

84

REPORTS AND STUDIES



GESAMP

Joint Group of Experts on the
Scientific Aspects of Marine
Environmental Protection

THE ATMOSPHERIC INPUT OF CHEMICALS TO THE OCEAN



GESAMP REPORTS AND STUDIES NO. 84

GAW REPORT NO. 203



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ISSN 1020-4873

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For bibliographic purposes this document should be cited as:

GESAMP (IMO/FAO/UNESCO-IOC/UNIDO/WMO/IAEA/UN/UNEP/UNDP Joint Group of Experts on the Scientific Aspects of Marine Environmental Protection). 2012. The Atmospheric Input of Chemicals to the Ocean. Rep. Stud. GESAMP No. 84/GAW Report No. 203. 69 pp.

**GESAMP**

Joint Group of Experts on the
Scientific Aspects of Marine
Environmental Protection

IMO FAO UNESCO-IOC UNIDO WMO IAEA UN UNEP UNDP

THE ATMOSPHERIC INPUT OF CHEMICALS TO THE OCEAN



IMO INTERNATIONAL
MARITIME
ORGANIZATION

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THE UNIVERSITY
OF ARIZONA

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Executive Summary

The atmospheric input of chemicals to the ocean is closely related to a number of important global change issues. The increasing input of atmospheric anthropogenic nitrogen species to much of the ocean may cause a low level fertilization of the ocean that could result in an increase in marine 'new' productivity of up to ~3% and thus impact carbon drawdown from the atmosphere. However, the increase in nitrogen inputs are also likely to increase the formation of nitrous oxide in the ocean. The increased emission of this powerful greenhouse gas will partially offset the climate forcing impact resulting from the increase in carbon dioxide drawdown produced by N fertilization. Similarly, much of the oceanic iron, which is a limiting nutrient in many areas of the ocean, originates from the atmospheric input of minerals as a result of the long-range transport of mineral dust from continental regions. The increased supply of soluble phosphorus from atmospheric anthropogenic sources (through large-scale use in fertilizers) may also have a significant impact on surface-ocean biogeochemistry, but estimates are highly uncertain. While it is possible that the inputs of sulphur and nitrogen oxides from the atmosphere can add to the rates of ocean acidification occurring due to rising levels of carbon dioxide, there is too little information on these processes to assess the potential impact. These inputs may be particularly critical in heavily trafficked shipping lanes and in ocean regions proximate to highly industrialized land areas. Other atmospheric substances may also have an impact on the ocean, in particular lead, cadmium, and POPs. GESAMP initiated Working Group 38, The Atmospheric Input of Chemicals to the Ocean, to address these issues.

Working Group 38 was initially formed to address the following Terms of Reference:

- 1) Assess the need for the development of new model and measurement products for improving our understanding of the impacts of the atmospheric deposition of nitrogen species and dust (iron) to the ocean;
- 2) Review the present information on the atmospheric deposition of phosphorus species to both the marine and terrestrial environments, considering both natural and anthropogenic sources, and evaluate the impact of atmospheric phosphorus deposition on marine and terrestrial ecosystems. Consider whether such a review of any other substance would be useful.
- 3) Work with the WMO Sand and Dust Storm Warning and Assessment System (SDS-WAS) and with the WMO Precipitation Chemistry Data Synthesis and Community Project to evaluate the needs of the marine community and assist in clearly articulating them in the development of these WMO efforts.

Additional tasks were later developed for the working group, in particular to more specifically elaborate the role of minerals carried by the dust which is responsible for marine production and to achieve more detailed and more specific description of the atmospheric transport and deposition process of iron- and phosphorus-carried minerals. To this end, the activities of Working Group 38 were extended with the aim of bringing together the SDS-WAS and GESAMP scientific communities and, as a result of their joint effort, to evaluate the following topics:

- | | |
|---------|--|
| Topic 1 | Improving the quantitative estimates of the geographical distribution of the transport and deposition of mineral matter and its content to the ocean. |
| Topic 2 | Developing case-studies of dust/Fe/P input to the ocean and the resultant marine response utilizing SDS-WAS transport modelling, remote-sensing, in-situ observations, and ocean biogeochemical modelling. |
| Topic 3 | Specifying test-bed regions for joint studies of the transport and deposition to the ocean of mineral matter. |

Charges 1) and 2) above were addressed by developing separate peer-reviewed scientific papers in the areas of phosphorus, nitrogen, sulphur, iron and organic matter deposition from the atmosphere to the ocean. Summaries of these papers are presented in this report. Charge 3) was addressed by the development of two advisory letter reports to the World Meteorological Organization in the areas of dust deposition to the ocean and precipitation chemistry over the ocean, and they are presented in this report. Topics 1, 2, and 3 were discussed in detail at a joint meeting of GESAMP WG38 and SDS-WAS, and separate analyses on each of these topics were developed and are presented in this report.

The results of the deliberations of this working group have significant implications for policy-makers. Atmospheric mineral dust often originates from very specific source areas and is then transported over long distances, influencing the climate and chemistry of the atmosphere on local, regional, and global scales. It has implications for

human health, visibility, and climate. It also provides essential components for ocean fertility, primarily the micronutrient iron. Measurements on various times scales have suggested strong correlations of dust emissions, transport and deposition with climate change. Given the importance of dust in the earth system, including deposition to the oceans, it is unfortunate that it represents one of the primary uncertainties in future climate change scenarios. Policy-makers must become aware of the importance of atmospheric mineral dust and its wide range of environmental impacts.

Continued support for research on mineral dust has multiple benefits ranging from improving short-term forecasting to improved understanding of the role of mineral dust in supplying nutrients to the world's oceans. Supplying iron to iron-depleted regions has been proposed as a form of *geo-engineering* to remove carbon dioxide from the atmosphere. While a discussion of the pros and cons of this approach is beyond the scope of the Working Group, we require a much better understanding of the role of mineral dust and related processes before we can make sound science-based decisions.

Absorption by the ocean of gases such as sulphuric and nitric acids will tend to decrease seawater pH which will in turn cause CO₂ to be released from the ocean to the atmosphere. This will moderate or cancel out the expected pH drop and concomitantly decrease the effectiveness of the seawater as a sink for carbon dioxide in areas of major strong acid deposition. Thus it is clearly desirable to reduce the emissions of the strong acid precursors SO₂ and NO_x from shipping and land-based sources so as to improve air quality both locally and regionally, but such reductions will probably have little effect on the pH of seawater. These policy-oriented remarks should be seen in the context of the almost certainty that growth and urban/industrial development for the foreseeable future will be primarily concentrated in coastal and near-coastal areas. This means that control of emissions of acidic gases to the atmosphere from such zones will continue to be a growing area of concern for air quality and of consequent significance for carbon dioxide uptake by affected marine waters.

Clearly models are essential to developing an understanding of the processes and impacts of the atmospheric input of chemicals to the ocean. The lack of high quality, harmonized deposition measurements that are needed for model verification is a serious issue. The existing network of WMO GAW sites could play a critical role in providing for extended measurements pertaining to nutrient and contaminant deposition and the related ocean biological and physical parameters. However, additional atmospheric sampling sites, especially in the Southern Hemisphere, are necessary. Therefore continuing long-term observations remains of highest priority for policy-makers, both for improving models and monitoring future changes.

Finally, institutional support for assessment activities, intercomparisons, and appropriate identification and documentation of models and measurements, remains a high priority. This support is necessary to ensure an improved understanding of the role of dust both now and on longer time scales.

I. INTRODUCTION AND TERMS OF REFERENCE

There is growing recognition of the impact of the atmospheric input of both natural and anthropogenic substances on ocean chemistry, biology, and biogeochemistry as well as climate. In the 1980s, GESAMP formed a working group sponsored by the World Meteorological Organization (WMO), UNESCO, and the United Nations Environment Programme (UNEP) that developed a comprehensive review of the input of atmospheric trace species to the global ocean (GESAMP, 1989). That benchmark effort led to a scientific publication in *Global Biogeochemical Cycles* (Duce, Liss *et al.*, 1991) that for almost 20 years has been the state-of-the-art reference in this area, leading to over 600 citations in the literature. However, the information in those reports is now over 20 years old, the documents are clearly out of date, and much new information on this topic is now available. A number of important environmental issues persist in this area and in many cases are considered to be more serious than previously thought, and new issues have arisen.

