AEOLIAN INPUTS

R. Chester, Liverpool University, Liverpool, Merseyside, UK

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Introduction

The oceans are an important reservoir in the global biogeochemical cycles of many elements, but until the recent past it was thought that material fluxes to the reservoir were dominated by fluvial inputs. Over the last two or three decades, however, it has become apparent that the atmosphere is a major transport pathway in the land-sea exchange of material. This atmospherically transported material differs from that introduced by fluvial inputs in two important ways. (i) It is delivered, albeit at different flux magnitudes, to all areas of the sea surface, whereas river inputs are initially delivered to the land-sea margins. (ii) It does not pass through the biogeochemically dynamic estuarine Rlter; a region of intense dissolved/particulate reactivity, which, under present day conditions, retains \sim 90% of fluvial particulate material. As a result, the atmosphere is the most important pathway for the long-range transport of much of the particulate material delivered directly to open-ocean regions. This material has an important influence on marine sedimentation; for example, in equatorial North Atlantic deep-sea sediments deposited to the east of the Mid-Atlantic Ridge and in central North Pacific deep-sea sediments, essentially all the land-derived components are aeolian in origin. Atmospheric aerosols can also exert an influence on climatic forcing by acting as cloud condensation nuclei and by processes such as the scattering of short-wave radiation by both anthropogenic and natural aerosols. Further, the presence of anthropogenic sulfate aerosols in the atmosphere can lead to an increase in albedo and so cool the planet; an effect, which, on a global scale, is comparable to that induced by the 'greenhouse' gases, but is opposite in sign.

The aeolian material delivered to the sea surface by the atmosphere is dispersed from the source regions via the major wind systems, such as the Trades and the Westerlies, within which relatively small-scale winds (e.g. the Sirocco and the Mistral in the Mediterranean) can be important locally. Large-scale meteorological phenomena can also affect aeolian transport; for example, long-term interannual variability in dust transport out of Africa to the Atlantic Ocean and the Mediterranean Sea has been linked to precipitation patterns induced by the North Atlantic Oscillation. Material in the marine atmosphere consists of gaseous and particulate components, both of which can originate from either natural or anthropogenic sources. Gasto-particle conversions are important in the generation of particulate material, especially that derived from anthropogenic sources; however, air/sea gaseous exchange is covered in articles on air-sea interactions, and attention here is largely confined to the particulate aerosol.

The sea surface itself is a major source of particulate material to the marine atmosphere in the form of sea salt. However, these sea salts are re-cycled components, and the globally important terrestrial sources of material to the marine atmosphere, i.e. those supplying material involved in land-sea exchange, are (i) the Earth's crust (mineral dust), and (ii) anthropogenic processes (sulfates, nitrates, etc). Other terrestrial sources, which include volcanic activity and the biosphere (e.g. direct release from vegetation, biomass burning), can also supply components to the atmosphere. Material is removed from the atmosphere by a combination of two depositional modes; (i) the 'dry' mode, which does not involve an aqueous phase, and (ii) the 'wet' (precipitation scavenging) mode, either by cloud droplets (in-cloud processes) or by falling rain (below-cloud processes).

Land^**sea Exchange of Individual Components**

Marine Aerosol: Major Components, Sources, and Distribution

Data are available on the concentrations of aerosols over many marine regions, and it is now apparent that there is an 'aerosol veil' over all oceans. Concentrations of material in the aerosol veil, however, vary from $\sim 10^3$ ng m⁻³ of air close to continental sources to $\sim 10^{-2}$ ng m⁻³ of air over pristine oceanic regions. The aerosol veil is composed mainly of mineral dust and anthropogenic components. On a global scale, the anthropogenic material is dominated by sulfate aerosols, together with smaller amounts of nitrates. The mineral dust aerosol consists of a wide variety of minerals, with quartz, the clay minerals and feldspars usually being predominant. The signatures of the major clay minerals

Figure 1 Aerosols: terrestrial sources and fluxes to the world ocean. (A) Terrestrial sources of aerosol production; light gray areas indicate regions of anthropogenic emissions, and dark gray areas indicate regions of mineral aerosol production. (Reproduced with permission from Gilman C and Garrett C (1994) Heat flux parameterizations for the Mediterranean Sea: The role of atmospheric aerosols and constraints from the water budget. Journal of Geophysical Research 99: 5119-5134.) (B) Mineral aerosol fluxes to the world ocean (units, mg m⁻² y⁻¹). (Reproduced with permission from Duce RA *et al.* (1991)).

