ATMOSPHERIC INPUT OF POLLUTANTS

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Introduction

For about a century oceanographers have tried to understand the budgets and processes associated with both natural and human-derived substances entering the ocean. Much of the early work focused on the most obvious inputs – those carried by rivers and streams. Later studies investigated sewage outfalls, dumping, and other direct input pathways for pollutants. Over the past decade or two, however, it has become apparent that the atmosphere is also not only a significant, but in some cases dominant, pathway by which both natural materials and contaminants are transported from the continents to both the coastal and open oceans. These substances include mineral dust and plant residues, metals, nitrogen compounds from combustion processes and fertilizers, and pesticides and a wide range of other synthetic organic compounds from industrial and domestic sources. Some of these substances carried into the ocean by the atmosphere, such as lead and some chlorinated hydrocarbons, are potentially harmful to marine biological systems. Other substances, such as nitrogen compounds, phosphorus, and iron, are nutrients and may enhance marine productivity. For some substances, such as aluminum and some rare earth elements, the atmospheric input has an important impact on their natural chemical cycle in the sea.

In subsequent sections there will be discussions of the input of specific chemicals via the atmosphere to estuarine and coastal waters. This will be followed by considerations of the atmospheric input to open ocean regions and its potential importance. The atmospheric estimates will be compared with the input via other pathways when possible. Note that there are still very large uncertainties in all of the fluxes presented, both those from the atmosphere and those from other sources. Unless otherwise indicated, it should be assumed that the atmospheric input rates have uncertainties ranging from a factor of 2 to 4, sometimes even larger.

Estimating Atmospheric Contaminant Deposition

Contaminants present as gases in the atmosphere can exchange directly across the air/sea boundary or they may be scavenged by rain and snow. Pollutants present on particles (aerosols) may deposit on the ocean either by direct (dry) deposition or they may also be scavenged by precipitation. The removal of gases and/or particles by rain and snow is termed wet deposition.

Direct Deposition of Gases

Actual measurement of the fluxes of gases to a water surface is possible for only a very few chemicals at the present time, although extensive research is underway in this area, and analytical capabilities for fast response m3easurements of some trace gases are becoming available. Modeling the flux of gaseous compounds to the sea surface or to rain droplets requires a knowledge of the Henry's law constants and air/sea exchange coefficients as well as atmospheric and oceanic concentrations of the chemicals of interest. For many chemicals this information is not available. Discussions of the details of these processes of air/sea gas exchange can be found in other articles in this volume.

Particle Dry Deposition

Reliable methods do not currently exist to measure directly the dry deposition of the full size range of aerosol particles to a water surface. Thus, dry deposition of aerosols is often estimated using the dry deposition velocity, v_d. For dry deposition, the flux is then given by:

$$F_d = v_d \cdot C_a \qquad (1)$$

where F_d is the dry deposition flux (e.g., in $\mathrm{g\,m^{-2}\,s^{-1}}$), v_d is the dry deposition velocity (e.g., in $\mathrm{m\,s^{-1}}$), and C_a is the concentration of the substance on the aerosol particles in the atmosphere (e.g., in $\mathrm{g\,m^{-3}}$). In this formulation v_d incorporates all the processes of dry deposition, including diffusion, impaction, and gravitational settling of the particles to a water surface. It is very difficult to parameterize accurately the dry deposition velocity since each of these processes is acting on a particle population, and they are each dependent upon a number of factors, including wind speed, particle size, relative humidity, etc. The following are dry deposition velocities that have been used in some studies of atmospheric deposition of particles to the ocean:

- Submicrometer aerosol particles, $0.001\,\mathrm{m\,s^{-1}} \pm$ a factor of three

- Supermicrometer crustal particles not associated with sea salt, $0.01\,\mathrm{m\,s^{-1}} \pm$ a factor of three
- Giant sea-salt particles and materials carried by them, $0.03\,\mathrm{m\,s^{-1}} \pm$ a factor of two

Proper use of eqn [1] requires that information be available on the size distribution of the aerosol particles and the material present in them.

Particle and Gas Wet Deposition

The direct measurement of contaminants in precipitation samples is certainly the best approach for determining wet deposition, but problems with rain sampling, contamination, and the natural variability of the concentration of trace substances in precipitation often make representative flux estimates difficult using this approach. Studies have shown that the concentration of a substance in rain is related to the concentration of that substance in the atmosphere. This relationship can be expressed in terms of a scavenging ratio, S:

$$S = C_r \cdot \rho \cdot C_{a/g}{}^{-1} \qquad (2)$$

where C_r is the concentration of the substance in rain (e.g., in $\mathrm{g\,kg^{-1}}$), ρ is the density of air ($\sim 1.2\,\mathrm{kg\,m^{-3}}$), $C_{a/g}$ is the aerosol or gas phase concentration in the atmosphere (e.g., in $\mathrm{g\,m^{-3}}$), and S is dimensionless. Values of S for substances present in aerosol particles range from a few hundred to a few thousand, which roughly means that 1 g (or 1 ml) of rain scavenges $\subseteq 1\,\mathrm{m}^3$ of air. For aerosols, S is dependent upon such factors as particle size and chemical composition. For gases, S can vary over many orders of magnitude depending on the specific gas, its Henry's law constant, and its gas/water exchange coefficient. For both aerosols and gases, S is also dependent upon the vertical concentration distribution and vertical extent of the precipitating cloud, so the use of scavenging ratios requires great care, and the results have significant uncertainties. However, if the concentration of an atmospheric substance and its scavenging ratio are known, the scavenging ratio approach can be used to estimate wet deposition fluxes as follows:

$$F_r = P \cdot C_r = P \cdot S \cdot C_{a/g} \cdot \rho^{-1} \qquad (3)$$

where F_r is the wet deposition flux (e.g., in $\mathrm{g\,m^{-2}\,year^{-1}}$) and P is the precipitation rate (e.g., in $\mathrm{m\,year^{-1}}$), with appropriate conversion factors to translate rainfall depth to mass of water per unit area. Note that $P \cdot S \cdot \rho^{-1}$ is equivalent to a wet deposition velocity.

Atmospheric Deposition to Estuaries and the Coastal Ocean

Metals

The atmospheric deposition of certain metals to coastal and estuarine regions has been studied more than that for any other chemicals. These metals are generally present on particles in the atmosphere. Chesapeake Bay is among the most thoroughly studied regions in North America in this regard. **Table 1** provides a comparison of the atmospheric and riverine deposition of a number of metals to Chesapeake Bay. The atmospheric numbers represent a combination of wet plus dry deposition directly onto the Bay surface. Note that the atmospheric input ranges from as low as 1% of the total input for manganese to as high as 82% for aluminum. With the exception of Al and Fe, which are largely derived from natural weathering processes (e.g., mineral matter or soil), most of the input of the other metals is from human-derived sources. For metals with anthropogenic sources the atmosphere is most important for lead (32%).

There have also been a number of investigations of the input of metals to the North Sea, Baltic Sea, and Mediterranean Sea. Some modeling studies of the North Sea considered not only the direct input pathway represented by the figures in **Table 1**, but also considered Baltic Sea inflow, Atlantic Ocean inflow and outflow, and exchange of metals with the sediments, as well as the atmospheric contribution to all of these inputs. **Figure 1** shows schematically some modeling results for lead, copper, and cadmium. Note that for copper, atmospheric input is relatively unimportant in this larger context,

Table 1 Estimates of the riverine and atmospheric input of some metals to Chesapeake Bay

Metal	*Riverine input ($10^6\,\mathrm{g\,year^{-1}}$)*	*Atmospheric input ($10^6\,\mathrm{g\,year^{-1}}$)*	*% Atmospheric input*
Aluminum	160	700	81
Iron	600	400	40
Manganese	1300	13	1
Zinc	50	18	26
Copper	59	3.5	6
Nickel	100	4	4
Lead	15	7	32
Chromium	15	1.5	10
Arsenic	5	0.8	14
Cadmium	2.6	0.4	13

(Data reproduced with permission from Scudlark JR, Conko KM and Church TM (1994) Atmospheric wet deposition of trace elements to Chesapeake Bay: CBAD study year 1 results. *Atmospheric Environment* 28: 1487–1498.)