The atmospheric input of chemicals to the ocean is closely related to a number of important global change issues (Duce, Galloway and Liss, 2009). For example, the increasing input to much of the ocean of atmospheric anthropogenic nitrogen species, including nitrate, ammonia, and water-soluble organic nitrogen, may cause a low-level fertilization of the ocean that could result in an increase in marine 'new' productivity of up to ~3%. This in turn could cause a possible sequestering of up to 0.3 Pg C/yr of atmospheric CO₂ in the ocean, which would affect the radiative properties of the atmosphere and thus climate (Duce *et al.*, 2008). The atmospheric input of this anthropogenic nitrogen may also lead to the increased oceanic production and emission of N₂O, a powerful greenhouse gas that could offset as much as 2/3 of the decrease in radiative forcing from the increased drawdown of CO₂. In addition, the recognition that much of the oceanic iron, which is a limiting nutrient in many areas of the ocean, originates from the atmospheric input of minerals as a result of the long-range transport of mineral dust has catalyzed an intense interest in the atmospheric and marine chemistry of iron, its chemical form, and rate of input to the ocean (Jickells *et al.*, 2005; Mahowald *et al.*, 2005). The transport of mineral dust and iron affects the large areas of the global ocean where iron is the limiting nutrient. There is also a close connection with climate here, as a windier and dryer climate would result in increased quantities of iron entering the ocean, with its consequent impact on marine productivity and thus both CO₂ drawdown and dimethyl sulfide release, both of which in turn would provide a climate feedback. In both of these examples (nitrogen and iron), the fates of these substances and changes in their fluxes in the future are potentially related to climate and climate change. The input of other substances that may have an impact on the ocean, such as phosphorus, lead, cadmium, and POPs, may also be of concern, but these have received little focused study to date. In addition, there is little information about whether inputs of sulphur dioxide from the atmosphere can add to the ocean acidification linked to rising levels of carbon dioxide. Such sulphur dioxide input may be particularly critical in heavily trafficked shipping lanes and in coastal waters proximate to industrialized land areas.

The development of atmospheric models and measurement programmes to simulate the long-range transport and deposition of chemicals to the Earth's surface has expanded significantly in the last twenty years. The concern and interest of the marine community about atmospheric inputs to the ocean has also grown significantly, as outlined above. However, to date there has been relatively little interaction between the atmospheric and oceanic communities in this area, with the exception of some excellent research as part of SOLAS. There is now an excellent opportunity for the inclusion of atmospheric transport and deposition studies to the ocean in new and developing atmospheric research and monitoring programmes. For example, WMO has initiated new and improved measurement and modelling programmes in the areas of precipitation chemistry. WMO has also developed a Sand and Dust Storm Warning and Assessment System (SDS-WAS) that links users to products of operational research forecasts of sand and dust. Until now there has been little involvement of the marine community in either of these efforts, although clearly both would be of significant interest and value to the ocean sciences. For all of the reasons outlined above, GESAMP decided to initiate a new working group, Working Group 38, The Atmospheric Input of Chemicals to the Ocean, to address these issues.

Working Group 38 was initially formed to address the following Terms of Reference:

- Charge 1) Assess the need for the development of new model and measurement products for improving our understanding of the impacts of the atmospheric deposition of nitrogen species and dust (iron) to the ocean.
- Charge 2) Review the present information on the atmospheric deposition of phosphorus species to both the marine and terrestrial environments, considering both natural and anthropogenic sources, and

evaluate the impact of atmospheric phosphorus deposition on marine and terrestrial ecosystems. Consider whether such a review of any other substance would be useful.

- Charge 3) Work with the WMO Sand and Dust Storm Warning and Assessment System and with the WMO Precipitation Chemistry Data Synthesis and Community Project to evaluate the needs of the marine community and assist in clearly articulating them in the development of these WMO efforts.

The membership of Working Group 38 is presented in Annex 1. The first meeting of Working Group 38 took place at the University of Arizona, Tucson, Arizona, USA from 10-14 December 2008. This meeting was organized and supported by the Global Atmosphere Watch (GAW) and the World Weather Research Programme (WWRP) of WMO, with additional support from SCOR (ICSU Scientific Committee for Oceanic Research), the International maritime Organization (IMO), the Swedish International Development Agency (SIDA), and the University of Arizona. Twelve of the 15 members of the Working Group were able to attend that meeting. Nations represented by membership on the Working Group include China, Germany, Greece, India, Italy, Japan, New Zealand, Thailand, Turkey, the United Kingdom, and the United States.

During the first meeting the working group addressed these three charges in detail. Charges 1) and 2) were addressed by gathering initial information for the development of separate scientific papers that the working group would subsequently write in the areas of phosphorus, nitrogen, sulphur, iron and organic matter deposition from the atmosphere to the ocean.

The second meeting of Working Group 38 took place at IMO in London in January, 2010. This meeting focused completely on the development of the three papers discussed above relative to Charges 1) and 2). A summary of these papers and information on where they are, or will be, published is presented in Section II of this report.

Charge 3) was addressed during the first meeting of the working group by the development of two advisory letter reports to the World Meteorological Organization. These letter reports provided advice to WMO in the area of dust deposition to the ocean and precipitation chemistry over the ocean. These reports are presented in detail in Section III of this report.

After the second meeting, additional Terms of Reference were developed for the working group. In order to more specifically elaborate the role of minerals carried by the dust which is responsible for marine production and in order to achieve more detailed and more specific description of the atmospheric transport and deposition process of iron- and phosphorus-carried minerals, WMO proposed the extension of the above activities with the aim to bring together the SDS-WAS and GESAMP scientific communities, and as a result of their joint effort to discuss the following specific topics:

- Topic 1 Improving the quantitative estimates of the geographical distribution of the transport and deposition of mineral matter and its content to the ocean.
- Topic 2 Developing case-studies of dust/Fe/P input to the ocean and the resultant marine response utilizing SDS-WAS transport modelling, remote-sensing, in-situ observations, and ocean biogeochemical modelling.
- Topic 3 Specifying test-bed regions for joint studies of the transport and deposition to the ocean of mineral matter.

These topics were discussed in detail at the third meeting of the working group in Malta in March 2011. At this meeting three separate reports on the three topics above were developed, and these reports are presented and discussed in Section IV of this report.

Annex 2 provides the agendas for and the attendees at each of the three meetings of the Working Group.

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II. SUMMARY OF THREE PAPERS PUBLISHED IN SCIENTIFIC JOURNALS

A. Summary of "Impacts of Atmospheric Nutrient Deposition on Marine Productivity: Roles of Nitrogen, Phosphorus and Iron"

(Gregory Okin, Alex Baker, Ina Tegen, Natalie Mahowald, Frank Dentener, Robert Duce, James N. Galloway, Keith Hunter, Maria Kanakidou, Nilgun Kubilay, Joseph Prospero, Manmohan Sarin, Vanisa Surapipith, Mitsuo Uematsu and Tong Zhu (2011))

This paper was published in *Global Biogeochemical Cycles* (Vol. 25, GB2022, doi:10.1029/2010GB003858, 2011)

As pointed out by Okin *et al.* (2011), "Nutrients are supplied to the mixed layer of the open ocean by either atmospheric deposition or mixing from deeper waters, and these nutrients drive nitrogen and carbon fixation. To evaluate the importance of atmospheric deposition, we estimate marine nitrogen and carbon fixation from present-day simulations of atmospheric deposition of nitrogen, phosphorus and iron", and these estimated depositions are shown in Figure 1. Spatial estimates of inorganic and organic N deposition, N_{Dep} , were obtained from an ensemble calculation of deposition using 24 different global transport-chemistry models. These authors also stated that "Total P deposition to the oceans, P_{Dep} , was calculated as the sum of P deposited in dust, P deposited from combustion sources, and P deposited from natural (non-dust) sources. Total bioavailable Fe deposition to the oceans, Fe_{Dep} , was calculated as the sum of soluble iron deposited in dust and iron deposited from combustions sources."

