

The impacts of atmospheric deposition to the ocean on marine ecosystems and climate

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Introduction

The transfer of chemicals from the atmosphere to the ocean has long had an impact on the ocean (e.g. nutrient source; pH influence). With the advent of the Anthropocene, the transfer of some chemicals has increased over natural levels and the transfer of new chemicals has commenced. This brief review examines the impact of the increased transfer of certain nutrients (nitrogen, iron and phosphorus), toxins (lead and mercury) and pH regulators (carbon dioxide) on ocean ecosystems and climate.

This topic has been investigated for over 100 years, with earlier papers focusing on carbon dioxide (Bolin, 1960). A substantial body of work began to accumulate on a number of substances in the late 1960s and 1970s (e.g. Murozumi et al., 1969; Goldberg, 1971). A series of reviews was produced by the UN Group of Experts on the Scientific Aspects of Marine Environmental Protection (GESAMP), with a major review of the topic (GESAMP, 1989; Duce et al., 1991). Two additional

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GESAMP reports (GESAMP, 1991; GESAMP, 1995) tied inputs to the sea surface to global change (Liss and Duce, 1997). WMO was a founding supporter of GESAMP and currently, through the Global Atmospheric Watch programme, is leading an effort to develop an integrated database on transfer of chemicals from the atmosphere to the ocean (www.wmo.int/pages/prog/arep/gaw/gesamp.html). A new GESAMP Working Group (No. 38, supported by WMO, the International Maritime Organization, the International Council for Science Scientific Committee on Oceanic Research and the Swedish International Development Cooperation Agency) has recently been formed to address the entire issue of the atmospheric input of chemicals to the ocean.

Several factors determine whether any part of the ocean will receive atmospheric inputs that could alter biogeochemical processes. Three important factors are the reactivity of the material being deposited; the residence time of the chemical in the atmosphere; and atmospheric transport patterns, relative to anthropogenic sources, i.e. where is the chemical emitted, how long does it stay in the atmosphere, and what does it do when transferred to the ocean? These factors will be addressed in the following sections.

The atmospheric residence time of a contaminant is perhaps the most critical factor in determining whether there will be significant transport of the contaminant to open ocean regions. In general, if the atmospheric residence time of a substance is short, i.e. days, the substance will only be transported on the local-to-regional scale. Substances with residence times

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of weeks can be transported on the hemispheric scale, while those with residence times of more than one or two years can be transported globally.

Substances present on particles, such as most heavy metals and dust, will generally have relatively short residence times (days to a few weeks) and their removal, either by wet or dry deposition to the ocean surface, will generally be on a local-to-regional scale, particularly close to coastlines for terrestrial sources or near major shipping lanes for ship-based sources. This is also the case for reactive gases with short residence times. Long-lived gases such as carbon dioxide and some of the persistent organic pollutants (POPs) which have atmospheric lifetimes of decades, are distributed more uniformly globally and their input to the ocean is largely independent of the distribution of their sources.

Nutrient transport to the ocean

Iron and dust

Iron (Fe) is an essential micronutrient for marine photosynthetic organisms and in approximately 30 per cent of the surface ocean, much in the Southern Ocean, it is the nutrient that limits biological primary productivity (Martin, 1990). The primary source for open ocean iron is atmospheric deposition, since the large iron inputs to the ocean from rivers are largely removed to the sediments close to the coast (Jickells et al., 2005; Mahowald et al., 2005). The iron is present primarily in terrestrial mineral dust, largely from arid regions.

Enhanced interest in iron was stimulated by Martin (1990), who also suggested that, during periods in the past when larger quantities of mineral dust, and thus iron, were transported to the ocean, the resulting increased

