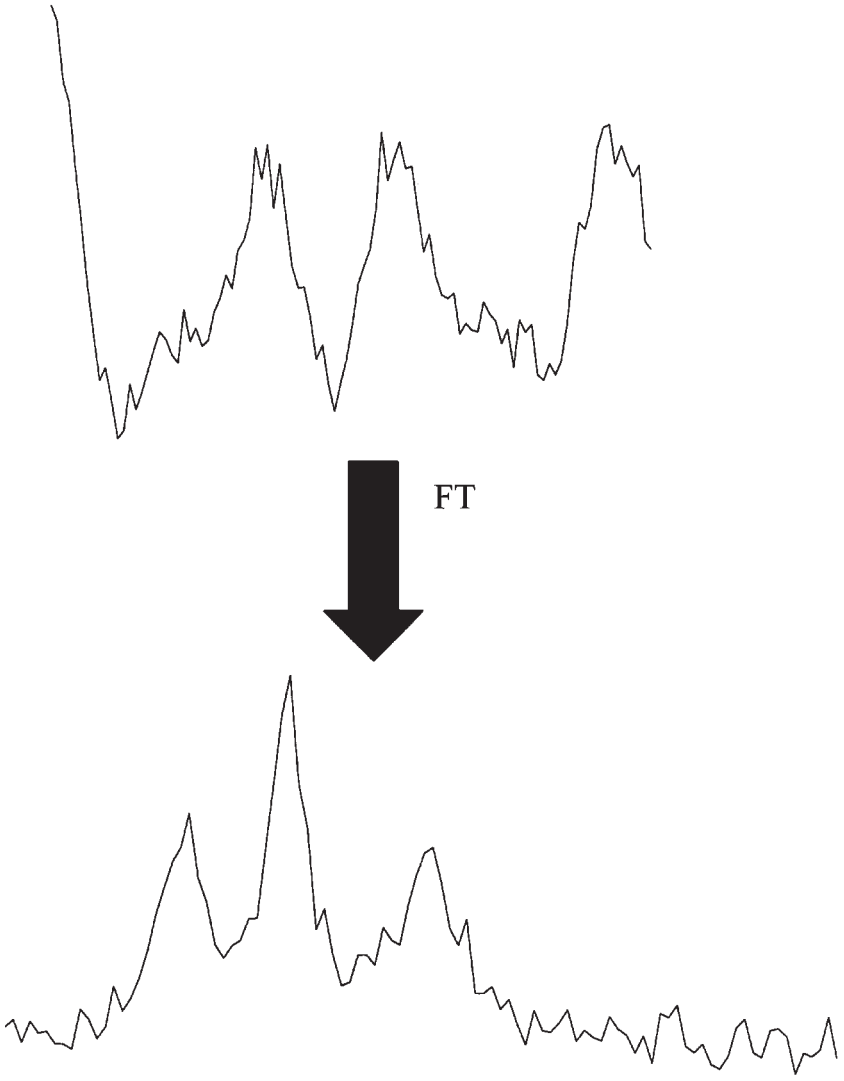

FIGURE 27.9 Fourier transform of a correlogram.

Quite different techniques are necessary for the analysis of noncyclic trends, but these are conventionally not called time-series analysis, and the aim of the techniques introduced in this chapter is to treat these trends as noise and reduce their influence.

Many methods for time-series analysis have their origins in economics, and some of the most comprehensive software packages are available to econometricians. It is easy to perform most straightforward calculations using common spreadsheet software such as Excel, which has functions for correlation coefficients and other simple manipulations, but more elaborate computations are available in most common economics packages or enhancements of statistical software.

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