(chlorite, kaolinite, illite, and montmorillonite) can be used as tracers to identify the sources of the dusts, the extent to which the material has been transported over the oceans, and its contribution to marine sedimentation.

The principal continental sources of both the mineral dust aerosol and anthropogenic (mainly sulfate) aerosol are concentrated in specific latitudinal belts, predominantly in the northern hemisphere (see **Figure 1A**). Quantitatively, the crust-derived mineral dust, which is derived mainly from the arid and semi-arid desert regions of the world (**Figure 1A**), imposes the strongest fingerprints on the marine aerosol. Mineral dust fluxes to the world ocean are listed in **Table 1**, and are illustrated in **Figure 2**. From this figure it can be seen that the highest dust fluxes to the sea surface are found off the major deserts, e.g. the Sahara in the North Atlantic and the Asian deserts in the North Pacific. Much of the material injected into the atmosphere from these arid sources is transported in the form of dust 'pulses'; these are related to dust storms on the

Adapted from Prospero JM (1981) and Prospero JM, Uematso M and Savoie DL (1989). In: Riley JP and Chester R (eds) Chemical Oceanography, vol. 10, pp. 137-218. London: Academic Press.

continental source regions, and are superimposed on background aerosol concentrations.

Organic Matter and Organic Compounds

Various classes of particulate organic carbon (POC) and vapour-phase organic carbon (VOC) are present in the atmosphere. The non-methane atmospheric global VOC burden has been estimated to be \sim 50 × 10¹² g, and the total POC burden to be $\sim 1-5 \times 10^{12}$ g. The principal terrestrial sources of organic matter to the atmosphere are vegetation, soils, biomass burning, and the freshwater biomass, together with a variety of anthropogenic processes. The sea surface also contributes to the organic matter burden in the marine atmosphere, with

 $\sim 14 \times 10^{12}$ g y⁻¹ of organic carbon being produced by the ocean surface; $> 90\%$ being on particles $>1 \mu m$ in diameter. Particulate organic matter (POM) is removed from the air via 'dry' and 'wet' deposition, and in addition the removal of VOM includes conversion to POM and transformation to inorganic gaseous products. Estimates of the 'wet' atmospheric depositional flux of carbon to the ocean surface range between $\sim 2.2 \times 10^{14}$ g y⁻¹ and $\sim 10 \times 10^{14}$ g y⁻¹, and for the 'dry' flux a value of $\sim 6 \times 10^{12}$ g y⁻¹ has been proposed. These are of the same order of magnitude as the estimates of fluvially transported POC entering the oceans $(\sim 1-2.5\times10^{14}$ g y⁻¹). The estimates of atmospherically transported carbon must be regarded with extreme caution, but nonetheless, even when the marine source is taken into account, the 'wet' and 'dry' flux estimates indicate that the oceans act as a major sink for organic carbon in the atmosphere. Atmospherically transported carbon, however, makes up a maximum of only $\sim 2\%$ of the carbon produced by primary productivity $(\sim 30 - 50 \times 10^{15} \text{ g y}^{-1}).$

Viable POC in the marine atmosphere includes material such as fungi, bacteria, pollen, algae, insects, yeasts, molds, mycoplasma, viruses, phages, protozoa, and nemotodes.