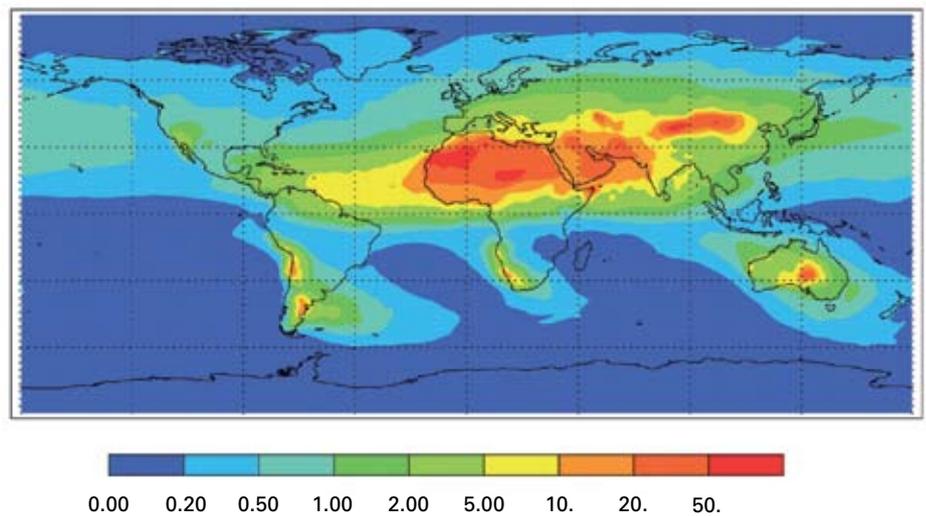


Figure 1— Average atmospheric dust deposition ($\text{g cm}^2/\text{yr}$) (from Jickells et al., 2005)

marine biological productivity caused additional drawdown of atmospheric carbon dioxide, thus affecting climate. Deserts and drylands currently occupy about one-third of the Earth's land surface. These regions are very sensitive to climate and other global changes, which can possibly alter the flux of mineral particles from the land surface to the atmosphere. The global atmospheric deposition of iron is shown in Figure 1.

Iron is present in very low concentrations in the ocean due to its low solubility in oxygenated waters. Biogeochemically, it is the soluble iron that is used as a nutrient. The iron content of soil dust averages ~3.5 per cent, but the iron solubility from soil dust is very low, generally from <1 per cent to 2 per cent in seawater. However, measurement of the solubility of iron in mineral aerosol samples indicates a higher solubility, possibly due to processing of the aerosol as it is transported over the ocean (Jickells and Spokes, 2001).

Factors that control aerosol iron solubility include photochemistry, especially the photo-reduction of Fe III to Fe II, and the acidic environment of the mineral aerosol, particularly during aerosol cloud processing (Jickells and Spokes, 2001). We know that the emissions of acid precursors

such as sulphur dioxide and nitrogen oxide have more than doubled as a result of anthropogenic activity and nitrogen oxide emissions are expected to continue to increase (Dentener et al., 2006).

Mineral dust particles primarily have diameters from 0.1 to 10 μm , with a mean diameter of ~2 μm . These particles have lifetimes that allow them to be transported thousands of kilometres, with subsequent deposition to the ocean (see Figure 1). Dust production, transport and deposition to the oceans depend on climatic factors that affect the uplift, wind velocity and rainfall (which is important for removal of particles). Human activities may have increased the production of atmospheric dust by up to 50 per cent (Mahowald, Engelstaedter et al., 2009).

The suggestion of Martin (1990) that iron is a limiting nutrient in large areas of the ocean has led to a series of mesoscale iron addition experiments to test this hypothesis. As pointed out by Boyd et al. (2007), these experiments “reveal that iron supply exerts controls on the dynamics of plankton blooms, which in turn affect the biogeochemical cycles of carbon, nitrogen, silicon and sulphur and ultimately influence the Earth climate system”.

Nitrogen and phosphorus

All organisms on Earth require nitrogen but less than 1 per cent of all biological species have the ability to convert ubiquitous molecular nitrogen (N_2) into bio-available reactive nitrogen (N_r). Because of its scarcity, nitrogen is often the limiting nutrient for croplands, forests and grasslands and coastal and open ocean ecosystems. Humans have, in principle, solved the problem of the nitrogen limitation of croplands through nitrogen fertilizer production. Since most of the nitrogen used in food production and all the reactive nitrogen produced by fossil fuel combustion is lost to the environment, however, there is a substantial leakage of reactive nitrogen to unmanaged systems, including terrestrial and marine ecosystems.

The atmosphere is the most important vector distributing anthropogenic reactive nitrogen to the global environment. In the mid-1990s, about 40 per cent of anthropogenic reactive nitrogen created was emitted to the atmosphere. By 2050, it will be 50 per cent. Thus, with the exception of coastal ecosystems (where rivers are an important reactive nitrogen source) atmospheric deposition is the most important process supplying anthropogenic reactive nitrogen to unmanaged terrestrial and marine ecosystems (Galloway et al., 2008).

