much interesting structure, but they lack the full detail of both boundary currents and mesoscale eddies. The art of 'parametrizing' the effects of eddies so as to allow their neglect in detail is an active area of current research.

Conclusion

We have argued that mesoscale eddies contain large kinetic energy, comparable with that of the time-averaged ocean circulation. Eddies are crucial to the transport of heat, momentum, trace chemicals, biological communities, and the oxygen and nutrients relating to life in the sea. They are also active in air–sea interaction, both through response to weather and in shaping the patterns of warmth that drive the entire atmospheric circulation.

As a member of the huge family of turbulent motions, eddies contribute to the stirring and mixing of the oceans, to the creation of its basic, layered density field, and to its general circulation. The fundamental physics of eddies is expressed in terms of its potential vorticity, which is a tracer-like property that 'moves with the fluid.' The distribution of potential vorticity can be turned into knowledge of the currents and fluid density variations. The smallness and great energy of mesoscale eddies, the great thermal and chemical capacity of the oceans, and the slowness of the circulation conspire to challenge computer models, but rapidly increasing computer power is producing ever better representations of the ocean's fabric. At present, rather short-lived experiments (a few decades duration) can be carried out that resolve the global field of eddies, intense currents, and wind-driven gyres, whereas the slower features important to long-term climate change cannot be examined while also resolving mesoscale eddies. Nevertheless, several important physical processes like turbulent mixing, convection, upper mixed layer dynamics, and interaction with complex bottom topography are not yet well simulated by computer models. Many of the important applications of physical circulation in the oceans involve vertical motion: for biological communities, for transport of trace gases and their exchange with the atmosphere, for ocean/atmospheric climate interaction. This vertical motion of the fluid is particularly difficult to predict without fully resolving the detail of mesoscale – and smaller – features.

See also

General Circulation Models. Ocean Circulation. Ocean Colour from Satellites. Rossby Waves. Satellite Remote Sensing SAR. Satellite Remote Sensing of Sea Surface Temperatures.

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METAL POLLUTION

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doi:10.1006/rwos.2001.0054

Introduction

Marine pollution has been defined as 'the introduction by man, directly or indirectly, of substances or energy to the marine environment resulting in deleterious effects such as hazards to human health; hindrance of marine activities, including fishing; impairment of the quality for the use of sea water; and reduction in amenities' (GESAMP, 1990). Approximately 45% of people on Earth live within 150 km of the coast and marine pollution occurs as a consequence of increases in population density and industrialization. The problems of marine pollution are generally limited to nearshore waters rather than the open ocean, with the main impacted areas being estuaries, fjords, rias, and their adjoining shelf seas (**Figure 1**).

In the marine environment, metals such as iron, vanadium, copper, and zinc are essential for certain biochemical reactions in organisms, but even in moderately contaminated estuaries these metals contribute to stress in marine biota. By virtue of their toxic and bioaccumulative properties both cadmium and mercury are regarded as 'Black List' substances, while lead is on the 'Grey List'. These elements have little or no biochemical function and, while tolerable in minute quantities, exhibit toxic effects above critical concentrations. Mercury has a complex marine chemistry and exists in various forms, such as inorganic mercury, organically complexed mercury (with natural dissolved organic carbon), as a dissolved gas, Hg^0, and as the methylated species