Non-viable POC includes carbonaceous material (which has a refractory 'soot' component) and individual organic species. Concentrations of carbonaceous aerosols in the marine atmosphere vary over the range $\sim 0.05-1.20 \,\mu g$ Cm⁻³ of air and display a distinct latitudinal distribution. In the northern hemisphere the carbon, which ranges in concentration between ~ 0.4 and $\sim 1.2 \,\mu$ g Cm⁻³ of air, has a predominantly anthropogenic continental source

Figure 2 Fluxes of lead to the world ocean (units, μ gm⁻²y⁻¹). From Duce RA *et al.* (1991).

from combustion processes. In the southern hemisphere POC concentrations are lower (range ~ 0.05 –0.30 µg C m⁻³ of air), and natural continental and marine sources are about equal.

A wide variety of individual species of both natural and synthetic organic compounds are transported from the continents to the sea surface via the atmosphere. The classes of organic compounds that have received particular attention include aliphatic hydrocarbons, wax esters, fatty alcohols, sterols, fatty acids, and long-chain unsaturated ketones. The most extensive investigation of atmospherically transported organic species on an ocean-wide basis was carried out in the Pacific as part of the SEXREX Program (Sea-Air Exchange Program). On the basis of data obtained from the Pacific it is apparent that in the remote marine atmosphere organic carbon accounts for \sim 10% of the total aerosol, although only $\sim 1\%$ of this has been characterized. The most abundant terrestrially derived components are the *n*-alkanes and the C_{21} - C_{36} fatty alcohols, which are common in the epicuticular waxes of vascular plants, and the most abundant marinederived species are the $C_{13}-C_{18}$ fatty acid salts.

The atmosphere is a major pathway for the transport of a number of organic pollutants that enter sea water. These include the synthetic trace organics, such as high molecular-weight halogenated hydrocarbons of the following compounds, or compound classes; chlorobenzenes (e.g. hexachlorobenzene, HCB), chlorocyclohexanes (e.g. hexachlorocyclohexanes, HCHs), polychlorobiphenyls (PCBs), dichlorodiphenyltrichloroethanes (DDTs), and non-halogenated coumpounds (e.g. polynuclear aromatic hydrocarbons, PAHs). Global atmospheric fluxes of HCHs, HCBs, DDTs, and PCBs to the world ocean are listed in **Table 2**, and two important conclusions can be drawn from the data. (i) The dominant deposition of the organochlorines is to the North Atlantic and North Pacific, which is consistent with their source derivations; with HCH and DDT compounds having their highest deposition rates in the North Pacific and PCBs in the North Atlantic. (ii) The atmospheric inputs of the organochlorines to the world ocean exceed those from fluvial inputs by 1 to 2 orders of magnitude.

Nutrients

These include nitrate, phosphate, and micro-nutrients such as iron. The main features in the atmospheric input of nitrogen nutrients to the world ocean can be summarized as follows. (i) The atmospheric input of total nitrogen (N) to the global ocean is $\sim 30.2 \times 10^{12}$ gNy⁻¹, made up of ~ 13.4 $\times 10^{12}$ g N y⁻¹ oxidized nitrogen species and ~ 16.8 $\times 10^{12}$ g N y⁻¹ reduced nitrogen species, which is similar in magnitude to the total (i.e. natural $+$ anthropogenic) fluvial nitrogen flux (\sim 21-49 \times 10^{12} g N y⁻¹). (ii) The overall flux of nitrogen to the sea surface is ~ 87 mg N m⁻² y⁻¹; the largest fluxes being to the North Atlantic and North Pacific. (iii) The 'wet' removal of reduced nitrogen species may be an important source of nutrients to the oceans. The atmospheric fluxes of nitrogen species usually include only inorganic forms, such as nitrate and ammonia; however, if dissolved organic nitrogen (DON), most of which has an anthropogenic source, is included in 'wet' deposition it would increase the anthropogenic input of fixed nitrogen to the oceans by a factor of \sim 1.5.