Not surprisingly, atmospheric reactive nitrogen deposition has increased substantially with the advent of

the industrial age and intensive agriculture. In 1860, reactive nitrogen deposition to most of the ocean was $<50 \text{ mg N m}^2/\text{yr}$, with very few areas $>200 \text{ mg N m}^2/\text{yr}$. Most oceanic deposition was from natural sources; anthropogenic sources impacted only a few coastal regions. By 2000, deposition over large ocean areas exceeded $200 \text{ mg N m}^2/\text{yr}$, reaching $>700 \text{ mg N m}^2/\text{yr}$ in many areas. Intense deposition plumes extend far downwind of major population centres in Asia, India, North and South America, around Europe and west of Africa (Figure 2) (Duce et al., 2008).

Atmospheric reactive nitrogen deposition is now approaching molecular nitrogen fixation as a result of the dramatic increase in the anthropogenic component. These increasing quantities of atmospheric anthropogenic fixed nitrogen entering the open ocean could account for up to about one-third of the ocean's external (non-recycled) nitrogen supply and up to ~ 3 per cent of the annual new marine biological production, ~ 0.3 petagram of carbon per year. This input could account for the production of up to ~ 1.6 teragrams of nitrous oxide per year. Although ~ 10 per cent of the ocean's drawdown of atmospheric anthropogenic carbon dioxide may result from this atmospheric nitrogen fertilization, leading to a decrease in radiative forcing, up to about two-thirds of this amount may be offset by the increase in emissions of nitrous oxide, a greenhouse gas. On the basis of future scenarios for anthropogenic emissions, the contribution of atmospheric anthro-

pogenic reactive nitrogen to primary production could approach current estimates of global nitrous oxide fixation by 2030 (Duce et al., 2008).

In addition to nitrogen and iron, phosphorus (P) can also be a limiting nutrient in the open ocean. A recent review (Mahowald, Jickells et al., 2009) suggests that there is a net loss of total phosphorus from many land ecosystems and a net gain of total phosphorus by the oceans (560 Gg P/yr). Mineral aerosols are the dominant source of total phosphorus on a global scale (82 per cent), with primary biogenic particles (12 per cent) and combustion sources (5 per cent) important in non-dusty regions. Globally averaged anthropogenic oceanic inputs are estimated to be ~ 5 per cent and 15 per cent for total phosphorus and phosphates, respectively, and may contribute as much as 50 per cent to the deposition over the oligotrophic ocean, where productivity may be phosphorus-limited. Mahowald, Jickells et al. (2009) also speculate that the increased injection of anthropogenic nitrogen into the ocean could also shift some marine regions from being nitrogen-limited to phosphorus-limited.

Toxic metal transport to the ocean

Lead

Large quantities of the toxic heavy metal lead (Pb) have been emitted

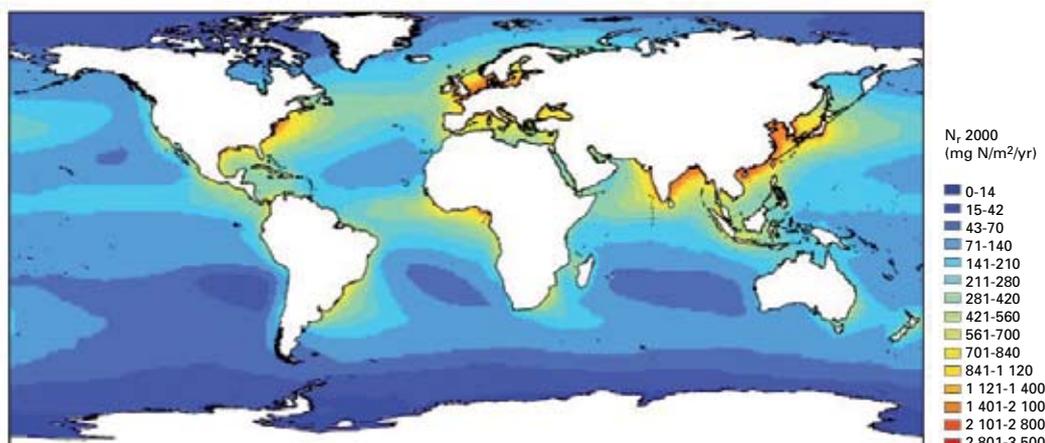


Figure 2 — Total atmospheric reactive nitrogen deposition in 2000 in $\text{mg m}^2/\text{yr}$ (from Duce et al., 2008)