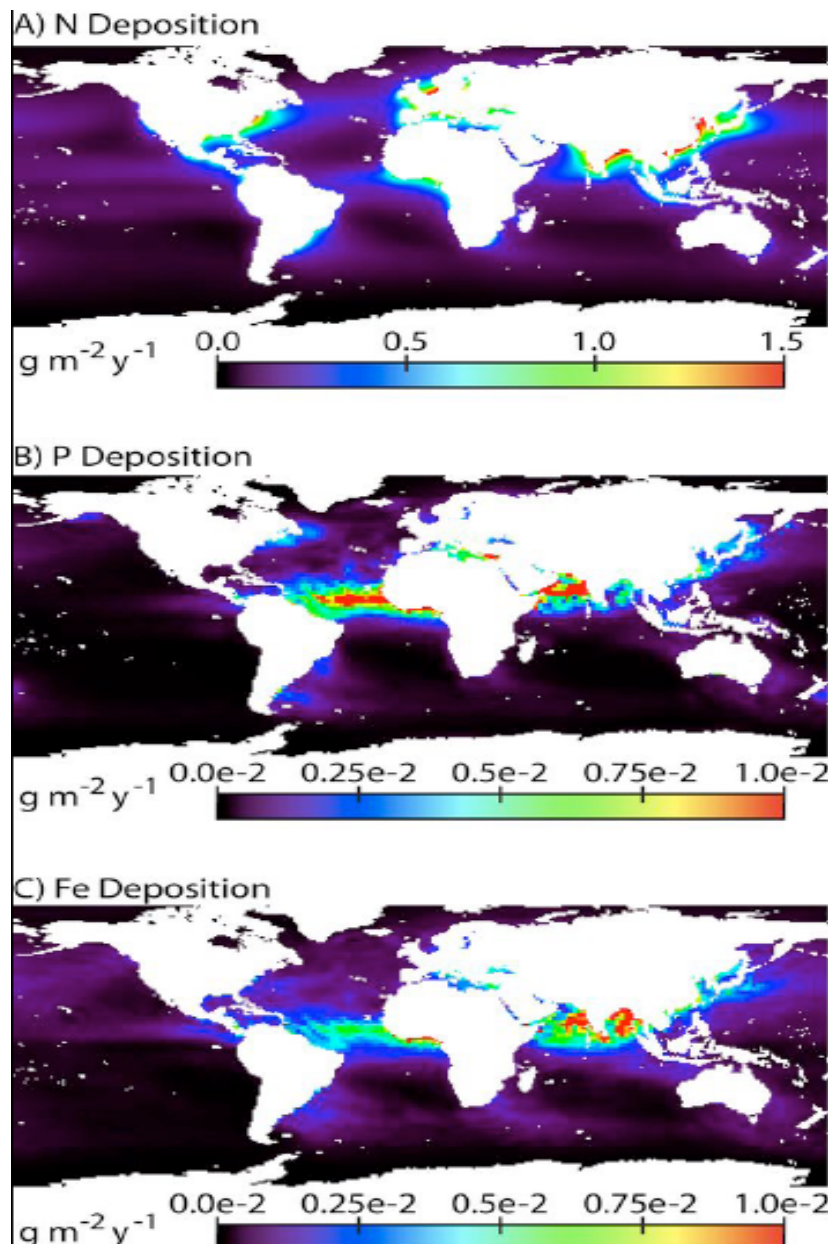


Figure 1 - Atmospheric deposition of nitrogen (A), phosphorus (B), and iron (C) to the global ocean (From Okin, G. *et al.*, Impacts of atmospheric nutrient deposition on marine productivity: roles of nitrogen, phosphorus and iron, *Global Biogeochemical Cycles*, 25, GB2022, doi:10.1029/2010GB003858, 2011. Copyright [2011] by the American Geophysical Union. Reproduced by permission of the American Geophysical Union)

N-fixation was calculated with reference to excess phosphate, $xsPO_4$, concentrations: $xsPO_4 = PO_4 - NO_3/16$. Okin et al. "considered that regions where $xsPO_4$ was less than $0.1 \mu M$ were likely to be phosphate-limited for nitrogen-fixation, and we assumed that in all other regions nitrogen-fixation was therefore likely to be subject to iron-limitation." Thus, the maximum potential rate of marine nitrogen-fixation due to atmospheric input, N_{Fix}^{Atm} , was calculated as:

$$N_{Fix}^{Atm} = \begin{cases} P_{Dep}(N/P)_{diaz} & \text{where P is limiting} \\ Fe_{Dep}(N/Fe)_{diaz} & \text{where Fe is limiting} \end{cases}$$

where $(N/P)_{diaz}$ and $(N/Fe)_{diaz}$ are N:P and N:Fe ratios for diazotrophic organisms, respectively. There are two competing views on the iron requirements for nitrogen fixation by *Trichodesmium* at present, so both estimates $(N/Fe)_{diaz} = 1050 \text{ g/g}$ and $(N/Fe)_{diaz} = 50 \text{ g/g}$ were used in this analysis. If the latitude was greater than 40° , N_{Fix}^{Atm} was considered negligible.

The direct carbon-fixation due to atmospheric input of N and Fe, $C_{Fix, Fe/N Dep}^{Atm}$, was calculated as follows:

$$C_{Fix, Fe/N Dep}^{Atm} = \begin{cases} Fe_{Dep}(C/Fe) & \text{where Fe is limiting} \\ N_{Dep}(C/N)_{Redfield} & \text{elsewhere} \end{cases}$$

Here $(C/N)_{Redfield}$ is the Redfield mass ratio of 7.2 g/g while (C/Fe) is $1.47 \times 10^5 \text{ g/g}$, which is the minimum C:Fe ratio reported for iron-depleted waters. Okin et al. then "defined ocean areas where primary productivity was likely to be Fe-limited (i.e., HNLC [high nutrient-low chlorophyll] regions) as those having annual average NO_3^- concentrations $>4 \text{ mM}$ " in the top 10 m. Phosphorus can limit C-fixation either directly as $C_{Fix, P Dep}^{Atm} = P_{Dep}(C/P)_{Redfield}$ or indirectly, and in combination with Fe, through its impact on N_{Fix}^{Atm} . Okin et al. also pointed out that "this indirect carbon fixation was calculated as $C_{Fix, N Fix}^{Atm} = N_{Fix}^{Atm}(C/N)_{Redfield}$ ". Values of atmospherically-supported carbon fixation (both direct and indirect) were compared with estimates of average net primary productivity (NPP) derived from the MODerate resolution Imaging Spectrometer (MODIS)."

"We find that for calculated values of $xsPO_4$, N_{Fix}^{Atm} in most of the surface oceans is Fe-limited, and the patterns of N_{Fix}^{Atm} are largely determined by the deposition of Fe in dust (Figure 2), with the northern Atlantic Ocean being most likely to be P-limited with respect to N_{Fix}^{Atm} . By far the largest impact on our estimates of N_{Fix}^{Atm} relate to the assumed values of N/Fe for diazotrophic organisms. In non-HNLC regions, the ratio of N:P in atmospheric deposition is always greater than the Redfield mass ratio, suggesting that P would limit productivity if only atmospheric inputs were considered. However, throughout much of the non-HNLC areas, N is considered to limit primary productivity" due to high concentrations of $xsPO_4$ in surface waters. Okin et al. also stated that "the amount of oceanic C-fixation (Table 1, column 2) that can be supported by Fe and N deposition where these elements limit primary productivity is several orders of magnitude greater than that which can be supported directly by P deposition (Table 1, column 4). Due to the high C:Fe ratio we assume for phytoplankton under Fe-limitation, HNLC areas experience significantly higher rates of atmospherically-supported C-fixation than non-HNLC (N-limited) areas. Furthermore, the indirect impact of deposition via N fixation is considerably greater than the direct effect of atmospheric P deposition would be, even if C-fixation in the surface oceans were P-limited."

"Our results are to some extent model dependent and subject to uncertainties associated with the assumptions we made about the bioavailable fraction of each nutrient input, but it is clear that there is significant variability in the contribution of the combined supply of atmospheric N, Fe and P to marine C-fixation." Okin et al. also stated that "in HNLC regions, on the other hand, atmospheric deposition of Fe can potentially contribute considerably to rates of marine productivity. Here, we find that the global NPP potentially supported by atmospheric deposition of N and Fe is $\sim 7.5 - 9.3 \text{ Pg/yr}$," whereas previous results have suggested that the total NPP resulting from atmospheric N deposition alone is about 0.4 Pg/yr . This indicates clearly that deposition of atmospheric Fe is likely much more important than deposition of atmospheric N in supporting NPP in the world ocean. Okin et al. pointed out that "globally, HNLC regions contribute significantly to the rate of carbon uptake by the surface oceans. Thus, the changes in atmospheric deposition to these regions could potentially have significant impacts on future oceanic carbon uptake. The Southern Ocean, in particular, is dominated by HNLC conditions. The major sources of Fe deposition to this basin are the arid regions of the South America, southern Africa, and Australia. Increasing atmospheric pollutants due to industrialization may contribute to atmospheric processing of Fe-bearing aerosols." This could make the iron more soluble and thus more available for use in the ocean, thus, as these authors point out, "having a significant potential to impact productivity in this area."