The atmospheric input of phosphate has been studied in detail in the Mediterranean Sea. However, the role played by atmospherically transported phosphorus in nutrient cycles is not clearly understood; for example, it has been proposed that Saharan dust may act as a *sink* for the removal of dissolved phosphorus in the water column by adsorption onto iron-rich particles, or as a *source* with up to \sim 8% of the phosphorus in the dusts being soluble in sea water. There is evidence that in summer months the atmosphere does provide a source of phosphorus to the Western Mediterranean and that this may account for new production, since the stratification of the surface waters prevents the input of nutrients from deep waters. For example, in the Ligurian Sea a strong summer desert dust transport episode was followed 10 days later by a significant

Table 2 The atmospheric input of some organochlorine compounds to the world oceans (units, 10^6 g y⁻¹)

| Compound ^a | North | South Atlantic | North Pacific | South Pacific | Indian Ocean | Global atmospheric | Global fluvial |
|-----------------------|----------|-------------------|-------------------------|------------------|-----------------|-----------------------|-------------------|
| | Atlantic | | | | | | |
| HCHs | 850 | 97 | 2600 | 470 | 700 | 4800 | $40 - 80$ |
| HCB | 17 | 10 | 20 | 19 | 11 | 77 | |
| DDTs | 16 | 14 | 66 | 26 | 43 | 170 | |
| PCBs | 100 | 14 | 36 | 29 | 52 | 240 | $40 - 80$ |

^aHCHs, hexachlorocyclohexanes; HCB, hexachlorobenzene; DDTs, dichlorodiphenyltrichloroethanes; PCBs, polychlorobiphenyls. Adapted from Duce RA et al. (1991).

increase in phytoplankton concentration, which could have resulted from the solubilization of phosphorus from the dusts.

In recent years there has been a renewed interest in the role played by iron as a limiting nutrient in primary production, especially in high-nitrogen, low-productivity (HNLP) regions in which there is sufficient light and nutrient concentrations but low productivity. The concentrations of iron in openocean waters are generally low, and it is thought that the element would run out before nitrate is exhausted. To provide sufficient iron it therefore has been suggested that it must be added to sea water from other sources, one of which is the long-range transport of atmospheric dust. However, iron oxyhydroxide particles and iron colloids are not directly available to phytoplankton, and the bioavailable forms of the metal are thought to be dissolved Fe(II), which is rapidly converted into Fe(III), and Fe(III) itself. As a result, iron must be dissolved from atmospheric dust before it becomes available to phytoplankton, and although adsorption onto particulate matter is the dominant control on the concentrations of dissolved iron in open-ocean waters, the deposition of mineral dust from high concentration episodic atmospheric events can result in a net addition of dissolved iron to surface waters. Further, during 'wet' deposition iron may undergo reductive dissolution to Fe(II), a form of iron that would be immediately available to phytoplankton. It also has been suggested that siderophores (compounds with a high affinity for ferric iron which are secreted by organisms) may play a role in the bioavailability of iron. Various small-scale laboratory simulations have shown that phytoplankton growth rates increase in response to the addition of iron to the system, but there is considerable disagreement over the interpretation of the results. Laboratory experiments also have been criticized on the grounds that they do not represent planktonic community response on an ocean-wide scale. To overcome this, the Fe-limitation hypothesis has been tested by large-scale intervention experiments, such as IronEx I and IronEx II, which were carried out in the equatorial Pacific. In these experiments patches of sea (defined by $SF₆$ tracer) were seeded with iron in the concentrations expected from natural events. Although there was a doubling of the plant biomass following iron addition, interpretation of the data from IronEx I was hampered as a result of the subduction of the seeded seawater patch below a layer of less dense water. During IronEx II, however, a massive phytoplankton bloom was triggered, providing direct evidence that in these HNLP waters phytoplankton growth is iron limited.