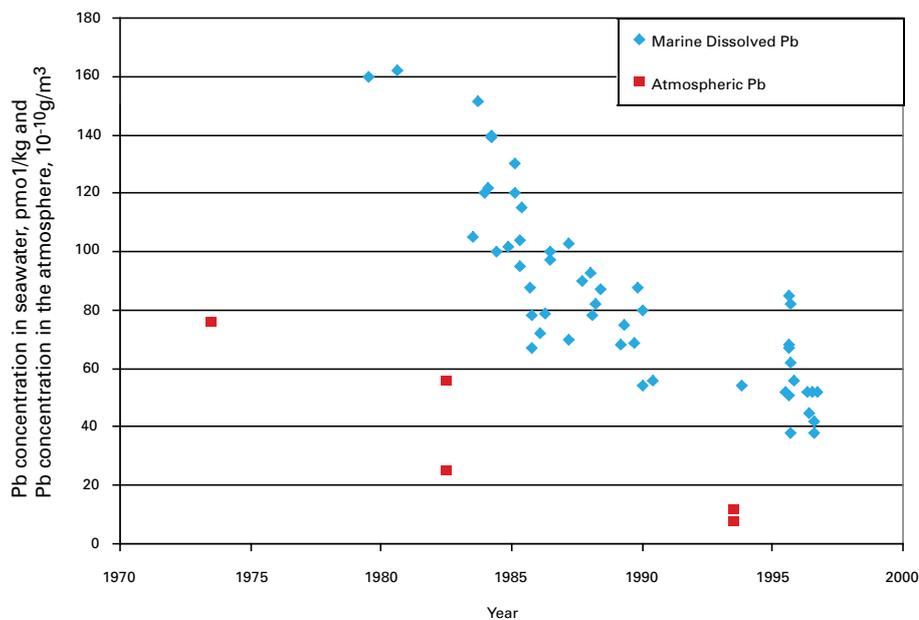


Figure 3 — Change in atmospheric and oceanic lead concentrations from the 1970s to the late 1990s near Bermuda (from Duce, 2001, using data from Huang et al., 1996 and Wu and Boyle, 1997)

to the atmosphere as a result of human activities. This lead is on very small submicrometre particles and can be transported thousands of kilometres before depositing in the ocean. Smelters and other industrial processes are important sources but the primary source for atmospheric lead until recently was the combustion of fuels containing tetraethyl lead. Atmospheric deposition of anthropogenic lead has resulted in a measurable increase in surface ocean water lead concentrations.

While this is most noticeable in the North Atlantic, it could even be seen 20-30 years ago in the South Pacific (Patterson and Settle, 1987). Lead is one of the few metals for which atmospheric deposition has observably affected its concentration in the surface ocean. However, because of the removal of lead from motor vehicle fuels, input to the ocean has decreased significantly over the past 20-30 years (Huang et al., 1996; Wu and Boyle, 1997). Figure 3 shows atmospheric and surface oceanic lead concentrations at or near Bermuda from the early 1970s to near 2000. The decrease in atmospheric lead is reflected in a similar decrease in lead in the surface ocean. Similar results

have been found near Hawaii. Because lead has a short oceanic residence time (~10-20 years), changes in the atmospheric input flux showed up relatively quickly in the surface-water concentrations.

Mercury

It is now well established that atmospheric deposition is the main source of mercury (Hg) in the ocean (Mason and Scheu, 2002). Most atmospheric mercury is present as gaseous elemental mercury, although gas-phase ionic mercury is also found. The primary form of mercury deposited to the ocean is divalent ionic mercury (Hg²⁺) in rain, but dry deposition of gas-phase ionic mercury may also be important (Fitzgerald et al., 2007). It has been estimated that, in the past 200 years, the global atmospheric burden of mercury has increased by a factor of 5 as a result of human activities, leading to increased inputs of mercury to the ocean over that time (Slemr and Langer, 1992). Human activities clearly dominate terrestrial natural sources for atmospheric mercury. Mercury input to the ocean may actually be decreasing now in some regions, however: there is evidence that, in the upper-ocean water

column near Bermuda, mercury may have decreased by a factor of about 2 between 1979 and 2000 (Mason and Gill, 2005).