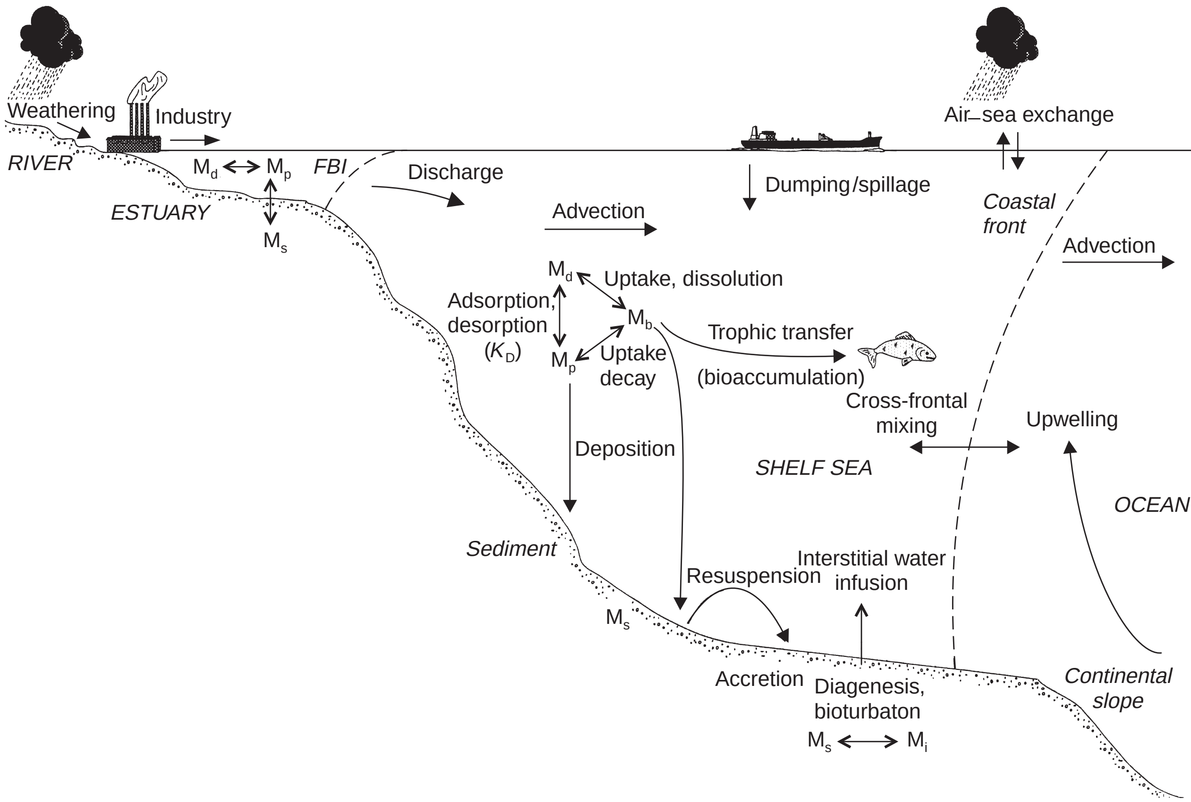

Figure 1 Processes affecting the transport and biogeochemistry of metal pollutants in estuaries and shelf seas. FBI = fresh water–brackish water interface. Metal compartments are designated. M_d, dissolved; M_p, suspended particulate; M_s, sediment; M_i, interstitial water; M_b, biogenic particulate.

monomethyl mercury (MMHg) and dimethyl mercury (DMHg). Both MMHg and DMHg are present in the water column in sediments and in the tissues of marine organisms. Thus, depending on their physicochemical state or bioavailability, metals will impact upon different parts of the marine food web and in some cases bioaccumulation and/or biomagnification occurs, which may, ultimately, expose humans to a potential health hazard.

When attempting to assess the biogeochemical pathways and health impact of metals it is crucial to determine the total concentration accurately and where possible to identify and quantify the physical and chemical forms, or species. The analytical determination of metals in sea water has had a difficult history and many measurements reported in the literature prior to about 1985 should be treated with caution. Major strides have been made in the minimization of contamination during sample collection, storage, and preparation and in the application of sensitive analytical techniques, sometimes coupled with methods for the separation of metal species. The concentrations of dissolved metals have been revised downwards in recent years as a consequence of the introduction of these advances, together with improvements in analytical quality assurance, including appropriate use of certified reference materials.

The sources and pathways of metals through the coastal environment are complex (see **Figure 1**). Interfacial processes play a key role in their passage from the land to the sea. In estuaries the composition of river water may be modified by physicochemical processes at the fresh water–brackish water interface (FBI), where strong gradients of salinity, temperature, concentration and type of suspended particulate matter (SPM), pH and dissolved oxygen exist. Metal exchanges, between the dissolved and particulate phases, take place under the influence of these gradients and this process is quantified by the partition coefficient (K_D, $\mathrm{l\,kg^{-1}}$) (eqn [1]).

$$K_D = \frac{[M_p]}{[M_d]} \qquad [1]$$

Here $[M_p]$ is the metal concentration of SPM in $\mathrm{nmol\,kg^{-1}}$ (or $\mathrm{\mu g\,kg^{-1}}$), and $[M_d]$ is the dissolved metal concentration in $\mathrm{nmol\,l^{-1}}$ (or $\mathrm{\mu g\,l^{-1}}$). Coastal sediments can contain elevated concentrations of dissolved metals in their interstitial waters which may be exchanged across the sediment–water interface via molecular diffusion or by resuspension and in soft sediments by enhanced diffusion due to bioturbation from burrowing organisms (**Figure 1**). The mercury cycle is complicated by the fact that microbial activity, in sediments and the water column, can produce DMHg and Hg^0, both of which are volatile and can exchange across the air–sea interface.