Trace Metals

Particulate trace metals in the marine atmosphere that are involved in land-sea exchange are derived from two principal terrestrial sources. The first is the Earth's crust. Crustal weathering involves lowtemperature generation processes, and crust-derived elements are found on particles with mass median diameters (MMDs) in the range \sim 1–3 µm. Relative to other sources, crust-derived elements are referred to as the non-enriched elements (NEEs). The second source comprises a variety of anthropogenic processes, which often involve high temperatures (e.g. fuel combustion, ore smelting). Anthropogenically derived elements (e.g. Pb, Cu, Zn, Cd, As, Hg) are largely found on smaller particles with $MMDs < 0.5 \mu m$, and are termed the anomalously enriched elements (AEEs). Less important terrestrial sources of trace metals to the marine atmosphere include volcanic activity and the biosphere. In addition, the sea surface supplies recycled elements to the marine atmosphere; this is a low-temperature source, and sea salt-associated elements are located on particles with MMDs in the range \sim 3-7 µm. Global elemental atmospheric emission rates from natural and anthropogenic sources are listed in **Table 3**.

The overall trace metal composition of the marine aerosol is dependent on the extent to which material from the various sources are mixed together in the atmosphere, and trace metal concentrations are a function of factors such as the distance the air mass transporting them has travelled from the source, the 'aging' of the aerosol in the air, and the relative effectiveness of the processes that remove material from the atmosphere. As a result, trace metals in the marine atmosphere have concentrations ranging over several orders of magnitude – see

Table 3 Global elemental emission rates to the atmosphere (units, 10^9 g y⁻¹)

| Element | Natural | Anthropogenic |
|---------|----------------|---------------|
| AI | 20940 | 4000 |
| As | 12 | 19 |
| Cd | 1.4 | 7.7 |
| Co | $6.1 - 7.3$ | 2.9 |
| Cr | 44 | 30.5 |
| Cu | $22 - 28$ | $35 - 52$ |
| Fe | 10370 | 6000 |
| Hg | 2.5 | 3.6 |
| Mn | $221 - 317$ | $39 - 408$ |
| Pb | $11.5 - 12$ | 332-404 |
| V | $41 - 45$ | $22 - 86$ |
| Zn | $45 - 280$ | 132-280 |

Adapted from Chester R (2000) (full references given in original table).

Table 4 Concentrations of particulate trace metals in the marine atmosphere (units, ng m^{-3} of air)

Adapted from Chester R (2000) (full references given in original table).

Table 4. It is apparent from the data in this table that, in general, the trace metal concentrations decrease with increasing remoteness from continental sources in the general rank order: coastal $seas$ > North Atlantic > North Pacific and tropical Indian $Ocean > South$ Pacific. This is reflected in trace metal fluxes, which decrease in the same sequence; lead atmospheric fluxes to the world ocean are illustrated in **Figure 2**. Despite the fact that trace metal concentrations decrease towards more pristine oceanic environments, atmospheric inputs can be the dominant source of some trace metals to the mixed layer in open-ocean regions where inputs from other sources are minimal. This is especially the case for the 'scavenged-type' metals (e.g. Al, Mn, Pb), which have a surface source and a relatively short residence time in sea water.

Aerosol-associated trace metals are removed from the air by 'dry' or 'wet' depositional processes, and once deposited at the sea surface the initial constraint on the manner in which the metals enter the major marine biogeochemical cycles is a function of the extent to which they undergo solubilization in sea water. There is considerable size-dependent fractionation between the parent aerosol and the deposited material in both the 'dry' and the 'wet' depositional modes. However, with respect to the seawater solubility of trace metals, the major difference between the two depositional modes is that they follow separate geochemical routes. In 'dry' deposition material is delivered directly to the sea surface and trace metal solubility is largely constrained by particle \leftrightarrow seawater reactivity; estimates of the seawater solubility of trace metals from aerosols are listed in **Table 5**. In contrast, in 'wet'

deposition there is an initial particle \leftrightarrow rainwater reactivity; much of this is pH-dependent, and can involve the dissolution of some trace metals prior to the deposition of the scavenged aerosol at the sea surface. Data on the trace metal composition of marine rainwaters from a number of regions are now available, and a selection are listed in **Table 6**, from which it can be seen that trace metals in rainwaters, like those in aerosols, have their highest concentrations in coastal regions and decrease towards more pristine oceanic regions.