Mercury is highly toxic and there have been a number of instances of its toxicity in coastal regions, starting with the infamous Minamata Bay incident. While there is no evidence that mercury in surface open ocean waters has caused any toxicity effects, there is considerable evidence that some fish in open ocean regions concentrate mercury sufficiently to be harmful to humans if too much of that fish is consumed. Given the bio-accumulation of mercury in fish, additional data on its deposition rates and the role that humans play in them, are needed.

Carbon dioxide and ocean acidification

As atmospheric carbon dioxide (CO₂) rises due to human activities, the amount of dissolved carbon dioxide in the oceans also increases. Since industrialization, about half the anthropogenic carbon dioxide emitted to the atmosphere has dissolved in the oceans. Because the pH of seawater (about 8.2 ± 0.3) is determined by the balance between dissolved alkaline (basic) substances entering the oceans from land weathering and the dissolution of atmospheric carbon dioxide (to produce acidity or hydrogen ions (H⁺) in the water), an increase in atmospheric carbon dioxide will cause seawater to become more acidic. Concomitantly, the concentration of carbonate (CO₃²⁻) ions will fall, making it harder for organisms to make their shells of calcium carbonate (CaCO₃), since they rely on the supersaturation provided by the concentration of carbonate ions.

Since the advent of major industrialization, it has been calculated that the pH of the surface oceans has decreased by 0.1 pH units, corresponding to a 30 per cent increase in hydrogen ion concentration. By assuming what the

level of atmospheric carbon dioxide will be in the future, it is possible to calculate that, at the end of this century, the pH of surface seawater may well be lowered by 0.5 pH units, corresponding to a 300 per cent increase in hydrogen ion concentration from pre-industrial times.

This increase is well outside the range of natural variation indicated above and the predicted pH is probably lower than has occurred for several hundreds of thousands of years—perhaps longer. Furthermore, the rate of hydrogen ion increase has been much more rapid than anything experienced by the oceans over this period (Royal Society, 2005). Given this profound and rapid change in the acid/base balance of seawater, what are the implications for biological life, marine ecology and biogeochemical feedbacks, including the very ability of the oceans to absorb anthropogenic carbon dioxide?

Corals are an obvious example of widespread calcium-carbonate-secreting organisms and they will very likely be adversely affected by

the lower availability of carbonate ions in a higher carbon dioxide world. This will add to the effect of raised seawater temperature that already appears to be affecting corals in tropical waters. In addition, microscopic phytoplankton having structures made of calcium carbonate (common throughout the oceans) will also be at a disadvantage (see Figure 4). In contrast, plankton that form their structures by fixation of carbon may well benefit from the availability of extra carbon from the increase in carbon dioxide. Indeed, this may even be the situation for some carbonate secretors according to a recent study (Iglesias-Rodriguez et al., 2008) that found evidence for increased calcification in one phytoplankton species under lowered seawater pH. Any effects are likely to be most pronounced in the Southern Oceans, where the low water temperature leads to enhanced dissolution of carbon dioxide. Clearly, organisms will respond and/or adapt in different ways to the lowered pH so that increased acidity will almost certainly lead to changes in marine biodiversity.

Changes are also likely to occur in the ocean's ability to absorb carbon dioxide, because the addition of acidity leads to a decrease in carbonate ions that provide seawater with much of its natural ability to absorb carbon dioxide. Thus, less of the carbon dioxide emitted into the atmosphere will be taken up by the oceans, having a potentially important feedback on global warming. Other gases important for climate and air quality such as dimethyl sulphide and organohalogens are also likely to be affected by pH-induced changes in microorganisms in near-surface seawater that produce these compounds.

Sulphur and nitrogen oxides are other acidic gases formed as a result of the combustion of fossil fuels. Like carbon dioxide, they also dissolve in water to form acidic solutions—indeed, they are generally stronger acid formers. Doney et al. (2007) report a modelling exercise to assess the relative importance of carbon dioxide versus sulphur and nitrogen oxides and conclude that, for the global oceans, carbon dioxide greatly outweighs the other two oxides.