Anthropogenic and Natural Inputs

Dissolved and particulate metals in rivers and estuaries are derived from natural weathering processes in the catchment area, and reflect the geological composition of the watershed (see **Table 1** for the crustal abundance of selected metals) and the local climatic conditions. Natural concentrations of metals can be augmented in catchment areas that are mineralized, and there may be a significant anthropogenic perturbation downstream because of mineral extraction and processing. In densely populated regions, metals originate from a wide range of industrial, domestic and agricultural uses, and their inputs into river systems have increased significantly over the past two centuries. Regulated dredging and dumping of metal pollutants at sea, inadvertent spills, and illegal discharge all add to the complexity of anthropogenic inputs to the aquatic environment. Thus, our ability to unravel natural versus anthropogenic inputs is often complicated by the significant and uncontrolled human perturbation of catchments and their river systems. Only where metal compounds are entirely of anthropogenic origin, such as tributyl tin, can the human impact be evaluated. In the case of lead, however, it has been possible to identify man-made inputs via the application of inductively coupled plasma mass spectrometry (ICP-MS) to the determination of lead isotopic ratios (e.g., ^{206}Pb to ^{207}Pb) which have distinct signatures in leaded gasoline.

Because a significant proportion of the marine environment has been altered by anthropogenic activities, natural concentrations for dissolved and particulate metals are difficult to obtain unambiguously. Baseline values are often assumed from analyses of samples from remote systems that are considered to be 'pristine' or from metal analyses of sediment horizons dated as being prior to the industrial revolution. Another approach to assessing man's impact on the global ocean is to compare the rates of metal emission to the atmosphere from natural and anthropogenic sources. In **Table 1** the 'interference factor' is > 1 for all metals, with relatively high values for lead and cadmium, suggesting that there is a significant anthropogenic alteration of their natural cycles.

Macrotidal estuaries have strong internal cycles and sediment particles may be retained within the system for years, and in large estuaries for decades. Thus, estuaries are a significant repository for metals, although no systematic inventories of the sediment metal burden have been made. Suspended particles advecting from estuaries into shelf seas are trapped in the coastal margin and estimates show that $\sim 90\%$ of the fluvial suspended load (and associated metals) of the Mississippi, St. Lawrence, Rhône, and rivers in the south east of the United States is deposited in the coastal margin. Early diagenesis of deposited material may result in release of metals into sediment pore waters and, since the dissolved phase is generally considered to be more bioavailable, the composition of interstitial waters could be more important in the overall toxicity of the sediments than is their total metal content. Accurate quantification of interstitial water composi-

Table 1 Fluxes of metals to the atmosphere from natural and anthropogenic sources. The interference factor is the ratio of the anthropogenic flux to the natural flux. The generic term 'combustion' refers to various combinations of coal, oil, and wood combustion and refuse incineration

Metal	*Crustal abundance (nmol g^{-1})*	*Atmospheric emission rate (t y^{-1})*			*Major uses of metals and their compounds*
		Natural	*Anthropogenic*	*Interference factor*	
Cadmium	2	1.4	7.6	5.3	Nonferrous metal production; cement/fertilizer manufacture; combustion
Copper	510	28	35	1.2	Nonferrous metal production; biocides; combustion
Mercury	0.4	2.5	3.6	1.5	Chlorine cells; gold mining operations; combustion
Lead	80	12	332	27	Petroleum additive; nonferrous metal production; combustion
Zinc	2000	45	131	3.0	Nonferrous metal production; steel/iron manufacturing; cement production

tion in estuaries and shelf seas is hindered because of the heterogeneous distribution of sediment texture and because a satisfactory method has not yet been developed for application in shallow waters that are highly dynamic.