Estimates of particulate and dissolved atmospheric and fluvial trace metal fluxes to the world ocean are listed in **Table 7**, from which a number of overall conclusions can be drawn. (i) Rivers are the principal source of particulate trace metals to the oceans; phosphorus being an exception. (ii) For iron, nickel, copper, and phosphorus the dissolved atmospheric and the dissolved fluvial inputs are the

Table 5 Seawater solubility of trace metals from particulate aerosols; % total element soluble

| Trace metal | Solubility (%) |
|-------------|----------------|
| Al | \sim 1–10 |
| Fe | \sim 1-50 |
| Mn | \sim 20-50 |
| Ni | $≤ 20-50$ |
| Cr | $≤ 10-20$ |
| V | $≤ 20-85$ |
| Cu | $≤ 10-85$ |
| Zn | $≤ 10-75$ |
| Pb | $≤ 10-90$ |
| | |

Data, which are from various sources, include both crustal and anthropogenic aerosols.

VWM, volume-weighted mean concentrations; this normalizes the trace metal concentration in a rain to the total amount of rainfall over the sampling period.

Adapted from Chester R (2000) (full references given in original table).

same order of magnitude. (iii) For lead, zinc, and cadmium the dissolved atmosphere fluxes are dominant; this will still be the case for lead even when allowance is made for the phasing out of leaded gasoline, which has accounted for a large fraction of the anthropogenic lead previously released into the atmosphere.

Conclusions

There is an 'aerosol veil' over all marine regions, and the atmosphere is a major transport route for the supply of mineral dust, organic matter, nutrients, and trace metals to the world ocean. Atmospheric fluxes decrease in strength away from the continental source regions, but in remote open-ocean areas they can be the dominant supply route for the deposition of land-derived particulate material and some trace metals to the ocean surface. Unlike fluvial inputs, which are delivered to the land-sea margins, the atmosphere supplies material to the 'mixed layer' over the whole ocean surface, and the material plays an important role in oceanic biogeochemical cycles and in the formation of marine sediments.

Table 7 Atmospheric and fluvial trace metal fluxes to the world ocean (units, 10^9 gy⁻¹)

| | Atmospheric input | | Fluvial input | | |
|---------|---------------------|------------------|----------------------|---------------------|--|
| Flement | Dissolved | Particulate | Dissolved | Particulate | |
| Fe | 3.2×10^{3} | 29×10^3 | 1.1×10^{3} | 110×10^{3} | |
| P | 310 | 640 | Total 300^a | Total 300 | |
| Ni | $8 - 11$ | $14 - 17$ | 11 | 1400 | |
| Cu | $14 - 45$ | $2 - 7$ | 10 | 1500 | |
| Pb | 80 | 10 | 2 | 1600 | |
| Zn | $33 - 170$ | $11 - 60$ | 6 | 3900 | |
| Cd | $1.9 - 3.3$ | $0.4 - 0.7$ | 0.3 | 15 | |
| As | $2.3 - 5.0$ | $1.3 - 2.9$ | 10 | 80 | |

Total phosphorus input to marine sediments. Adapted from Duce RA et al. (1991).

See also

Air+**Sea Gas Exchange. Air**+**Sea Transfer: Dimethyl** Sulphide, COS, CS₂, NH₄, Non-methane Hydrocarbons, Organo-halogens; N₂O, NO, CH₄, CO. An**thropogenic Trace Elements in the Ocean. Atmospheric Input of Pollutants. Metal Pollution. Nitrogen Cycle. Phosphorus Cycle. Photochemical Processes. Refractory Metals. Transition Metals and Heavy Metal Speciation.**

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