Geo-engineering schemes to moderate climate change directly (e.g. mirrors in space, injection of particles into the stratosphere) will do nothing to solve the ocean acidification problem. The only realistic way to do that is to decrease the amount of carbon dioxide emitted into the atmosphere. Although the physical chemistry behind the role of carbon dioxide in seawater is straightforward, the effect of decreasing pH on biological life in the ocean and feedbacks to the global system are far from clear. Because of this, it is a subject in need of urgent further study; indeed, several major research programmes are currently in progress or will soon be initiated.

Conclusion

The atmospheric transport of chemicals to the ocean has been investigated for over a century. With time, we have found that the

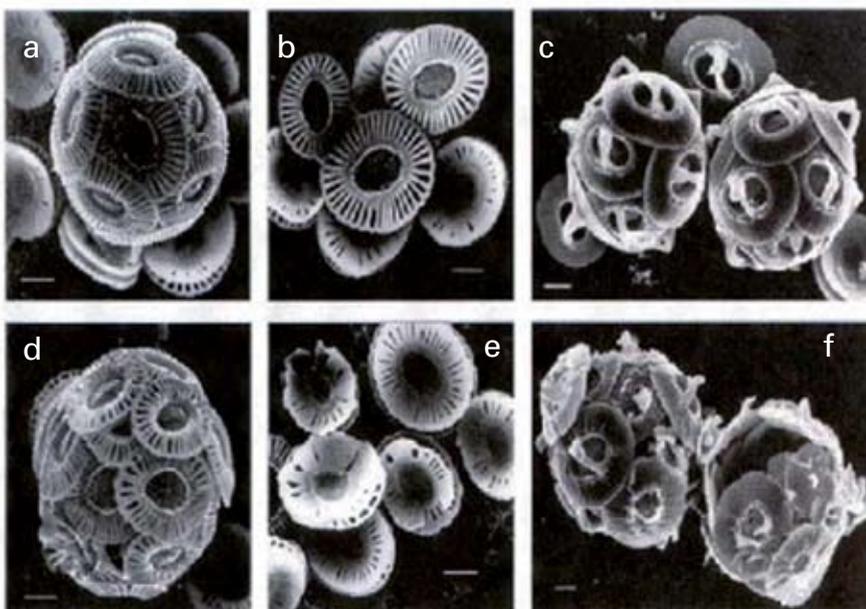


Figure 4 — Scanning electron microscope pictures of coccolithophorids grown under low and high carbon dioxide conditions, corresponding to carbon dioxide levels of about 300 ppmv ((a)-(c)) and 780-850 ppmv ((d)-(f)). Note the difference in the coccolith structure (including malformations) and in the degree of calcification of cells grown at normal and elevated carbon dioxide levels (from Riebesell et al., 2000).

atmosphere is a critical source of nutrients, toxins and acids. We have also found that there no region of the oceans escapes the influence of human action and that this influence will increase in the future as both the human population and the per capita use of resources continue to grow.