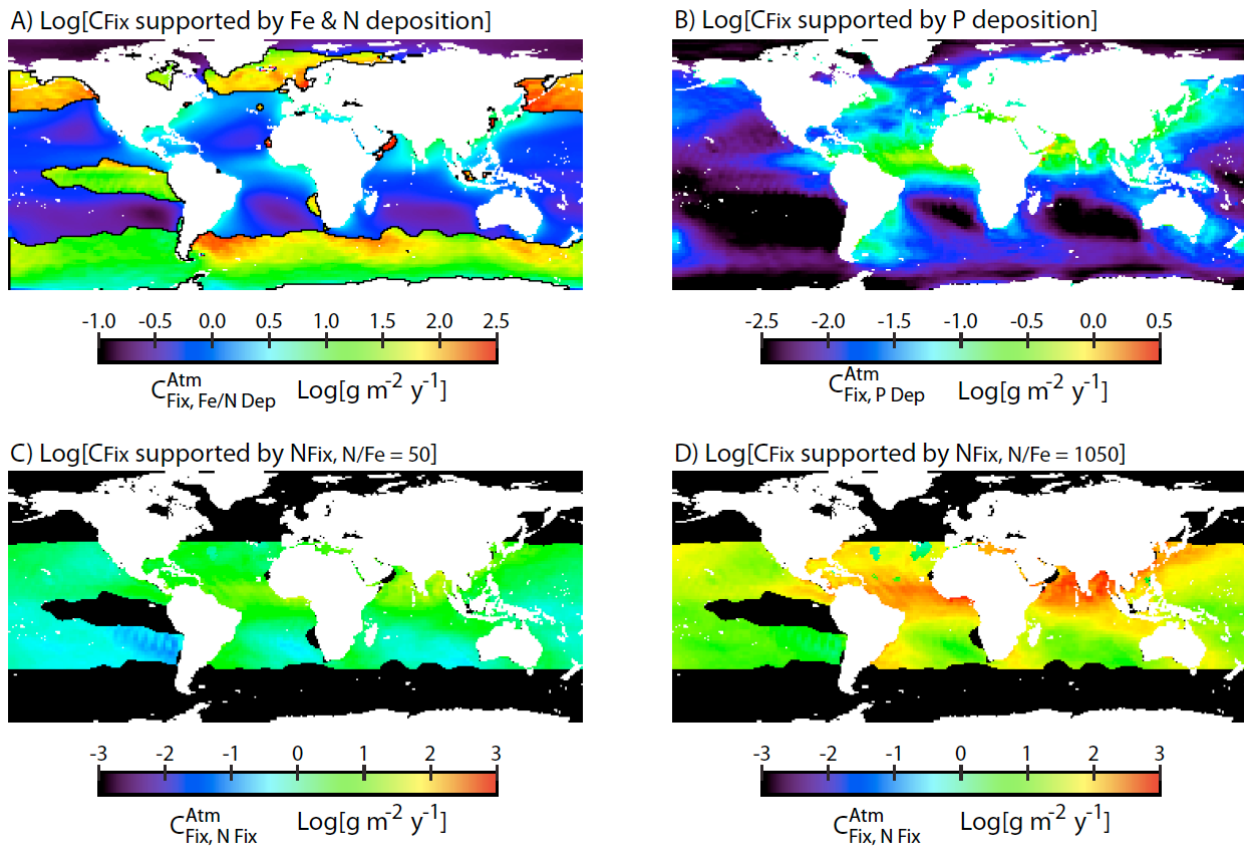


Figure 2 - Carbon fixation supported by iron, nitrogen, and phosphorus deposition and carbon fixation supported by nitrogen fixation from this deposition

(From *Okin, G. et al.*, Impacts of atmospheric nutrient deposition on marine productivity: roles of nitrogen, phosphorus and iron, *Global Biogeochemical Cycles*, 25, GB2022, doi:10.1029/2010GB003858, 2011.

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Table 1* - Estimated Rates of Nitrogen Fixation, Carbon Fixation, and Satellite-Derived NPP for Major Ocean Basins¹

	$N_{\text{Fix}}^{\text{Atm}}$ (1)		$C_{\text{Fix,Fe/N Dep}}^{\text{Atm}}$ (2)	$C_{\text{Fix,N Fix}}^{\text{Atm}}$ (3)		$C_{\text{Fix,P Dep}}^{\text{Atm}}$ (4)	NPP (5)	% (6)	
	Tg/yr		Pg/yr	Pg/yr		Tg/yr	Pg/yr		
N/Fe Ratio (g/g) (7)	50	1050	n/a	50	1050	n/a	n/a	50	1050
Global Ocean	15	323	7.5	0.085	1.8	15	42.6	16	20
Atlantic	5.0	104	0.82	0.028	0.59	6.1	9.84	6.1	13
North Atlantic	0.42	8.0	0.63	0.0024	0.046	1.0	3.68	15	17
North Central Atlantic	1.8	38	0.083	0.010	0.21	2.3	2.18	2.2	14
Equatorial Atlantic	2.4	50	0.053	0.014	0.29	2.6	2.27	2.0	16
South Atlantic	0.39	8.2	0.062	0.0021	0.044	0.24	1.71	1.7	5.1
Indian	5.1	106	0.55	0.028	0.59	3.5	5.12	2.9	12
North Indian	2.0	42	0.46	0.011	0.22	2.1	1.41	12	29
Equatorial Indian	2.4	51	0.073	0.014	0.29	1.2	1.86	2.1	16
South Indian	0.62	13	0.013	0.0036	0.075	0.26	1.84	0.8	4.4
Pacific	4.2	88	2.9	0.022	0.46	3.2	15.9	12	15
North Pacific	0.91	19	2.1	0.0046	0.10	1.2	4.58	43	45
North Central Pacific	1.8	37	0.09	0.010	0.21	1.0	3.09	1.7	8.5
Equatorial Pacific	1.1	24	0.58	0.0053	0.11	0.84	5.16	9.4	12
South Pacific	0.37	7.7	0.072	0.0020	0.041	0.19	3.06	1.7	3.4
Southern Ocean	0.77	16	3.2	0.0039	0.083	1.5	11.4	51	52

(1) $N_{\text{Fix}}^{\text{Atm}}$ assuming that diazotrophic N fixation is -P or Fe-limited and N/Fe ratio of either 50 or 1050 g/g.

(2) C fixation from N_{Dep} and Fe_{Dep} only

(3) C fixation from $N_{\text{Fix}}^{\text{Atm}}$ only

(4) C fixation from P_{Dep} only

(5) Average MODIS-derived NPP from July, 2002 to June, 2007.

(6) $\left(C_{\text{Fix, Fe/N Dep}}^{\text{Atm}} + C_{\text{Fix, N Fix}}^{\text{Atm}} \right) / \text{NPP}$

(7) Calculations of $N_{\text{Fix}}^{\text{Atm}}$ were made using the range of ratios of N/Fe representing different estimates in the literature

* (From Okin, G. et al., *Impacts of atmospheric nutrient deposition on marine productivity: roles of nitrogen, phosphorus and iron*, *Global Biogeochemical Cycles*, 25, GB2022, doi:10.1029/2010GB003858, 2011. Copyright [2011] by the American Geophysical Union. Reproduced by permission of the American Geophysical Union)

B. Summary of "Impacts of Anthropogenic SO_x, NO_x and NH₃ on Acidification of Coastal Waters and Shipping Lanes"

(Keith Hunter, Peter S. Liss, Vanisa Surapipith, Frank Dentener, Robert Duce, Maria Kanakidou, Nilgun Kubilay, Natalie Mahowold, Greg Okin, Manmohan Sarin, Mitsuo Uematsu and Tong Zhu (2011))

This paper was published in *Geophysical Research Letters* (Vol. 38, L13602, doi:10.1029/2011GL047720, 2011)

As pointed out by *Hunter et al. (2011)*, "the acidification of the surface ocean by anthropogenic carbon dioxide (CO₂) absorbed from the atmosphere is now well-recognized and is considered to have lowered surface ocean pH by 0.1 units" (corresponding to an approximately 25% increase in the acidity of the surface oceans) since the mid-18th century. Further acidification in the future may lead to under-saturation of calcium carbonate, making growth difficult for calcifying organisms, ranging from microscopic calcareous plankton to massive coral reefs.

For this reason, in recent years, *Hunter et al.* stated that there has been "considerable concern about the effects of anthropogenic CO₂ absorbed by the ocean on its carbonate chemistry, and associated pH-dependent processes, collectively termed *ocean acidification* (OA). This process is independent of human-derived global warming, but shares a common cause," i.e., increases in CO₂ entering the atmosphere/ocean system as a result of fossil fuel combustion. "A number of potential effects of OA are recognized, including making calcification of marine organisms more difficult, and altering the availability of CO₂ for metabolism," with resultant ecosystem changes (as described in a report from the Royal Society of London in 2005). However, as recently pointed out by Scott Doney and co-workers, "other anthropogenic gases can also alter ocean pH by absorption from the atmosphere, specifically oxides of sulphur and nitrogen (which enter the ocean mainly after oxidation to H₂SO₄ and HNO₃ respectively) and ammonia."

Hunter et al. further stated that Doney and colleagues have "presented a detailed analysis of the impact of these gases on the pH of the global surface ocean. Their approach comprised a 3-Dimensional general circulation model of the ocean combined with estimated regional air-to-sea fluxes of the relevant gases. They found that the net effect is negative (becoming more acidic) in temperate regions of the North Atlantic that are dominated by fossil fuel sources of SO₂ and NO_x but that it is positive (becoming more alkaline) in the tropics because of a dominance of NH₃ input. The latter position is reversed if a substantial portion of the ammonia undergoes nitrification (conversion of ammonia to nitric acid by bacterial action in seawater). On a global scale, these workers concluded that the alterations in surface water chemistry from anthropogenic nitrogen and sulphur input are rather small, only a few percent at most of those caused by the uptake of anthropogenic CO₂. However, they did conclude that more substantial impacts might be expected in coastal waters." *Hunter et al. (2011)* examined this possibility in more detail.

Recently, Nick Bates and Andrew Peters from the Bermuda Biological Laboratory have used rainfall measurements of pH and chemical compositions at Bermuda to confirm that in this region of the subtropical North Atlantic the contribution to OA from sulphur and nitrogen gases was at most 2% of that caused by anthropogenic CO₂. *Hunter et al.* point out that "while this agrees with the predictions of the global model referred to above, Bermuda is not a heavily impacted region, and there appears to be no comparable analysis made for coastal waters adjacent to industrialized and urbanized land areas or with major shipping routes where the impacts of sulphur and nitrogen gases are expected to be greater. It is known that the global distribution of shipping density correlates well with emissions of various pollutants derived from ship exhausts, including SO₂, NO_x and particulates. Therefore, we have conducted a feasibility analysis on the likely relative impacts of CO₂ versus the other anthropogenic gases in such waters, focusing in more detail on these areas than was done by Doney and co-workers as well as considering the impacts in a non-model based framework." To illustrate the effects of strong acid/alkali atmospheric inputs on coastal waters, we have applied our calculation to three areas: the North Sea, the Baltic Sea and the South China Sea. There are other significant regions where similar effects may apply, e.g. the Bay of Bengal with high atmospheric acid inputs from shipping and industrial activity of the Indian eastern seaboard, but for which we could find sufficient data in order to make the equivalent calculations.