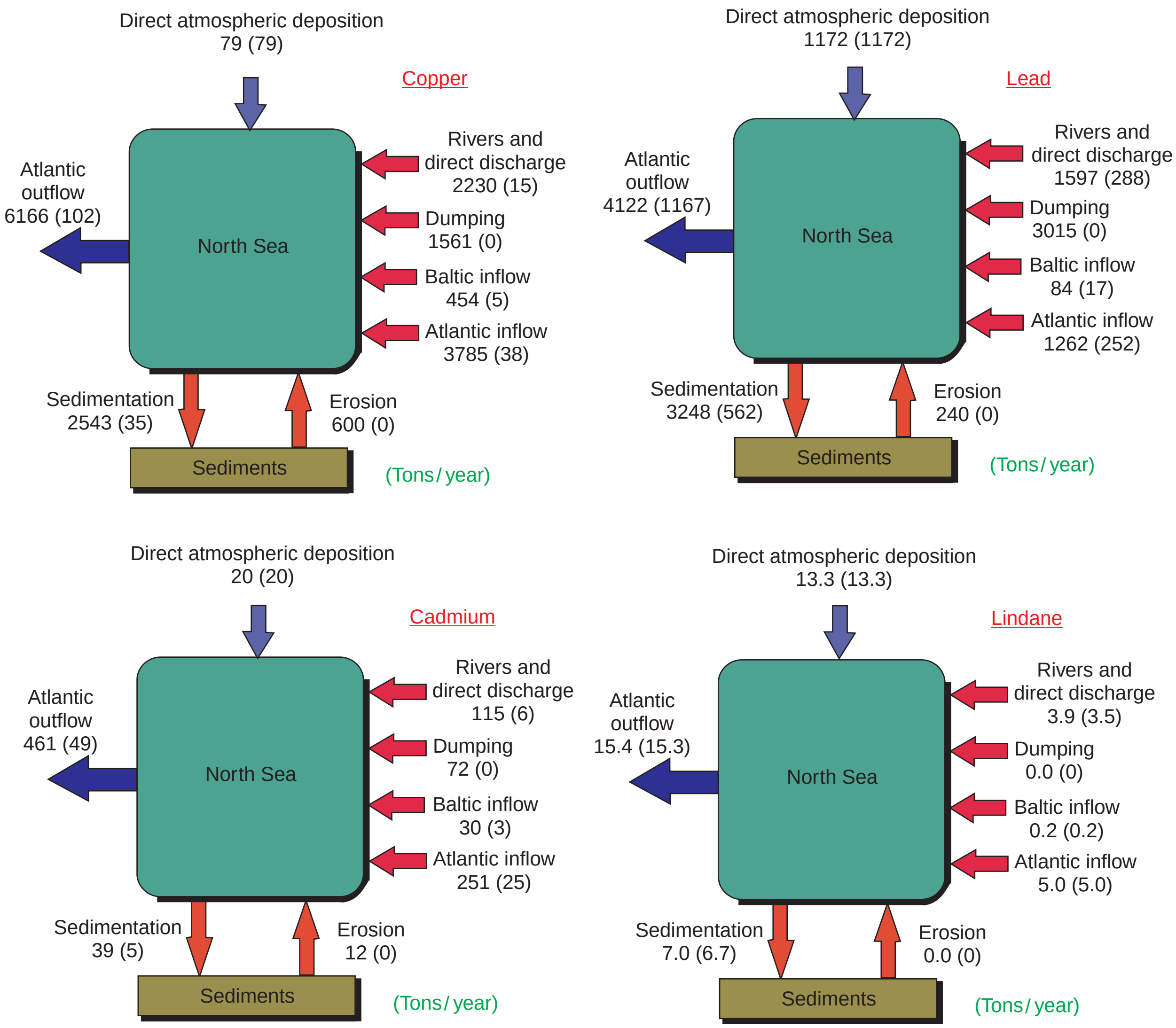

Figure 1 Input of copper, lead, cadmium, and lindane to the North Sea. Values in parentheses denote atmospheric contribution. For example, for copper the atmospheric contribution to rivers and direct discharges is 15 tons per year. (Figure reproduced with permission from Duce, 1998. Data adapted with permission from van den Hout, 1994.)

while atmospheric input is somewhat more important for cadmium, and it is quite important for lead, being approximately equal to the inflow from the Atlantic Ocean, although still less than that entering the North Sea from dumping. As regards lead, note that approximately 20% of the inflow from the Atlantic to the North Sea is also derived from the atmosphere. This type of approach gives perhaps the most accurate and in-depth analysis of the importance of atmospheric input relative to all other sources of a chemical in a water mass.

Nitrogen Species

The input of nitrogen species from the atmosphere is of particular interest because nitrogen is a necessary nutrient for biological production and growth in the ocean. There has been an increasing number of studies of the atmospheric input of nitrogen to estuaries and the coastal ocean. Perhaps the area most intensively studied is once again Chesapeake Bay. **Table 2** shows that approximately 40% of all the nitrogen contributed by human activity to Chesapeake Bay enters via precipitation falling directly on the Bay or its watershed. These studies were different from most earlier studies because the atmospheric contributions were considered not only to be direct deposition on the water surface, but also to include that coming in via the atmosphere but falling on the watershed and then entering the Bay. Note from **Table 2** that atmospheric input of

Table 2 Estimates of the input of nitrogen to Chesapeake Bay

Source	*Total input (10^9 g year^{-1})*	*Areal input rate (g m^{-2} year^{-1})*	*% of the total*
Animal waste	5	0.4	3
Fertilizers	48	4.2	34
Point sources	33	2.9	24
Atmospheric precipitation			
nitrate	35	3.1	25
ammonium	19	1.7	14
Total	140	12.3	100

(Data reproduced with permission from Fisher D, Ceroso T, Mathew T and Oppenheimer M (1988) *Polluted Coastal Waters: The Role of Acid Rain*. New York: Environmental Defense Fund.)

nitrogen exceeded that from animal waste, fertilizers, and point sources. In the case of nitrate, about 23% falls directly on the Bay, with the remaining 77% falling on the watershed. These results suggest that studies that consider only the direct deposition on a water surface (e.g., the results shown in **Table 1**) may significantly underestimate the true contribution of atmospheric input. The total nitrogen fertilizer applied to croplands in the Chesapeake Bay region is ~ 5.4 g m^{-2} year^{-1}, while the atmospheric nitrate and ammonium nitrogen entering the Bay is ~ 4.8 g m^{-2} year^{-1}. Chesapeake Bay is almost as heavily fertilized from atmospheric nitrogen, largely anthropogenic, as the croplands are by fertilizer in that watershed!

Results from studies investigating nitrogen input to some other estuarine and coastal regions are summarized in **Table 3**. In this table atmospheric sources for nitrogen are compared with all other sources, where possible. The atmospheric input ranges from 10% to almost 70% of the total. Note that some estimates compare only direct atmospheric deposition with all other sources and some include as part of the atmospheric input the portion of the deposition to the watershed that reaches the estuary or coast.