References

- BOLIN, B., 1960: On the exchange of carbon dioxide between the atmosphere and the sea, *Tellus*, 12, 274-281.
- BOYD, P.W., T. JICKELLS et al., 2007: Mesoscale iron enrichment experiments 1993-2005: Synthesis and future directions, *Science*, 315, 612, doi: 10.1126/science.1131669.
- DENTENER, F., J. DREVET et al., 2006: Nitrogen and sulfur deposition on regional and global scales: A multimodel evaluation, *Global Biogeochem. Cycles*, 20, GB4003, doi:10.1029/2005GB002672.
- DONEY, S.C., N. MAHOWALD et al., 2007: Impact of anthropogenic atmospheric nitrogen and sulfur deposition on ocean acidification and the inorganic carbon system, *Proc. National Academy of Sciences*, 104, 14580-14585.
- DUCE, R.A., 2001: Atmospheric input of pollutants, *Encyclopedia of Ocean Sciences*, Academic Press, New York, 192-201.
- DUCE, R.A., P.S. LISS et al., 1991: The atmospheric input of trace species to the world ocean, *Global Biogeochemical Cycles*, 5, 193-259.
- DUCE, R.A., J. LAROCHE et al., 2008: Impacts of atmospheric nitrogen on the open ocean, *Science* 320, 893-897.
- FITZGERALD, W.F., C.H. LAMBORG and C.R. HAMMERSCHMIDT, 2007: Marine biogeochemical cycling of mercury, *Chem. Rev.*, 107, 641-662.
- GALLOWAY, J.N., A.R. TOWNSEND et al., 2008: Transformation of the nitrogen cycle: recent trends, questions and potential solutions, *Science*, 320, 889-892.
- GESAMP, 1989: The atmospheric input of trace species to the world ocean, Rep. Stud., GESAMP 38, 111 pp.
- GESAMP, 1991: Global changes and the air/sea exchange of chemicals, Rep. Stud., GESAMP 48, 69 pp.
- GESAMP, 1995: The sea-surface microlayer and its role in global change, Rep. Stud., GESAMP 59, 76 pp.
- GOLDBERG, E.D., 1971: Atmospheric dust, the sedimentary cycle and man, *Comments in Geophysics: Earth Sci.* 1, 117-132.
- HUANG, S., R. ARIMOTO and K. RAHN, 1996: Changes in atmospheric lead and other pollution-derived trace elements at Bermuda, *J. Geophys. Res.*, 101, 21033-21040.
- IGLESIAS-RODRIGUEZ, M.D. et al., 2008: Phytoplankton calcification in a high-CO₂ world, *Science*, 320, 336-240.
- JICKELLS, T.D. and L. SPOKES, 2001: *Atmospheric iron inputs to the ocean, in Biogeochemistry of Iron in Seawater* (D. Turner and K.A. Hunter (Eds.)), John Wiley, Hoboken, New Jersey, 85-121.
- JICKELLS, T., Z.S. AN et al., 2005: Global iron connections between desert dust, ocean biogeochemistry and climate, *Science*, 308, 67-71.
- LISS, P.S. and R.A. DUCE (Eds.), 1997: *The Sea Surface and Global Change*, Cambridge University Press, 519 pp.
- MAHOWALD, N., A.R. BAKER et al., 2005: Atmospheric global dust cycle and iron inputs to the ocean, *Global Biogeochem. Cycles*, 19, GB4025, doi:10.1029/2004GB002402.
- MAHOWALD, N., S. ENGELSTAEDTER et al., 2009: Atmospheric iron deposition: global distribution, variability and human perturbations, *Annual Review of Marine Science*, 1, 248-278.
- MAHOWALD N., T.D. JICKELLS et al., 2009: The global distribution of atmospheric phosphorus sources, concentrations and deposition rates and anthropogenic impacts, *Global Biogeochemical Cycles* (in press).
- MARTIN, J.H., 1990: Glacial-interglacial CO₂ change: The iron hypothesis, *Paleoceanography*, 5, 1-13.
- MASON, R. P. and G.A. GILL, 2005: Mercury in the marine environment. In: *Mercury: Sources, Measurements, Cycles and Effects* (M.B. PARSONS and J.B. PERCIVAL (Eds.)). Mineralogical Association of Canada, 2005; Vol. 34, Chapter 10.
- MASON, R. P. and G.R. SHEU, 2002: Role of the ocean in the global mercury cycle, *Global Biogeochem. Cycles*, 16 (<http://dx.doi.org/10.1029/2001GB001440>).
- MUROZUMI, N., T.J. CHOW and C.C. PATTERSON, 1969: Chemical concentrations of pollutant lead aerosols, terrestrial dusts and sea salts in Greenland and Antarctic snow strata, *Geochim. Cosmochim. Acta*, 33, 1247-1294.
- PATTERSON, C.C. and D. SETTLE, 1987: Review of data on eolian fluxes of industrial and natural lead to the lands and seas in remote regions on a global scale, *Marine Chemistry*, 22, 137-1620.
- RIEBESELL, U., I. ZONDERVAN et al., 2000: Reduced calcification of marine plankton in response to increased atmospheric CO₂, *Nature*, 407, 634-637.
- ROYAL SOCIETY, 2005: Ocean acidification due to increasing atmospheric carbon dioxide. Policy Document 12/05, Royal Society, London, 60 pp.
- SLEMR, F. and E. LANGER, 1992: Increase in global atmospheric concentrations of mercury inferred from the measurement over the Atlantic Ocean, *Nature*, 355, 434-437.
- WU, J. and E.A. BOYLE, 1997: Lead in the western North Atlantic Ocean: Completed response to leaded gasoline phaseout, *Geochim. Cosmochim. Acta*, 61, 3279-3283.