



Editorial

Marine chemistry special issue: Aerosol chemistry and impacts on the ocean

Aerosol particles consist of many natural and anthropogenic components, including mineral dust, soot, organic molecules, sea salt crystals, spores, bacteria, and other microscopic particles (Duce, 2005). Atmospheric aerosol deposition has been recognized as an important source of nutrients and trace metals (Mahowald et al., 2005, 2008) to the open ocean that can enhance ocean productivity and carbon sequestration and thus influence atmospheric carbon dioxide concentrations and climate.

As a result, studies of aerosol chemistry are a significant component of major international science programs including GEOTRACES and SOLAS. The GEOTRACES Science Plan emphasizes that atmospheric deposition may be the critical pathway for maintaining the concentrations of biologically-required trace elements such as Fe, Co, and perhaps Zn in surface waters of the open ocean. Atmospheric deposition is important for other trace elements and isotopes (TEIs) that are used to study ocean biogeochemical cycles. It is critical to quantify the extent to which aerosol material is soluble in the oceans, and to understand the factors controlling this solubility well enough to be able to reliably model them. (Web REF: <http://www.geotraces.org/>). In the SOLAS Science Plan, it is noted that the atmospheric input of aerosols containing iron and other essential trace metals will be affected by natural and anthropogenic changes in climate and global biogeochemistry. This may alter carbon partitioning and biogenic air-sea gas fluxes due to changes in phytoplankton productivity and the food web structure (Web REF: <http://www.solas-int.org/>).

Aerosol inputs to the ocean vary considerably both spatially and temporally and their contribution of nutrient and trace metal loads depends on the origin and sources of the aerosols particles (e.g. mineral dust, combustion products, volcanic ash etc), chemical processes occurring on particle surfaces in the atmosphere, the solubility of the various aerosol constituents and the physical, chemical and biological characteristics at the site of deposition. Because of the recognized importance of aerosol deposition to the ocean and the dynamic nature of aerosol inputs, this topic has gained considerable interest over the past decade from both atmospheric scientists and the oceanographic community. This special issue, which reflects the current areas of discussion and research within this interdisciplinary field, includes 18 manuscripts that fall into three categories (1) discussion on the various processes that may impact aerosol solubility with particular emphasis on the solubility of iron in aerosols; (2) new time series data that report atmospheric deposition rates in various regions of the world; and (3) studies focusing on the biogeochemical implications of atmospheric deposition to the ocean.

1. Various controls on aerosol chemistry and solubility

A variety of factors acting in concert control the solubility of aerosols in the surface ocean (e.g. aerosol source, mineralogy, particle

size, and chemical alteration during transport). Before we can reliably model the biogeochemical response to aerosol deposition, we must understand these factors. Five papers in this issue are devoted to studies of these processes and to quantifying the fractional solubility of aerosol Fe and other chemical tracers.

Baker and Croot (2010-this issue) discuss the factors that are believed to affect aerosol iron solubility in seawater, and use the analogy of electrical resistors in parallel to develop a conceptual model for the overall solubility of aerosol iron in the oceans. They also point out the wide variety of experimental methods used to measure aerosol iron solubility, and the need to conduct additional studies in this area. Buck et al. (2010a-this issue) report on the size distribution and solubility of aerosols samples collected in the North Atlantic as part of the CLIVAR/Repeat Hydrography program. Their data confirm earlier reports that the majority of the total and soluble aerosol Fe is found on particles larger than 1 μm . In contrast to expectations, they did not find that the aerosol Fe solubility increased on fine particles. Aguilar-Islas et al. (2010-this issue) present aerosol Fe solubility results from a newly developed semi-continuous batch protocol, and conclude that colloidal Fe dominates the soluble fraction. They also suggest that differences in aerosol source and type, rather than differences in leaching methods, are responsible for most of the reported variability in aerosol Fe solubility. Mendez et al. (2010-this issue) conducted laboratory experiments to study the kinetics and thermodynamics of aerosol Mn and Fe solubility in seawater. In their experiments, aerosol Mn solubility was controlled by the amount of available Mn on the particles surfaces, while aerosol Fe solubility was controlled by the concentration of Fe binding ligands in the seawater. Finally, Anderson et al. (2010-this issue) used a sequential leaching scheme to study the phase association of phosphorus in anthropogenic and natural mineral aerosols in the Gulf of Aqaba. They report that while mineral phases account for the majority of the soluble aerosol P, that P is more soluble from anthropogenic aerosols.

2. Time series data on aerosol deposition at various regions

Several papers in this volume report new estimates of atmospheric deposition of various constituents to different region of the world's ocean ranging from open ocean areas of relatively low deposition to areas of high deposition fluxes. These papers increase the data archive for atmospheric deposition and expand our appreciation of the spatial and temporal variability of this source of nutrients and trace metals to the surface ocean. Buck et al. (2010b-this issue) discuss the solubility and deposition of trace elements in the North Atlantic Ocean and relate this to factors thought to influence aerosol solubility such as chemical weathering and aerosol source. They observe that aerosol concentrations varied spatially with the highest concentrations observed between 23°N and 8.7°N. Trapp et al. (2010-this issue)