Hunter et al. also stated that "this analysis, while obviously simplistic, shows that the effects of atmospheric inputs of strong acid gases, at deposition rates likely to be encountered in coastal waters, are to largely eliminate the pH reduction which would normally accompany ocean acidification by uptake of acidic gases, but at the expense of the important contribution of surface waters as a sink for anthropogenic CO₂." The results are illustrated in Figure 1 below. The H⁺ and CO₂ lines correspond to the effect on seawater pH of the addition of strong acid or CO₂, respectively. The 'After buffering' line shows the seawater pH with re-equilibration of the system by exchange of CO₂ across the air-sea interface. This almost zero change in pH with re-equilibration arises because the surface ocean - lower atmosphere

system is an open one, which means that gases can cross from one medium to the other on reasonably short timescales (days to months). Thus, absorption by the ocean of gases such as sulphuric and nitric acids will lead to a decrease in pH which will in turn cause CO_2 to be released to the atmosphere. This will moderate or cancel out the expected pH drop and concomitantly decrease the effectiveness of the seawater as a sink for carbon dioxide in areas of major strong acid deposition.

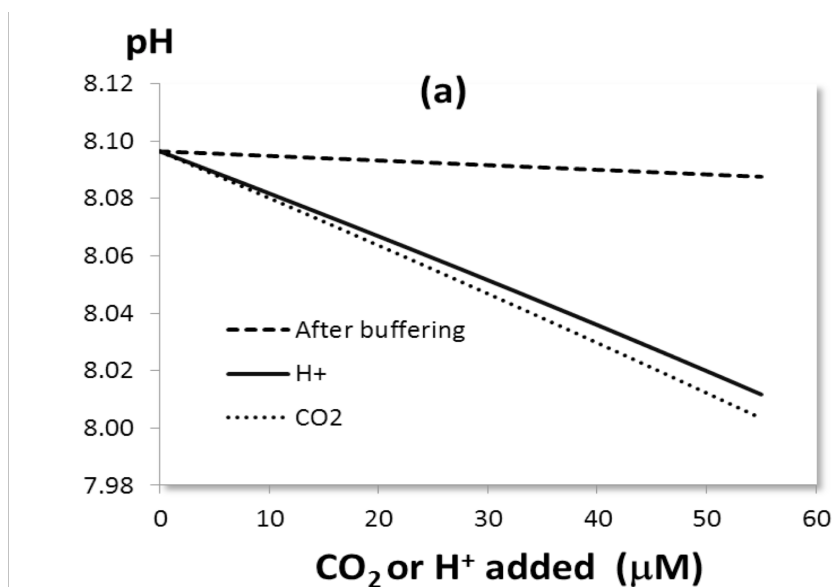


Figure 1 - Calculated change in pH of seawater as a function of the absorbed concentrations of either CO_2 or strong acid H^+ from H_2SO_4 or HNO_3 , both before and after buffering by re-equilibration with the atmosphere. Initial conditions $\text{DIC} = 1960 \mu\text{mol kg}^{-1}$, $A_T = 2290 \mu\text{mol kg}^{-1}$, $S = 35$, $T = 25^\circ\text{C}$, pH on the total scale. The solid line shows the initial changes in pH after addition of strong acid H^+ while the dotted line show the corresponding changes caused by CO_2 uptake. The dashed line shows the final pH changes from H^+ addition after re-equilibration of CO_2 with the atmosphere.

(From Hunter, K., et al., "Impacts of Anthropogenic SO_x , NO_x and NH_3 on acidification of coastal waters and shipping lanes, *Geophysical Research Letters*, 38, L13602, doi:10.1029/2011GL047720, 2011. Copyright [2011] by the American Geophysical Union. Reproduced by permission of the American Geophysical Union)

The reduction in emissions of the strong acid precursors SO_2 and NO_x from shipping and land-based sources is clearly a desirable activity in terms of improving air quality both locally and regionally. Our analysis indicates that there is an additional benefit in that the less strong acid that enters coastal seawater, the more the natural CO_2 sink that seawater provides will be maintained. This result arises from the fact that the coupled atmosphere/near-surface seawater system is an open one in which gases are easily transferred across the air-sea interface. On the other hand any proposals to dispose of acids in the deep(er) oceans, which are not subject to gas transfer to the atmosphere on short timescales, must take in to account that there will be no amelioration of any impacts of the acid addition due to such transfers.

These policy-oriented remarks should be seen in the context of the near-certainty that growth and urban/industrial development for the foreseeable future will be primarily concentrated in coastal and near-coastal areas. This means that control of emissions of acidic gases to the atmosphere from such zones will continue to be a growing area of concern for air quality and of consequent significance for seawater chemistry, as discussed above.

C. Summary of "Atmospheric Fluxes of Organic N and P to the Global Ocean"

(Maria Kanakidou, Robert Duce, Joseph Prospero, Alex R. Baker, Claudi Benitez-Nelson, Frank J. Dentener, Keith A. Hunter, Peter S. Liss, Natalie Mahowald, Greg S. Okin, Manmohan Sarin, Kostas Tsigaridis, Mitsuo Uematsu, Lauren M. Zamora and Tong Zhu)

This paper was submitted to *Global Biogeochemical Cycles* and was under review when this report was published.

Why is organic material important?

It is known that organic phosphorus (OP) and organic nitrogen (ON) are very important components of the cells of plants and animals. The C/N/P cycles are primarily coupled through photosynthetic fixation of these elements by biological activity. Photosynthetic organisms utilize P, C, N and other essential nutrients to build their tissues and for biological productivity. Thus the atmospheric CO₂ sink to the ocean relies on the availability of these nutrients.

Human activities have modified the atmospheric content and deposition fluxes of organic carbon (OC), ON and OP by emissions and atmospheric transformation of organic material in both gas and particulate forms. These cycles, perturbed by humans, are also sensitive to climate change, since emissions from the biosphere are the primary source of many organics in the global atmosphere. In addition, the partitioning of organics between the gas and particulate phases as well as the properties of organics in the atmosphere depend on interactions between natural and anthropogenic emissions. These interactions are known to lead to more organic aerosols in the atmosphere and also to chemically bind anthropogenically emitted substances, e.g., different forms of inorganic nitrogen, to organic substances. Thus, critical biochemical feedbacks exist between chemistry, climate, and the terrestrial and marine biosphere that involve the coupling of the C/N/P atmosphere/ocean cycles. Atmospheric processing and subsequent input to the ocean has been proposed as an important source of the marine nutrients nitrogen and phosphorus, especially for marine oligotrophic regions. The increased atmospheric pool of anthropogenically-derived nitrogen currently supplies significant amounts of bioavailable nitrogen to marine ecosystems. Until recently, little attention has been paid to the contribution and significance of organic forms of phosphorus and nitrogen, whereas the involvement of Fe-organic complexes in the assimilation of iron by marine organisms has been investigated.

Observational evidence

There is increasing observational evidence that a significant fraction of the atmospheric N and P deposition to the ocean occurs as ON and OP, with some fraction of this nitrogen and phosphorus either emitted directly or chemically transformed in the atmosphere to an organic form. The observed ON fraction of total N (deduced by the difference between the total nitrogen and the inorganic nitrogen determination) in rainwater exhibits a large range of values. Depending on location this fraction ranges from ~3% to 90%. There are few studies of the bioavailability of ON, and they lack information on the iron and phosphorus co-limiting effects on N-fixation. However, these few studies show that between ~20 and 75% of the dissolved organic nitrogen (DON) in atmospheric deposition is bioavailable. For phosphorus, the observed fractions of dissolved organic phosphorus (DOP) (deduced by the difference between the dissolved total phosphorus and the dissolved inorganic phosphorus) to total soluble phosphorus (TSP) range from ~10-60%. However, the observational data remain limited and require standardization, making it difficult to derive a concise global picture. The deposited amounts of the organic forms of N and P to the global ocean as well as their assimilation by marine organisms, and thus their environmental impact, are still an open question.