Synthetic Organic Compounds

Concern is growing about the input of a wide range of synthetic organic compounds to the coastal ocean. To date there have been relatively few estimates of the atmospheric fluxes of synthetic organic compounds to the ocean, and these estimates have significant uncertainties. These compounds are often both persistent and toxic pollutants, and many have relatively high molecular weights. The calculation of the atmospheric input of these compounds to the coastal ocean is complicated by the fact that many of them are found primarily in the gas phase in the atmosphere, and most of the deposition is related to the wet and dry removal of that phase. The atmospheric residence times of most of these compounds are long compared with those of metals and nitrogen species. Thus the potential source regions for these compounds entering coastal waters can be distant and widely dispersed.

Table 3 Estimates of the input of nitrogen to some coastal areas[a]

Region	*Total atmospheric input[b] (10^9 g year^{-1})*	*Total input all sources (10^9 g year^{-1})*	*% Atmospheric input*
North Sea	400[c]	1500	27[c]
Western Mediterranean Sea	400[c]	577[d]	69[c]
Baltic Sea	500	~ 1200	42
Chesapeake Bay	54	140	39
New York Bight	–	–	13[c]
Long Island Sound	11	49	22
Neuse River Estuary, NC	1.7	7.5	23

[a] Data from several sources in the literature.

[b] Total from direct atmospheric deposition and runoff of atmospheric material from the watershed.

[c] Direct atmospheric deposition to the water only.

[d] Total from atmospheric and riverine input only.

Table 4 Estimates of the input of synthetic organic compounds to the North Sea

Organic compound	*Atmospheric input (10^6 g year^{-1})*	*Input from other sources (10^6 g year^{-1})*	*% Atmospheric input*
PCB	40	3	93
Lindane	36	3	92
Polycyclic aromatic hydrocarbons	80	90	47
Benzene	400	500	44
Trichloroethene	300	80	80
Trichloroethane	90	60	94
Tetrachloroethene	100	10	91
Carbon tetrachloride	6	40	13

(Data reproduced with permission from Warmerhoven JP, Duiser JA, de Leu LT and Veldt C (1989) *The Contribution of the Input from the Atmosphere to the Contamination of the North Sea and the Dutch Wadden Sea*. Delft, The Netherlands: TNO Institute of Environmental Sciences.)

Figure 1 shows the input of the pesticide lindane to the North Sea. Note that the atmospheric input of lindane dominates that from all other sources. **Table 4** compares the atmospheric input to the North Sea with that of other transport paths for a number of other synthetic organic compounds. In almost every case atmospheric input dominates the other sources combined.

Atmospheric Deposition to the Open Ocean

Studies of the atmospheric input of chemicals to the open ocean have also been increasing lately. For many substances a relatively small fraction of the material delivered to estuaries and the coastal zone by rivers and streams makes its way through the near shore environment to open ocean regions. Most of this material is lost via flocculation and sedimentation to the sediments as it passes from the freshwater environment to open sea water. Since aerosol particles in the size range of a few micrometers or less have atmospheric residence times of one to several days, depending upon their size distribution and local precipitation patterns, and most substances of interest in the gas phase have similar or even longer atmospheric residence times, there is ample opportunity for these atmospheric materials to be carried hundreds to thousands of kilometers before being deposited on the ocean surface.

Metals

Table 5 presents estimates of the natural and anthropogenic emission of several metals to the global atmosphere. Note that ranges of estimates and the best estimate are given. It appears from **Table 5** that anthropogenic sources dominate for lead, cadmium, and zinc, with essentially equal contributions for copper, nickel, and arsenic. Clearly a significant fraction of the input of these metals from the atmosphere to the ocean could be derived largely from anthropogenic sources.

Table 6 provides an estimate of the global input of several metals from the atmosphere to the ocean and compares these fluxes with those from rivers. Estimates are given for both the dissolved and particulate forms of the metals. These estimates suggest that rivers are generally the primary source of particulate metals in the ocean, although again a significant fraction of this material may not get past the coastal zone. For the dissolved phase atmospheric and riverine inputs are roughly equal for metals such as iron, copper, and nickel; while for zinc, cadmium, and particularly lead atmospheric inputs appear to dominate. These estimates were made based on data collected in the mid-1980s. Extensive efforts to control the release of atmospheric lead, which has been primarily from the combustion of

Table 5 Emissions of some metals to the global atmosphere

Metal	*Anthropogenic emissions (10^9 g year^{-1})*		*Natural emissions (10^9 g year^{-1})*	
	Range	*Best estimate*	*Range*	*Best estimate*
Lead	289–376	332	1–23	12
Cadmium	3.1–12	7.6	0.15–2.6	1.3
Zinc	70–194	132	4–86	45
Copper	20–51	35	2.3–54	28
Arsenic	12–26	18	0.9–23	12
Nickel	24–87	56	3–57	30

(Data reproduced with permission from Duce *et al.*, 1991.)