Particulate metals deposited in the coastal margin are slowly advected onto the continental slope by seabed currents and wave action. Sediment diagenesis and diffusion releases dissolved metals into the oceanic water column, where they may be involved in upwelling processes at the shelf break (**Figure 1**). Comparisons of the relative magnitudes of the combined river and atmospheric fluxes with the upwelling flux suggests that the latter is greater by a factor 2 for copper, of 2–7 for zinc, and of about 10 for cadmium. In contrast, for inorganic mercury the upwelling flux to shelf seas is half the magnitude of the combined river and atmospheric input, while for methylated mercury the main source to shelf seas is the upwelling flux.

Distributions

The temporal and spatial distributions of dissolved metal pollutants are highly dependent on two important processes in the coastal boundary zone.

Local hydrodynamics. Water is dispersed in estuaries and coastal waters according to the local hydrodynamics, which can be characterized by the flushing time. The dispersion and dilution of metal pollutants from point and diffuse sources, and therefore their range of concentrations, will be affected by the flushing time. A flushing time of 0.5 y for coastal waters is typical for the North Sea and Irish Sea, a value of 2 y is representative of the waters around Bermuda, while a value of 5 y is representative of a semi-enclosed sea such as the Baltic. Waters with longer flushing times will register a slower response to changes in metal inputs, whereas changes in metal concentrations will be detected earlier in waters with shorter flushing times.

Particle–water interactions. Metal partitioning between the dissolved and particulate phases is a crucial factor because solutes are transported in a different way to particles. The latter experience gravitational settling and aggregation, as well as advection and mixing. The concentrations of SPM and the types of SPM play a significant role on the fraction of metal carried in the particulate phase. Lead has a relatively high K_D, largely owing to its tendency to complex with carboxyl and phenolic groups that dominate the surfaces of natural particles. In contrast, the relatively low K_D for cadmium is the result of its ability to complex with chloride ions in sea water. **Figure 2** shows the fraction of metals in the dissolved phase (f_d) calculated as a function of SPM concentration, using representative K_D values for sea water. In estuaries and coastal waters, significant fractions of the metals are associated with particulate matter, but, as the SPM concentration declines through the coastal margin and into the ocean, the dissolved phase assumes more importance. Because of their reactivity with particles many metals have short residence times in the coastal ocean, in the range 50–1000 y.

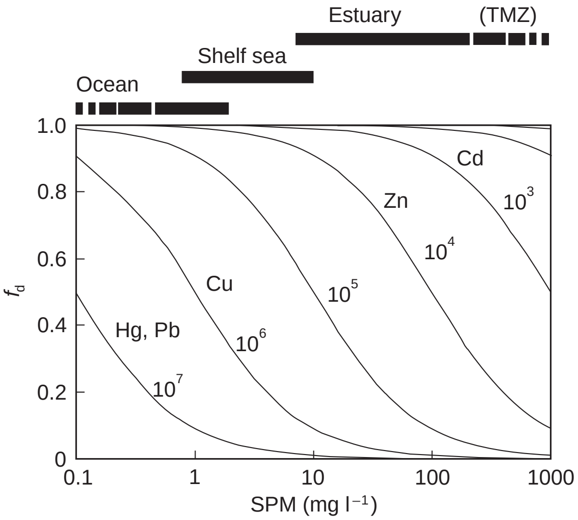

Figure 2 The fraction of metal in the dissolved phase (f_d) as a function of the concentration of suspended particulate matter (SPM). The bands at the top of the diagram represent the general ranges of SPM concentrations from the open ocean through to the estuarine turbidity maximum zone (TMZ). The numbers next to the lines are values of the partition coefficients, K_D, used to estimate the value of f_d. Metals are associated with their typical K_D values and are shown next to the appropriate line.

Table 2 Distributions of concentrations of dissolved cadmium, mercury, and lead (pmol l^{-1}) in rivers, estuaries, the English Channel and the North Atlantic

Location	*Cadmium*	*Mercury*	*Lead*
River background	90	2–20	1 000
Scheldt, Belgium	180–800	3.4–14	240–810
Seine, France	900–1 800	2.5–40	< 2 300–16 000
English Channel	100–130	1.5–2.5	115–150
N. Atlantic Surface	1–10	1–7	100–150
N. Atlantic Deep	350	1	20

Distributions in Estuaries and Coasts

Table 2 illustrates the trends in the concentrations of dissolved metals from river to ocean. The Scheldt and Seine estuaries have important anthropogenic sources of the metals compared to the riverine inputs. Estuarine chemistry in the Scheldt is complicated by the discharge of a high organic load that renders the waters of the upper estuary anoxic during most of the year. Thus, the concentrations of dissolved cadmium, mercury and lead in the water column can be relatively low as a result of the formation of sparingly soluble metal sulfides. However, the sediment interstitial waters of the Scheldt can contain up to 25 000 pmol l^{-1} of dissolved cadmium. In the Scheldt and Seine estuaries, analyses of mercury speciation have shown the presence of the Hg^0 form and microbial mediation appears to have transformed inorganic mercury into MMHg and DMHg.