Modelling effort to construct a global picture

GESAMP Working Group 38 revisited the role of non-methane organic carbon in the global troposphere as a source for organic nitrogen and organic phosphorus. This provided an updated picture of the role of organic material in atmospherically transporting the nutrients nitrogen and phosphorus globally, and specifically to the oceans (see Figure 1). Dedicated global 3-dimensional chemistry transport model simulations were then utilized to understand the global distribution of the fluxes of organic carbon, nitrogen, and phosphorus to the ocean. As an example of the results, Figure 2 shows maps of the model-calculated deposition of atmospheric organic nitrogen and inorganic nitrogen to the ocean. Table 1 then presents the calculated total atmospheric deposition of organic and inorganic nitrogen to the ocean and to the globe. These combined model simulations suggest that the global ON budget has a strong anthropogenic component. Overall about 45% of the primary (direct emissions) and secondary (chemical formation) sources of atmospheric ON are estimated to be associated with anthropogenic activities. On the other hand, a smaller fraction of the OP comes from human activities. Therefore it is expected that the continuously increasing anthropogenic emissions in the atmosphere might modify the ON cycle faster than the OP atmospheric budget. This would then modify the N:P composition of atmospheric deposition of nutrients to both the ocean and to terrestrial ecosystems. An increasing N:P

ratio could favour assimilation of part of the OP by the marine ecosystems, in particular those that exhibit P-limitation. However, the response of marine ecosystems to these changes requires laboratory and field investigations, since the effectiveness of the atmospheric inputs of nutrients to the ocean in stimulating productivity will depend on the bioavailability of these nutrient inputs from the atmosphere.

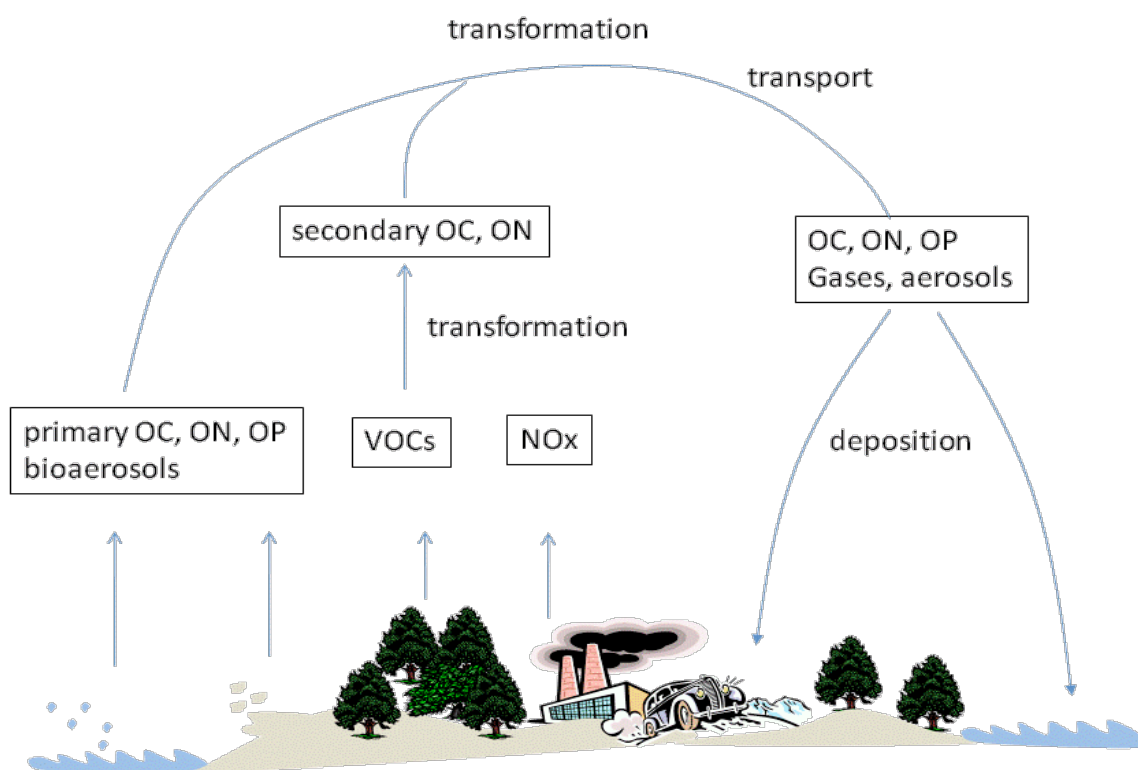


Figure 1 - Simplified illustration of the atmospheric cycle of organic material

Table 1 - Estimates from this work of the annual global deposition of atmospheric organic nitrogen (ON), inorganic nitrogen (IN), and total nitrogen (TN)

Deposition in Tg-N/yr	Total	
	World	Ocean
ON	38	19
IN	90	37
TN	128	56
ON/TN (%)	30	34

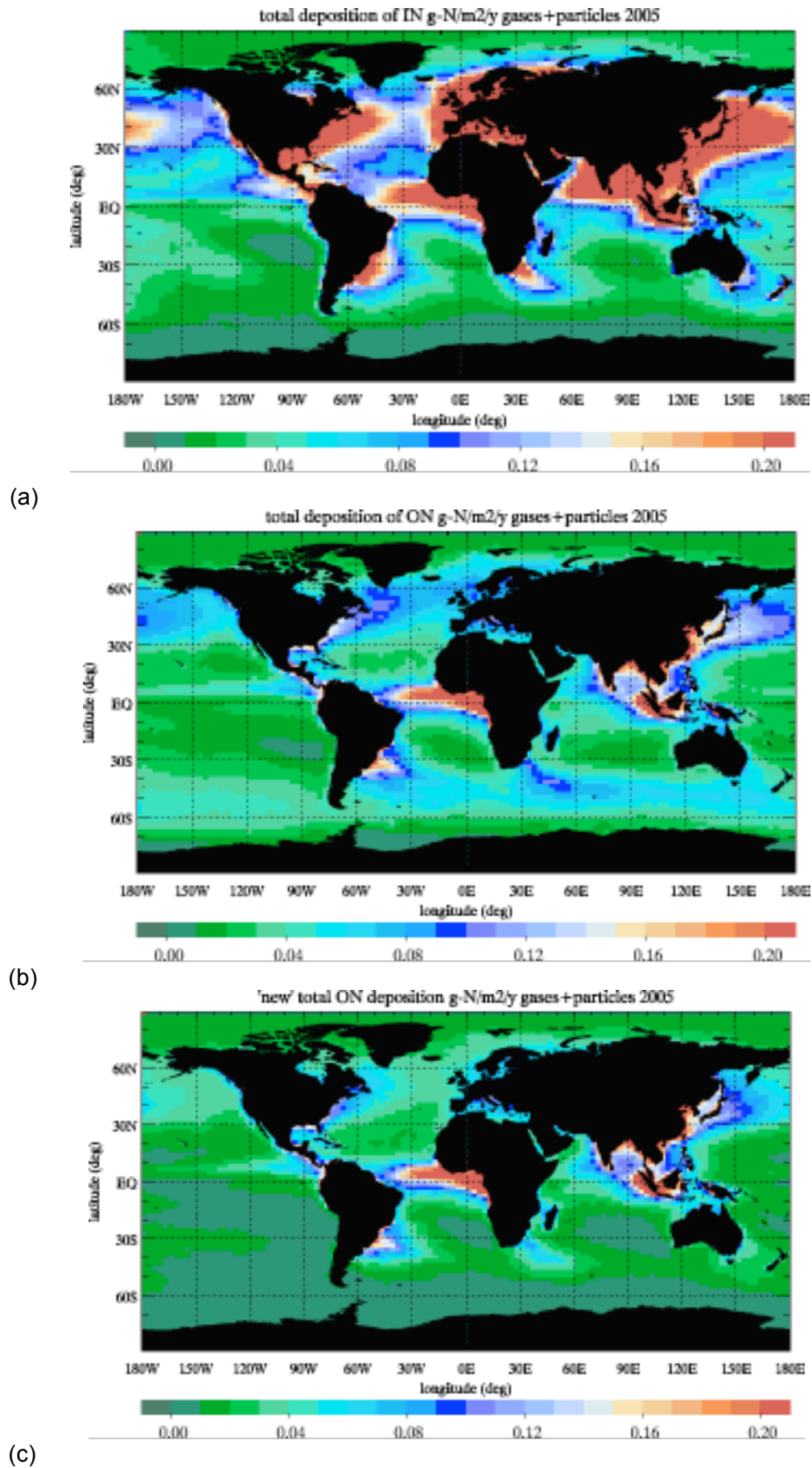


Figure 2 - Comparison of the deposition of (a) inorganic nitrogen (IN), (b) organic nitrogen (ON) and (c) ON of anthropogenic and natural terrestrial origin to the world ocean

Impact evaluation

Recently, Duce *et al.* [2008] presented a first evaluation of the impact of organic nitrogen deposition to the global ocean. They estimated that about a third of the ocean's external nitrogen supply is entering the open ocean via deposition of atmospheric anthropogenic nitrogen, with ~30% of that being organic nitrogen. They also estimated that this external supply could account for about 3% of the annual new marine biological production, implying that the organic nitrogen deposition could account for ~1% of the annual new marine biological productivity. Although highly uncertain, that estimate of the impact of ON deposition is indicative of the potential importance of human-driven ON deposition to the ocean. There is no similar estimate for organic phosphorus deposition and its potential impact.

What needs to be investigated?

There is a clear need for documenting the direct emissions to the atmosphere of the organic fraction of N and P, measuring their deposition to the ocean, and understanding their importance for marine ecosystems. This is important in view of the large anthropogenic contribution to the atmospheric nitrogen cycle and the more moderate anthropogenic contribution to the atmospheric phosphorus cycle. This disequilibrium of the human impact on nutrient deposition to the oceans is expected to alter the responses of the ecosystems and favour growth and sustainability of species that are able to adapt to the changes, making use of the deposited OP and ON. Further research is needed to measure OP and ON deposition and assimilation by marine ecosystems.