Table 6 Estimates of the input of some metals to the global ocean

Metal	*Atmospheric input*		*Riverine input*	
	Dissolved (10^9 g year^{-1})	*Particulate (10^9 g year^{-1})*	*Dissolved (10^9 g year^{-1})*	*Particulate (10^9 g year^{-1})*
Iron	1600–4800	14 000–42 000	1100	110 000
Copper	14–45	2–7	10	1500
Nickel	8–11	14–17	11	1400
Zinc	33–170	11–55	6	3900
Arsenic	2.3–5	1.3–3	10	80
Cadmium	1.9–3.3	0.4–0.7	0.3	15
Lead	50–100	6–12	2	1600

(Data reproduced with permission from Duce *et al*., 1991.)

leaded gasoline, are now resulting in considerably lower concentrations of lead in many areas of the open ocean. For example, **Figure 2** shows that the concentration of dissolved lead in surface sea water near Bermuda has been decreasing regularly over the past 15–20 years, as has the atmospheric lead concentration in that region. This indicates clearly that at least for very particle-reactive metals such as lead, which has a short lifetime in the ocean (several years), even the open ocean can recover rather rapidly when the anthropogenic input of such metals is reduced or ended. Unfortunately, many of the other metals of most concern have much longer residence times in the ocean (thousands to tens of thousands of years).

Figure 3 presents the calculated fluxes of several metals from the atmosphere to the ocean surface and from the ocean to the seafloor in the 1980s in the tropical central North Pacific. Note that for most metals the two fluxes are quite similar, suggesting the potential importance of atmospheric input to the marine sedimentation of these metals in this region. Lead and selenium are exceptions, however, as the atmospheric flux is much greater than the flux to the seafloor. The fluxes to the seafloor represent average fluxes over the past several thousand years, whereas the atmospheric fluxes are roughly for the present time. The atmospheric lead flux is apparently much larger than the flux of lead to the sediments, primarily because of the high flux of anthropogenic lead from the atmosphere to the ocean since the introduction of tetraethyllead in gasoline in the 1920s. (The atmospheric flux is much lower now than in the 1980s, as discussed

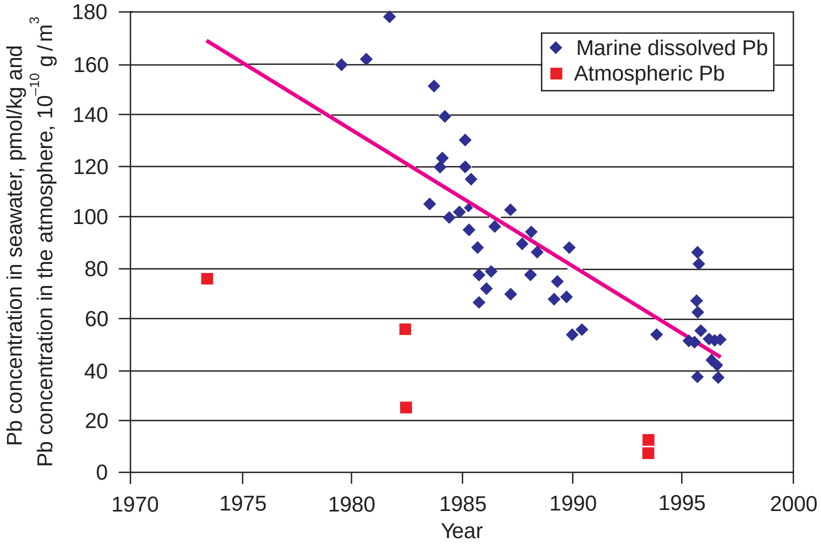

Figure 2 Changes in concentration of atmospheric lead at Bermuda and dissolved surface oceanic lead near Bermuda from the mid-1970s to the mid-1990s. (Data reproduced with permission from Wu J and Boyle EA (1997) Lead in the western North Atlantic Ocean: Completed response to leaded gasoline phaseout. *Geochimica et Cosmochimica Acta* 61: 3279–3283; and from Huang S, Arimoto R and Rahn KA (1996) Changes in atmospheric lead and other pollution elements at Bermuda. *Journal of Geophysical Research* 101: 21 033–21 040.)

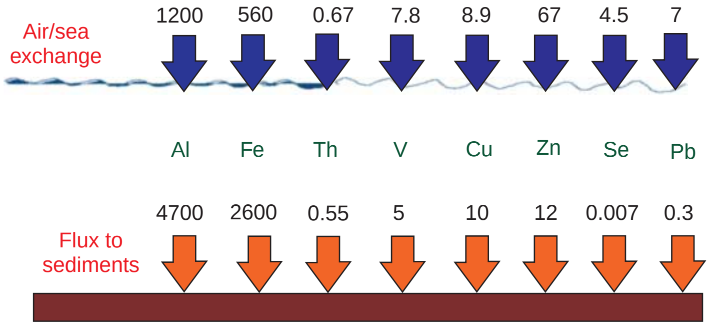

Figure 3 A comparison of the calculated fluxes of aluminum (Al), iron (Fe), thorium (Th), vanadium (V), copper (Cu), zinc (Zn), selenium (Se), and lead (Pb) (in $10^{-9}\,\mathrm{g\,cm^{-2}\,year^{-1}}$) from the atmosphere to the ocean and from the ocean to the sediments in the central tropical North Pacific. For each metal note the relative similarity in the two fluxes, except for lead and selenium. (Reproduced with permission from Duce, 1998.)

above.) However, in the case of selenium the apparently higher atmospheric flux is an artifact, because most of the flux of selenium from the atmosphere to the ocean is simply marine-derived selenium that has been emitted from the ocean to the atmosphere as gases, such as dimethyl selenide (DMSe). DMSe is oxidized in the atmosphere and returned to the ocean, i.e., the selenium input is simply a recycled marine flux. Thus, care must be taken when making comparisons of this type.