In assessing the distributions of dissolved metals in the coastal margin, their concentrations should be normalized with respect to salinity because a higher concentration at one location may be due to lower salinity (or greater fluvial influence). Distributions of dissolved metals in estuarine waters can vary linearly with salinity, the slope of which is dependent on the relative dissolved metal concentrations in the river and the sea, i.e., the 'end-member' concentrations. An example of conservative behavior, in which the concentration of dissolved cadmium varies in proportion to the amount of mixing between river water and sea water, is shown in **Figure 3A** for the Humber estuary plume. The observed behavior for cadmium is due to its affinity for the dissolved phase, even in turbid waters. The temporal change in the slope also shows that the distribution of the metal is highly responsive to changing inputs between different flow regimes. Total dissolved mercury (**Figure 3B**) displays non-conservative behaviour with a maximum concentration as a result of inputs from point sources along the banks of the Humber Estuary. Dissolved lead also behaves non-conservatively (**Figure 3C**) and the scatter of data arises because of diffuse atmospheric inputs. The dissolved lead is maintained at relatively low concentrations by its propensity to react with particles (**Figure 2**).

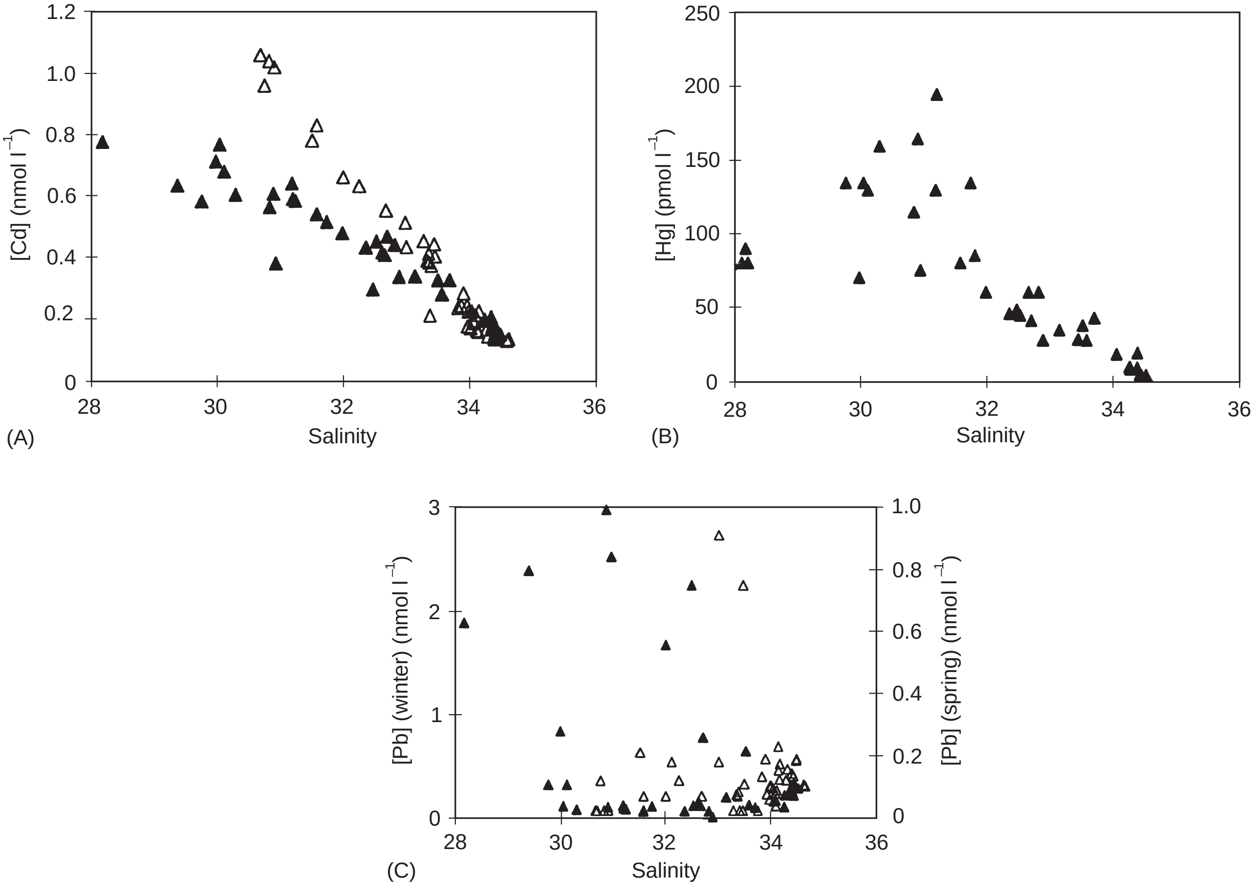

Figure 3 Concentrations of dissolved metals in the Humber Estuary as a function of salinity in winter with high fluvial input (solid symbols) and spring with reduced fluvial input (open symbols): (A) cadmium; (B) total mercury; (C) lead.