Specific recommendations

- Standardize sampling and analytical procedures for ON and OP. Determine the nature (major chemical groups) of organic nitrogen and organic phosphorus deposition.
- Use innovative methods (e.g., isotopes) to track the origin and fate of nutrients.
- Support an observational network of ON and OP deposition (dry + wet deposition, supported by additional observations of atmospheric gases and aerosols) - maximize the use of existing networks.
- Support studies to investigate how and under what circumstances ON and OP are assimilated by marine ecosystems. The impact of atmospheric deposition will vary with the types of organisms in the ocean and on the limiting factors in the region (light, nutrients etc.). There is therefore a need for analysis of data accounting for differences in season, organisms, circulation patterns, etc.
- Account for the deposition of ON and OP in ocean biogeochemistry/climate models.

Policy-relevant comments

This paper should be seen in the context of the continuously growing anthropogenic nitrogen and phosphorus emissions foreseen for the future. Human activities have changed and will further modify the atmospheric deposition fluxes of the nutrients ON and OP to the ocean, stimulating the marine ecosystems (bacteria or new productivity) and thus the carbon cycle.

Reference

Duce, R.A., J. LaRoche, K. Altieri, K. Arrigo, A. Baker, D. G. Capone, S. Cornell, F. Dentener, J. Galloway, R. S. Ganeshram, R. J. Geider, T. Jickells, M. M. Kuypers, R. Langlois, P. S. Liss, S. M. Liu, J. J. Middelburg, C. M. Moore, S. Nickovic, A. Oschlies, T. Pedersen, J. Prospero, R. Schlitzer, S. Seitzinger, L. L. Sorensen, M. Uematsu, O. Ulloa, M. Voss, B. Ward, L. Zamora, "Impacts of atmospheric anthropogenic nitrogen on the open ocean", *Science*, 320, 893-897 (2008).

III. ADVISORY LETTERS TO THE WORLD METEOROLOGICAL ORGANIZATION

A. Report of GESAMP Working Group 38 to the WMO Precipitation Chemistry Data Synthesis and Community Project

1. Introduction

GESAMP Working Group 38 (GESAMP WG 38) was established by GESAMP to assess the atmospheric input of chemicals to the ocean. One of the charges to GESAMP WG 38 was as follows:

“Work with the WMO Sand and Dust Storm Warning Advisory and Assessment System and with the WMO Precipitation Chemistry Data Synthesis and Community Project to evaluate the needs of the marine community and assist in clearly articulating them in the development of these WMO efforts.”

During its first meeting in Tucson, AZ, USA, from 11-14 December 2008, GESAMP WG 38 members identified a number of issues relevant to global atmospheric nutrient inputs and their effects on the oceans. GESAMP WG 38's effort resulted in two advisory reports to WMO (one related to the WMO Precipitation Chemistry Data Synthesis and Community Project as indicated above, and a second to the WMO Sand and Dust Storm Warning Advisory and Assessment System), as well as several targeted scientific papers. The charge related to the WMO Precipitation Chemistry Data Synthesis and Community Project is to advise that group on the types of measurements of wet deposition over the ocean that should be included in a potential database, and to identify where such measurements are needed. This report addresses that charge.

Our recommendations are based on the growing evidence that significant quantities of a number of chemicals enter the global ocean from the atmosphere. We show as examples Figures 1 and 2, which present model estimates of the annual atmospheric deposition of nitrogen species and mineral dust, respectively, to the global ocean. These figures clearly demonstrate that over large areas of the global ocean deposition is directly linked to, and dominated by, continental sources.

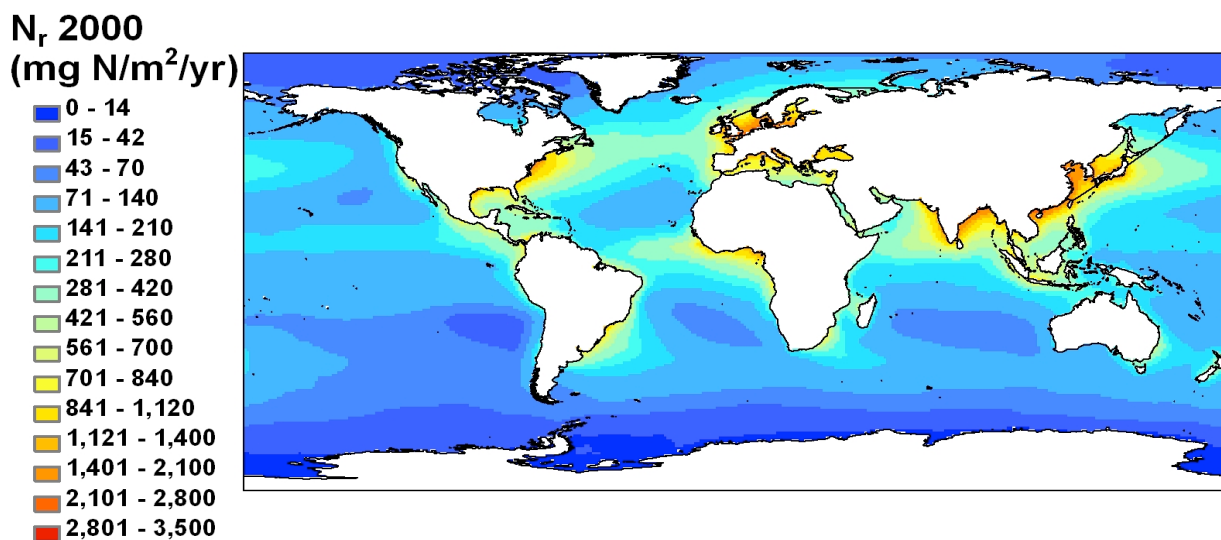


Figure 1 - Atmospheric reactive nitrogen deposition to the world ocean in 2000 in mg m⁻² yr⁻¹. Total atmospheric reactive nitrogen deposition to the ocean in 2000 was ~67 Tg N yr⁻¹, of which 44 Tg N yr⁻¹ was anthropogenic. (From Duce *et al.*, “Impacts of atmospheric anthropogenic nitrogen on the open ocean”, *Science*, 320, 893-897 (2008)). (Reprinted with permission from AAAS)

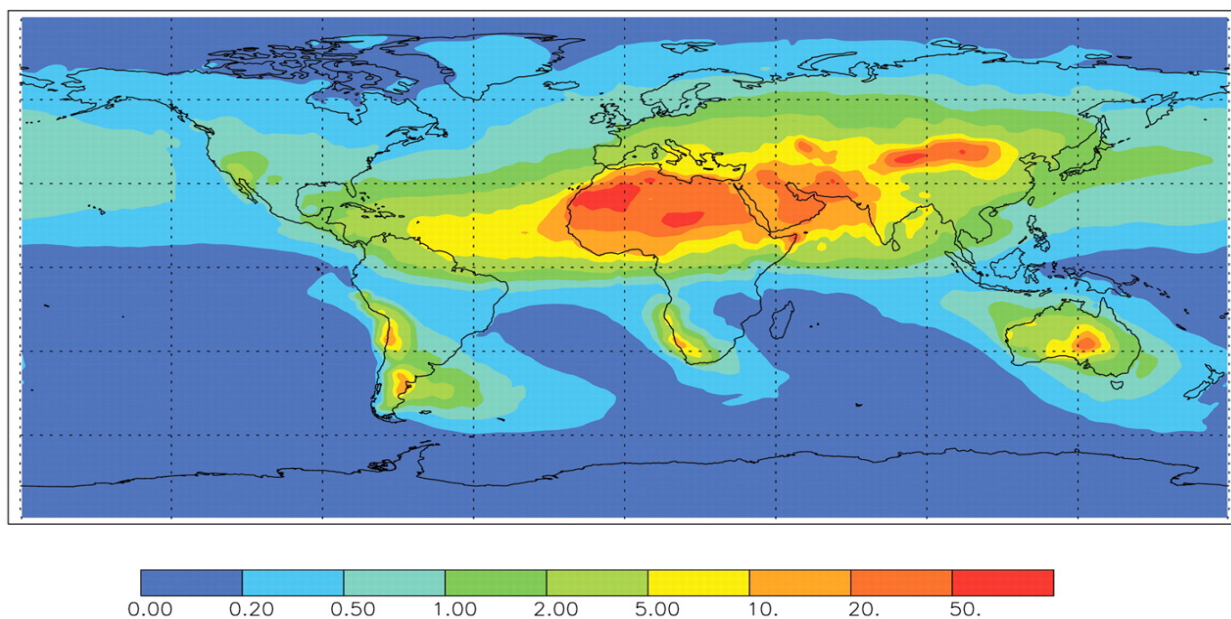


Figure 2 - Mineral dust deposition to the world ocean, in $\text{g m}^{-2} \text{yr}^{-1}$, based on a composite of three published modelling studies that match satellite optical depth, in situ concentration, and deposition observations. Total atmospheric dust deposition to the ocean = $\sim 450 \text{ Tg yr}^{-1}$. (From Jickells et al., "Global iron connections between desert dust, ocean biogeochemistry, and climate", *Science*, 308, 67-71 (2005)). (Reprinted with permission from AAAS)

In general, GESAMP WG 38 recognizes a critical need for coastal and open ocean measurements of wet deposition. Such data are essential if we are to improve our knowledge on the input and impact of chemicals into the oceans. Our advice here pertains primarily to measurements of precipitation chemistry. However, we also recognize that our understanding of ocean deposition would be greatly augmented by matching measurements of dry deposition and atmospheric concentrations of the species of interest.