Nitrogen Species

There is growing concern about the input of anthropogenic nitrogen species to the global ocean. This issue is of particular importance in regions where nitrogen is the limiting nutrient, e.g., the oligotrophic waters of the central oceanic gyres. Estimates to date suggest that in such regions atmospheric nitrogen will in general account for only a few percent of the total 'new' nitrogen delivered to the photic zone, with most of the 'new' nutrient nitrogen derived from the upwelling of nutrient-rich deeper waters and from nitrogen fixation in the sea. It is recognized, however, that the atmospheric input is highly episodic, and at times it may play a much more important role as a source for nitrogen in surface waters. **Table** 7 presents a recent estimate of the current input of fixed nitrogen to the global ocean from rivers, the atmosphere, and nitrogen fixation. From the numbers given it is apparent that all three sources are likely important, and within the uncertainties of the estimates they are roughly equal. In the case of rivers, about half of the nitrogen input is anthropogenic For atmospheric input perhaps the most important information in **Table** 7 is that the organic nitrogen flux appears to be equal to or perhaps significantly greater than the inorganic (i.e., ammonium and nitrate) nitrogen flux. The source of the organic nitrogen is not known, but there are indications that a large fraction of it is anthropogenic in origin. This is a form of atmospheric nitrogen input to the ocean that had not been considered until very recently, as there had been few measurements of organic nitrogen input to the ocean before the mid-1990s. The chemical forms of this organic nitrogen are still largely unknown.

Of particular concern are potential changes to the input of atmospheric nitrogen to the open ocean in the future as a result of increasing human activities. The amount of nitrogen fixation (formation of reactive nitrogen) produced from energy sources (primarily as NO_x, nitrogen oxides), fertilizers, and legumes in 1990 and in 2020 as a result of human activities as well as the current and predicted future geographic distribution of the atmospheric deposition of reactive nitrogen to the continents and ocean have been evaluated recently. **Table** 8 presents estimates of the formation of fixed nitrogen from energy use and production and from fertilizers, the two processes which would lead to the most important fluxes of reactive nitrogen to the

Table 7 Estimates of the current input of reactive nitrogen to the global ocean

Source	*Nitrogen input ($10^{12}\,\mathrm{g\,year^{-1}}$)*
From the atmosphere	
Dissolved inorganic nitrogen	28–70
Dissolved organic nitrogen	28–84
From rivers (dissolved inorganic + organic nitrogen)	
Natural	14–35
Anthropogenic	7–35
From nitrogen fixation within the ocean	14–42

(Data reproduced with permission from Cornell S, Rendell A and Jickells T (1995) Atmospheric inputs of dissolved organic nitrogen to the oceans. *Nature* 376: 243–246.)

Table 8 Estimates of anthropogenic reactive nitrogen production, 1990 and 2020

Region	*Energy (NO_x)*					*Fertilizer*				
	1990 (10^{12} g N year^{-1})	*2020*	Δ	*Factor*	*% of total increase*	*1990 (10^{12} g N year^{-1})*	*2020*	Δ	*Factor*	*% of total increase*
USA/Canada	7.6	10.1	2.5	1.3	10	13.3	14.2	0.9	1.1	1.6
Europe	4.9	5.2	0.3	1.1	1	15.4	15.4	0	1.0	0
Australia	0.3	0.4	0.1	1.3	0.4	—	—	—	—	—
Japan	0.8	0.8	0	1.0	0	—	—	—	—	—
Asia	3.5	13.2	9.7	3.8	39	36	85	49	2.4	88
Central/South America	1.5	5.9	4.4	3.9	18	1.8	4.5	2.7	2.5	5
Africa	0.7	4.2	3.5	6.0	15	2.1	5.2	3.1	2.5	6
Former Soviet Union	2.2	5.7	3.5	2.5	15	10	10	0	1.0	0
Total	21	45	24	2.1	100	79	134	55	1.7	100

(Data adapted with permission from Galloway *et al.*, 1995.)

atmosphere. Note that the most highly developed regions in the world, represented by the first four regions in the table, are predicted to show relatively little increase in the formation of fixed nitrogen, with none of these areas having a predicted increase by 2020 of more than a factor of 1.3 nor a contribution to the overall global increase in reactive nitrogen exceeding 10%. However, the regions in the lower part of **Table 8** will probably contribute very significantly to increased anthropogenic reactive nitrogen formation in 2020. For example, it is predicted that the production of reactive nitrogen in Asia from energy sources will increase $\leq$ fourfold, and that Asia will account for almost 40% of the global increase, while Africa will have a sixfold increase and will account for 15% of the global increase in energy-derived fixed nitrogen. It is predicted that production of reactive nitrogen from the use of fertilizers in Asia will increase by a factor of 2.4, and Asia will account for $\sim$ 88% of the global increase from this source. Since both energy sources (NO_x, and ultimately nitrate) and fertilizer (ammonia and nitrate) result in the extensive release of reactive nitrogen to the atmosphere, the predictions above indicate that there should be very significant increases in the atmospheric deposition to the ocean of nutrient nitrogen species downwind of such regions as Asia, Central and South America, Africa, and the former Soviet Union.