Distribution in the North Atlantic Ocean

Dissolved cadmium has a higher concentration in the deep waters of the North Atlantic Ocean owing to its uptake by phytoplankton in surface waters and recycling at depth; it exhibits nutrient-like behavior. Dissolved mercury has almost no gradient through the water column, because of a significant loss of Hg^0 to the atmosphere. However, in the deep waters of the North Atlantic, higher concentrations of MMHg and DMHg have been detected, possibly as a consequence of remineralization of phytoplankton. In contrast, lead has higher concentrations in the surface waters of the Atlantic, reflecting an atmospheric input. The strength of the atmospheric lead source appears to be declining as a result of a decrease in the use of leaded petrol. The monitoring of dissolved lead in the waters around Bermuda over a 15-year period shows that lead concentrations have decreased significantly. Since the SPM concentrations in these waters are low, the changes in dissolved lead concentrations are controlled almost exclusively by the flushing time of the water and the changing lead inputs. Following the decline in the atmospheric input, these waters have relaxed to near-background concentrations of dissolved lead (**Figure 4**).

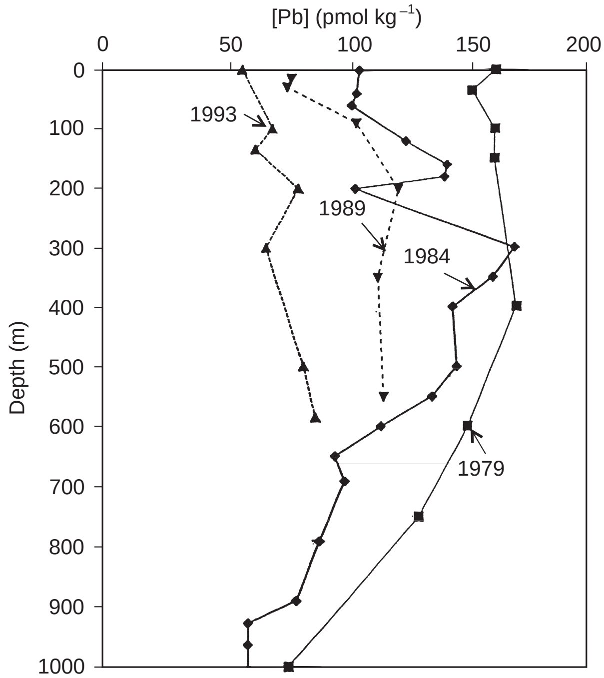

Figure 4 Vertical profiles of dissolved lead in the north Atlantic near Bermuda. The low point at 200 m in 1984 could not be accounted for by the authors, even though the analysis had been replicated and checked, and was thought to be a residual from the deep mixed layer from the previous winter. (Reprinted from Wu and Boyle (1997), copyright 1997, with permission from Elsevier Science.)