show both that significant temporal and spatial variability of the elemental composition of aerosols is evident at Barbados and Miami. They analyze a large suite of elements and conclude that most of these constituents are very close to average upper crustal abundances. The greatest enrichments and the largest variability were seen for As, Cd, Cu, Cr, Ni, Pb, V, and Zn, elements known to have major anthropogenic sources. They conclude that the uniformity of dust composition suggests that a major fraction of the dust is either derived from regions having similar composition or from multiple different sources followed by mixing during transport. Knapp et al. (2010-this issue) and Wankel et al. (2010-this issue) use the flux and isotopic composition of nitrogen in Bermuda rain and Eilat dry deposition respectively to assess sources of N in aerosols. Both studies detect seasonality in the isotope ratio of N species in atmospheric deposition and both suggest that the low $\delta^{15}\text{N}$ of the TN flux will cause it to have an effect on the $\delta^{15}\text{N}$ of thermocline NO_3^- that is in the same sense as the effect of N_2 fixation complicating fixation rate estimates based on natural abundance of N isotopes. Theodosi et al. (2010a-this issue) report on iron speciation, solubility and temporal variability in wet and dry deposition in the Eastern Mediterranean and suggest that Fe solubility is enhanced by acidic species in aerosols. They further conclude that dissolved iron in the Mediterranean Sea could be exclusively attributed to atmospheric deposition. The biogeochemical implications of atmospheric dissolved iron on phytoplankton growth and nitrogen fixation were also investigated. During summer and autumn dissolved Fe was deposited in quantities much higher than those required for phytoplankton growth and nitrogen, indicating the significant role of atmospheric deposition in the biogeochemical N cycle in the Mediterranean. Two studies report on the atmospheric transport and deposition of anthropogenic substances (Uematsu et al., 2010-this issue) and trace elements (Hsu et al., 2010-this issue) to the East China Sea. Uematsu et al. (2010-this issue) use ratios of various constituents to assess the sources of aerosols that highlight the fact that atmospheric pollutants from Asia, including heavy metals and major ions, are carried to the East China Sea even during non-dusty periods. Similarly, Hsu et al. (2010-this issue) use the elemental ratios in aerosols to conclude that total concentrations of both the chemical species of dust origin and of anthropogenic origin were higher during the Asian dust period, suggesting that the Asian outflow of air pollutants often accompanies the Asian dust advection. A variety of controlling factors of the solubilities of the elements were discussed in this study.

3. Impacts of atmospheric deposition on ocean biogeochemistry

Finally, several of the manuscripts in this special volume focus on the potential impacts and interactions that atmospheric deposition have on biological processes in the surface ocean. Boyd et al. (2010-this issue) investigate the relationship between modes of iron supply (mechanisms, dissolution rate and timescales) to the upper ocean and the subsequent biological responses. They find that the biological response in the ocean to aerosol iron deposition is relatively limited and attribute that to a wide range of confounding factors including seasonality of environmental factors controlling phytoplankton production (light, silicic acid, phosphate, iron), and the elemental stoichiometry of the aerosols (iron and other nutrients) during dissolution. They explore the mode of iron release using a simple dust/biota assessment test and conclude that dust deposition can easily be mistakenly attributed as a primary cause of enhanced biological activity and that, due to the slow dissolution of iron, dust-mediated phytoplankton blooms are probably rare in the modern ocean. Measures et al. (2010-this issue) also investigate the mode of release of metals from aerosols when added to seawater and find that like Fe much of the Al is released rapidly and attribute this to the interaction of mineral dust with atmospheric acids. They emphasize the need for the development of a common protocol for treating

aerosol samples as also emphasized by the suite of papers published in this volume that deal with the controls on aerosol solubility. Two papers discuss the significance of atmospheric inputs of a suite of trace metals to different regions of the Mediterranean. Theodosi et al. (2010b-this issue) find that atmospheric deposition of major and trace metals was sufficient to balance metals in the water column, indicating the predominant role of atmospheric deposition as an external source of trace elements in the eastern Mediterranean Sea. Guieu et al. (2010-this issue) conclude that atmospheric iron deposition has a strong impact on the iron marine cycle in the Mediterranean Sea and that atmospheric phosphate inputs during summer can sustain the new primary production during the stratification period on the scale of the whole open Mediterranean. Violaki et al. (2010-this issue) studied dissolved organic nitrogen (DON) atmospheric deposition in the eastern Mediterranean and found that DON consisted about 23% of the total N annual atmospheric flux and that 20–30% of the new production which could be stimulated by the atmospheric TDN deposition in the Eastern Mediterranean basin can be attributed to DON. Markaki et al. (2010-this issue) also studied deposition of dissolved nitrogen and phosphorus in the Mediterranean and suggested that this may explain the anomalous seawater N/P ratio of the Mediterranean and may suggest a relationship between atmospheric deposition and seawater productivity of this area.

4. The future for aerosol chemistry

Rapid advances in our understanding of the processes that affect the solubility of aerosol trace elements and isotopes, and the impacts this has on biogeochemical cycles in the oceans, can be expected due to improved analytical instrumentation and development of new experimental methodologies. These studies will help calibrate proxies used to study past ocean conditions, they will inform us on how atmospheric deposition influences ocean productivity, and they will contribute to our understanding of future global climate change. Recognition of the importance of atmospheric deposition in international science programs (e.g. GEOTRACES, SOLAS) provides a framework for aerosol scientists, marine biogeochemists, and modelers to work towards the common goals of understanding how the whole “Earth system” functions.

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