This prediction has been supported by numerical modeling studies. These studies have resulted in the generation of maps of the 1980 and expected 2020 annual deposition of reactive nitrogen to the global ocean. **Figure 4** shows the expected significant

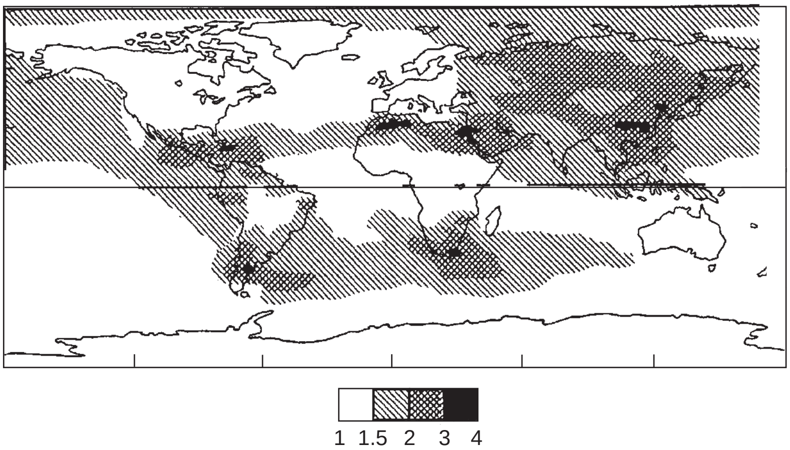

Figure 4 The ratio of the estimated deposition of reactive nitrogen to ocean and land surfaces in 2020 relative to 1980. (Figure reproduced with permission from Watson AJ (1997) Surface Ocean–Lower Atmosphere Study (SOLAS). *Global Change Newsletter, IGBP* no. 31, 9–12; data in figure adapted with permission from Galloway JN, Levy H and Kasibhatla PS (1994) Year 2020: Consequences of population growth and development on deposition of oxidized nitrogen. *Ambio* 23: 120–123.)

increase in reactive nitrogen deposition from fossil fuel combustion to the ocean to the east of all of Asia, from Southeast Asia to the Asian portion of the former Soviet Union; to the east of South Africa, northeast Africa and the Mideast and Central America and southern South America; and to the west of northwest Africa. This increased reactive nitrogen transport and deposition to the ocean will provide new sources of nutrient nitrogen to some regions of the ocean where biological production is currently nitrogen-limited. There is thus the possibility of significant impacts on regional biological primary production, at least episodically, in these regions of the open ocean.

Synthetic Organic Compounds

The atmospheric residence times of many synthetic organic compounds are relatively long compared with those of the metals and nitrogen species, as mentioned previously. Many of these substances are found primarily in the gas phase in the atmosphere, and they are thus very effectively mobilized into the atmosphere during their production and use. Their long atmospheric residence times of weeks to months leads to atmospheric transport that can often be hemispheric or near hemispheric in scale. Thus atmospheric transport and deposition in general dominates all other sources for these chemicals in sea water in open ocean regions.

Table 9 compares the atmospheric and riverine inputs to the world ocean for a number of synthetic organochlorine compounds. Note that the atmosphere in most cases accounts for 90% or more of the input of these compounds to the ocean. **Table 9** also presents estimates of the input of these same organochlorine compounds to the major ocean basins. Since most of these synthetic organic compounds are produced and used in the northern hemisphere, it is not surprising that the flux into the northern hemisphere ocean is greater than that to southern hemisphere marine regions. There are some differences for specific compounds in different ocean basins. For example, HCH (hexachlorocyclohexane) and DDT have a higher input rate to the North Pacific than the North Atlantic, largely because of the greater use of these compounds in Asia than in North America or Europe. On the other hand, the input of PCBs (polychlorinated biphenyls) and dieldrin is higher to the North Atlantic than the North Pacific, primarily because of their greater use in the continental regions adjacent to the North Atlantic.