Environmental Impact

The sediments of coastal regions reflect the long-term accumulation of metal contamination. Assessments of the anthropogenic component of metals in sediments require that the grain size must be accounted for and the corrected metal concentration compared with an uncontaminated reference material. For sediments with similar grain sizes, normalization is achieved with respect to a major element that is unaffected by anthropogenic inputs, such as aluminum, lithium, or rubidium. The enrichment factor (*EF*) is then defined as in eqn [2].

$$EF = \frac{[M_p]/[Al_p]}{[M_r]/Al_r]} \qquad [2]$$

Here $[M_p]$ and $[M_r]$ are the metal concentrations in particulate matter and in crustal rock, respectively, and $[Al_p]$ and $[Al_r]$ are the concentrations of aluminum (or any suitable reference element) in particulate matter and crustal rock, respectively. **Table 3** lists *EF*s for SPM or fine sediment in contrasting estuaries. Enrichment factors are close to unity for the baseline sediment and in the 'pristine' Lena Estuary, while the greatest *EF* values are encountered for cadmium in the Rhine (impacted by the production of phosphate fertilizers) and the Scheldt, and for copper in Restronguet Creek (impacted by historical mining activity). The general sequence of *EF*s is $Cd > Pb > Cu, Zn$; reflecting the relative significance of anthropogenic inputs to the estuarine environment and modification by different particle–water reactivities. The Scheldt Estuary has a history of metal pollution; and in comparison with other estuaries, Baeyens (see Further Reading) classifies the Scheldt as 'moderately polluted for all

Table 3 Enrichment factors calculated according to eqn [2] for metals in suspended particulate matter or fine sediment from estuarine and coastal environments

Location	*Cadmium*	*Copper*	*Lead*	*Zinc*
Rhine Estuary, The Netherlands	310	21	84	23
Scheldt Estuary, Belgium	38	3.1	8.9	4.9
Seine Estuary, France	18	3.1	9.6	3.3
Humber Estuary, UK	N/A	2.1	7.4	2.4
Restronguet Creek, UK	N/A	88	28	28
Lena Estuary, Russia	N/A	0.8	1.4	1.1
Baseline (Norwegian Coastal Sediments)	0.6	0.2	2.2	1.9

N/A, not available.

metals in the dissolved phase and fairly highly polluted in the particulate phase, especially for cadmium.' Efforts are being made to reduce the concentrations of cadmium in SPM in the Scheldt, and in the low-salinity region concentrations have declined from 400 nmol g^{-1} in 1978 to 79 nmol g^{-1} in 1995.

Metal contamination can also be registered in indicator organisms (that is, organisms that are able to accumulate metals rather than regulate them), affording a measure of the contamination of the marine food chain. Across a broad range of phyla (from macroalgae to dophins), copper, zinc, and possibly cadmium exhibit a relatively low spread of concentrations, indicating efficient regulation of these metals. For lead, the concentrations are lower in vertebrates, which may be due to effective regulation or reduced bioavailability of the metal. Mercury is exceptional because of its biomagnification along the food chain as a result of its being present mainly as methyl mercury which is eliminated slowly from the organism. Mercury is retained by long-lived species, such as seals and dolphins, owing to their biochemical ability to isolate mercury as mercuric selenide granules. *Fucus* is a representative indicator species and baseline concentrations of selected metals occur in samples from an uncontaminated area of the Western Irish Sea (**Table 4**). Concentrations of copper, lead, and zinc are generally highest in industrialized estuaries (e.g., Humber) and fiords (e.g., Hardangefjord) and those that drain mineralized catchments and old mine workings (e.g., Restronguet Creek). Elevated concentrations of metals impact the growth, respiration, reproduction, recruitment and species diversity of marine organisms, for example in Restronguet Creek the absence of bivalves has been ascribed to high levels of copper and zinc which prevent the settlement of juvenile bivalves.

Human Health

The toxicity of metals depends on their rate of excretion from an organism and their chemical form. The adverse effects of metals on human health were recognized in the 1950s and 1960s following catastrophic events involving mercury. Inorganic mercury is normally excreted by humans and poses little hazard to the general public. However, organic mercury compounds, such as methylated forms, are not readily excreted. Methylated mercury compounds can pass to all tissues in the body after absorption from the gastrointestinal tract. They can cross diffusion barriers and penetrate membranes, such as the blood–brain barrier (causing irreversible brain damage) and the placenta (rendering methylated mercury concentrations in fetal blood higher than those in the mother). The most significant outbreak of neurological, and often fatal illnesses occurred among the residents of Minamata in Japan. Chemical companies had discharged or dumped tonnes of mercury compounds into Minamata Bay for decades and these accumulated in the tissues of shellfish and fish. Consequently, large doses were passed onto the local, fish-eating population. Eventually the Bay was sealed off with nets to prevent organisms contaminated with mercury from escaping and affecting other areas. Over several decades biogeochemical processes and hydrodynamic flushing of mercury from the Bay have resulted in concentrations of mercury falling below government standards. Presently, the World Health Organization (WHO) regards a tolerable daily intake of total mercury (inorganic + organic) to be 50 μg d^{-1} for an adult of 70 kg.

Table 4 Mean concentration (nmol g^{-1}) of metals in *Fucus* spp. in estuaries and coastal waters

Location	*Cadmium*	*Copper*	*Lead*	*Zinc*
Hardangefjord, Norway	63	330	220	21 000
Humber Estuary, UK	46	680	39	8 500
Restronguet Creek, UK	7.3	14 000	140	26 000
Baseline (Western Irish Sea)	4.4	60	6	1 100

Human exposure to high concentrations of cadmium are rare and current concern centers around the chronic toxicity caused by long-term exposure to low levels of the metal. Bone disorders are one manifestation of chronic cadmium exposure. Cadmium is present in all tissues of adults, with the most significant amounts found in the liver and kidney, and the concentrations tend to increase with age. The WHO regards a tolerable daily intake of cadmium to be 70 μg d^{-1} for an adult of 70 kg.

Conclusions

Despite coastal waters in the vicinity of urban and industrial regions being contaminated with metals, there exists no evidence of significant pollution that poses a threat to human health, except on a local scale (and usually in shellfish) or where control has been poor. Since the dominant temporary or ultimate sink for metal contaminants is the sediment, an important goal of current research is to understand the mechanisms and extent to which contaminants are extracted by organisms (i.e., contaminant bioavailability) and transferred within the marine food chain.

Glossary

Advection Horizontal water motion.

Bioavailable metals Dissolved and particulate metals that are accessible to organisms during normal metabolic activity.

Bioaccumulative metals Metals that can be regulated and reside in the organism and are added to over its life.

Biomagnified metals Metals that are not regulated by organisms that can acquire an even larger body burden of metals.

Bioturbation Reworking of bottom sediment by burrowing marine organisms.

Diagenesis Release of particulate metals into the dissolved phase under suboxic conditions.

Flushing time The time required for an existing body of water to be exchanged with surrounding water.

Upwelling Vertical, upward movement of water at the shelf break, often tidally induced.

See also

Aeolian Inputs. Anthropogenic Trace Elements in the Ocean. Anti-fouling Materials. Atmospheric Input of Pollutants. Estuarine Circulation. Land–Sea Global Transfers. Metalloids and Oxyanions. Ocean Margin Sediments. Pollution: Effects on Marine Communities. Pore Water Chemistry. Refractory Metals. Regional and Shelf Sea Models. River Inputs. Temporal Variability of Particle Flux. Transition Metals and Heavy Metal Speciation. Trapped Particulate Flux. Shelf-sea and Slope Fronts.

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METALLOIDS AND OXYANIONS

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doi:10.1006/rwos.2001.0283

Introduction

The concentrations and distributions of dissolved trace elements (typically called trace 'metals,' though not all trace elements are metals) in the world's oceans are due to a complex interaction between their purely chemical behavior (e.g., acid/base properties, oxidation state, solubility), the way in which they are delivered to the ocean (atmosphere, rivers, submarine hydrothermal vents), biological reactions, and water circulation (e.g., currents). To organize this somewhat chaotic and confusing situation, the kinds of trace element behavior are classified into four types: conservative, nutrient-like or recycled, scavenged, and hybrid or mixed. A conservative trace element behaves like the major dissolved elements that make up the bulk of the ocean's salinity (e.g., Na^+). These elements are only effected by the physical processes of mixing, or the addition (dilution) or removal (evaporation) of water. Since there are no chemical or biological reactions that affect these elements, they have rather uniform concentrations with ocean depth. In contrast, the nutrient-like trace element is taken up by phytoplankton in surface waters during photosynthesis (like the nutrient nitrate), and this organic matter-bound element begins to gravitationally settle into deep waters. However, organic matter is