Conclusions

The atmosphere transports materials to the ocean that are both harmful to marine life and that are essential for marine biological productivity. It is now apparent that atmospheric transport and deposition of some metals, nitrogen species, and synthetic organic compounds can be a significant and in some cases dominant pathway for these substances entering both estuarine and coastal waters as well as some open ocean regions. Atmospheric input clearly must be considered in any evaluation of material fluxes to marine ecosystems. However, the uncertainties in the atmospheric fluxes of these materials to the ocean are large. The primary reasons for these large uncertainties are:

- The lack of atmospheric concentration data over vast regions of the coastal and open ocean, particularly over extended periods of time and under varying meteorological conditions;
- The episodic nature of the atmospheric deposition to the ocean;
- The lack of accurate models of air/sea exchange, particularly for gases;

Table 9 Estimates of the atmospheric input of organochlorine compounds to the global ocean

Ocean	*ΣHCH (10^6 g year^{-1})*	*ΣDDT (10^6 g year^{-1})*	*ΣPCB (10^6 g year^{-1})*	*HCB (10^6 g year^{-1})*	*Dieldrin (10^6 g year^{-1})*	*Chlordane (10^6 g year^{-1})*
North Atlantic	850	16	100	17	17	8.7
South Atlantic	97	14	14	10	2.0	1.0
North Pacific	2600	66	36	20	8.9	8.3
South Pacific	470	26	29	19	9.5	1.9
Indian	700	43	52	11	6.0	2.4
Global input via the atmosphere	~ 4700	~ 170	~ 230	~ 80	~ 40	~ 22
Global input via rivers	~ 60	~ 4	~ 60	~ 4	~ 4	~ 4
% Atmospheric input	~ 99%	~ 98%	~ 80%	~ 95%	~ 91%	~ 85%

(Data reproduced with permission from Duce *et al.*, 1991.)

- The inability to measure accurately the dry deposition of particles; and
- The inability to measure accurately the air/sea exchange of gases.

See also

Chlorinated Hydrocarbons. Metal Pollution. Refractory Metals. Transition Metals and Heavy Metal Speciation.

Further Reading

Duce RA (1998) *Atmospheric Input of Pollution to the Oceans*, pp. 9–26. Proceedings of the Commission for Marine Meteorology Technical Conference on Marine Pollution, World Meteorological Organization TD-No. 890, Geneva, Switzerland.

Duce RA, Liss PS, Merrill JT *et al.* (1991) The atmospheric input of trace species to the world ocean. *Global Biogeochemical Cycles* 5: 193–259.

Galloway JN, Schlesinger WH, Levy H, Michaels A and Schnoor JL (1995) Nitrogen fixation: anthropogenic enhancement – environmental reponse. *Global Biogeochemical Cycles* 9: 235–252.

Jickells TD (1995) Atmospheric inputs of metals and nutrients to the oceans: their magnitude and effects. *Marine Chemistry* 48: 199–214.

Liss PS and Duce RA (eds) (1997) *The Sea Surface and Global Change*. Cambridge: Cambridge University Press.

Paerl HW and Whitall DR (1999) Anthropogenically-derived atmospheric nitrogen deposition, marine eutrophication and harmful algal bloom expansion: Is there a link? *Ambio* 28: 307–311.

Prospero JM, Barrett K, Church T *et al.* (1996) Nitrogen dynamics of the North Atlantic Ocean – Atmospheric deposition of nutrients to the North Atlantic Ocean. *Biogeochemistry* 35: 27–73.

van den Hout KD (ed.) (1994) *The Impact of Atmospheric Deposition of Non-Acidifying Pollutants on the Quality of European Forest Soils and the North Sea.* Report of the ESQUAD Project, IMW-TNO Report No. R 93/329.

AUTHIGENIC DEPOSITS

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Introduction

There are many kinds and forms of authigenic mineral deposits in the deep-sea. Here we concentrate on the more abundant and, in some cases, potentially economic types, namely ferromanganese deposits, phosphorites, marine barite, and the authigenic silicate minerals in deep-sea sediments. Hydrothermal deposits and a class of sedimentary iron and manganese oxides associated with seafloor hydrothermal activity – the metalliferous sediments found as a basal sequence in the deep-sea sedimentary column and in deep basins adjacent to active spreading centers – are described elsewhere in the encyclopedia. Ferromanganese deposits are here divided into nodules and crusts on the basis of morphology and environment of formation. The sources of the major and minor metal enrichments in these deposits are contrasted between continental weathering and submarine volcanism, with important enrichment influences from the marine biosphere. Marine barite has a similar mixed origin with strong biological influence. Knowledge of the origins of submarine phosphorites has been greatly aided by studies of recent seafloor deposits. There are a variety of authigenic silicate minerals in deep-sea sediments. The more abundant zeolites and clays such as smectite form mainly from diagenetic alteration of metastable volcanic glasses, but many other reaction paths are known and suggested.

Ferromanganese Deposits

Marine ferromanganese deposits are complex assemblages of authigenic minerals and detrital components. They are broadly characterized by shape and by environment of formation as deep-sea nodules and crusts. Ferromanganese nodules are commonly found on the abyssal seafloor at and near the top of the underlying pelagic sediment cover. Crusts are usually found on the steep slopes of islands and seamounts but are also found with the pelagic sediment on the deep-sea floor where sedimentation is extremely low. Occasionally, nodules may grow to coalesce into a pavement or crust of ferromanganese deposits. Conversely, crusts can grow around small fragments of the usually lithified sediment or basalt substrate of a seamount or island slope to create ‘pseudo’ or ‘seamount nodules’ that are otherwise indistinguishable from crustal pavements.