2. Recommendations for Precipitation Measurements

2.1 Locations

Although GESAMP WG 38 recognizes that measurements on the continents provide useful information on natural and anthropogenic sources, it recommends that to properly characterize the inputs of chemicals into the ocean, we must obtain measurements at coastal and open-ocean sites (ideally, a few 100 km or more from the continents). Ship-borne measurements could also be potentially useful. At present wet deposition measurements are highly concentrated in continental regions affected by enhanced contamination resulting from human activities. Coastal and open ocean measurements would provide information on the magnitude of continental outflow and the input into the oceans. GESAMP WG 38 is aware of a number of past and ongoing wet deposition measurements that could be included in the WMO data compilation. We can also identify a suite of potential locations that could help to improve our knowledge concerning the atmospheric input of particles and chemical species into the ocean. Many of these presently are in operation or have been in the recent past.

The precipitation network initiated by the University of Virginia (James Galloway - jng@virginia.edu) in the early 1980s at Amsterdam Island, Bermuda, and Barbados provided unique information on wet deposition to the oceans; if these were to be re-established they would provide valuable information, including evidence of changes that occurred since the 1980s.

Rainfall studies were carried out at a number of locations carefully chosen by the AEROCE (Atmosphere/Ocean Chemistry Experiment) network to provide a representative set of locations in the major surface wind regimes over this region. These stations operated from the late 1970s until the mid-late 1990s by the University of Miami (Joseph Prospero - jprospero@rsmas.miami.edu). Some of these sites continued the work of the University of Virginia group who was a participant in AEROCE. Consideration should be given to re-establishing some of these stations. Among the sites in this network that would be most useful are:

Mace Head, Ireland (53.32N, 9.85W); data from 1988 to 1994
Davids Head, Bermuda (32.35N, 64.65W); data from 1992 to 1998
Tudor Hill, Bermuda (32.27N, 64.87W); data from 1988 to 1998
Miami, Florida, USA (25.75N, 80.25W); data from 1974 to 1998
Ragged Point, Barbados (13.17N, 59.43W); data from 1972 to 1998

Other possible locations include:

North Atlantic Ocean:

- Sao Vicente, Cape Verde Atmospheric Observatory (16.51N, 24.52W); the SOLAS (Surface Ocean/Lower Atmosphere Study) field station
- Irafoss, Iceland (64.0N, 21.0W); this is an EMEP (European Monitoring and Evaluation Programme) precipitation station

Mediterranean Sea:

- Crete, Greece; Finokalia station (35.20N, 25.40E); operating discontinuously since 1997
- Corsica, France; operating discontinuously since the 1990s

South Atlantic Ocean:

- Ascension/St. Helena, South Georgia / Falkland Islands; the University of Miami group operated an aerosol station in the Falklands (51.7S, 57.8E) from 1987 to 1996

North Indian Ocean:

- Port Blair, Andaman Islands, Bay of Bengal
- Hanimadu, Maldives Islands, Arabian Sea (6.75S, 73.15E); this was a station in the INDOEX (Indian Ocean Experiment) Programme

South Indian Ocean:

- Amsterdam Island (37.47S, 77.31E); precipitation data from 1980-1987, since then operating discontinuously – probably has the longest DMS dataset, atmospheric observations continuous since 1987
- Reunion Island (21.2S, 55.83W); the University of Miami group had an aerosol station here from 1990 to 1996
- Mauritius (20.2S, 57.5E)

North Pacific Ocean:

- Hawaii, Hawaii (19.4N, 155.2W); NADP (US National Atmospheric Deposition Programme) operated sites here at Mauna Loa and Volcano National Park but they are no longer active
- Oahu, Hawaii (21.35 N, 157.68 W); the University of Hawaii and Texas A&M University have operated an air sampling station here intermittently since 1966
- Midway (28.22N, 177.4W); the University of Miami group operated here from 1981 to 2001

South Pacific Ocean:

- American Samoa (14.3S, 170.6W); US NADP operated a site at the NOAA facility on Tutuila from 1980 to 1992 but it is no longer active
- Cape Grim, Tasmania, Australia (40.68S, 144.68E); Australian background monitoring station

Western North Pacific Ocean:

- Ogasawara (Bonin Islands), Japan; Chichi-Jima Island (27.05N, 142.13E); data available since 2001
- Okinawa, Japan; Cape Hedo (26.52N, 128.15E); data available since 2001

2.2 Substances, Concentrations, and Precipitation Amounts

The variables of primary interest to the oceanographic community that is concerned with atmospheric deposition to the ocean include:

- Precipitation amount (rainfall or snowfall)
- Atmospheric concentrations and/or deposition of:
 - All ions needed to obtain ion balance; (See GAW (WMO Global Atmosphere Watch) Report No. 160 for protocols for major ions)

- NO₃⁻; NH₄⁺; organic nitrogen; nss (non sea-salt) SO₄⁼; MSA (methane sulfonic acid); phosphorus (speciated in phosphate/total phosphorus if possible); Fe and other trace metals such as Pb, Hg, etc.; organic compounds (if possible speciated into acidic component, organic nitrates and methylamines and others);
- Insoluble components (organics; elemental carbon; mineral dust)
- POPs and other compounds (especially endocrine-disruptors) from a variety of continental sources, particularly with respect to deposition at higher latitudes

2.3 Quality criteria

GESAMP 38 recommends that in some cases the low concentration levels of micro-nutrients, such as phosphorus, iron, and possibly other trace metals, would require specific attention to measurement quality assurance beyond that normally accorded to precipitation studies. In particular, this concerns the instrumental and analytical analysis of trace metals, which because of their lower concentrations requires a special effort to avoid contamination in collection and storage. In a supplemental paragraph below GESAMP WG 38 provides recommendations for the collection of trace metal rainfall samples.

GESAMP WG 38 is aware that it is not always possible for stringent data quality criteria to be met. Metadata should be generated for all distinct samples/datasets, conforming to the appropriate ISO metadata standard. This facilitates data exchange and helps to ensure the longer-term stewardship of data.

2.4 Sample time resolution

Seasonality is important and monthly datasets are useful. There is a difference between sample time resolution and analysis averaging time. The former is needed for sample integrity and should be on a daily or at most weekly mean. However, this may be difficult at some remote marine sites.

2.5 Data source

Data should always include the names, addresses and other contact information for contact persons for any further information.

3. *Interaction Between GESAMP WG 38 and the WMO Precipitation Chemistry Data Synthesis and Community Project*

GESAMP WG 38 has identified several products that could be provided to the WMO Precipitation Chemistry Data Synthesis and Community Project to aid their work. These include:

A compilation of wet deposition measurements made during extensive ship cruises in the Atlantic - Alex Baker, United Kingdom (alex.baker@uea.ac.uk)

A similar compilation of atmospheric concentrations and fluxes from Pacific cruises and the EANET (Acid Deposition Monitoring Network in East Asia) ground sites in East Asia - Mitsuo Uematsu, Japan (uematsu@ori.u-tokyo.ac.jp)

A database of wet deposition measurements made during oceanic ship cruises is currently being compiled (EU COST Action 735 initiative - Alex Baker, United Kingdom (alex.baker@uea.ac.uk)

A data set is being developed for aerosol composition and deposition over the Bay of Bengal - Manmohan Sarin, India (sarin@prl.res.in)

The atmospheric and marine community concerned with atmospheric deposition to the ocean critically depends on the various data compilations that will be provided by the WMO Precipitation Chemistry Data Synthesis and Community Project. GESAMP WG 38 believes that the brief recommendations outlined above will enable this WMO project to enhance significantly the usefulness of the information that it can provide.

4. References

- Duce, R.A., J. LaRoche, K. Altieri, K. Arrigo, A. Baker, et al., "Impacts of atmospheric anthropogenic nitrogen on the open ocean", *Science*, 320, 893-897 (2008).
- Jickells, T.D., Z. S. An, K. K. Andersen, A. R. Baker, G. Bergametti, N. Brooks, J. J. Cao, P. W. Boyd, R. A. Duce, K. A. Hunter, et al., "Global iron connections between desert dust, ocean biogeochemistry, and climate", *Science*, 308, 67-71 (2005).

5. Supplemental Recommendation on Procedures to be Used for Trace Metal Rainwater Collection

Funnels and bottles for trace metal sampling should be soaked for at least 48 hours in 10% v/v HNO₃ and rinsed with ultrapure water, and bottles stored filled with ultrapure water acidified with 1 mL/L concentrated Aristar HNO₃. All rain sampling equipment should be stored in double, sealed plastic bags until use and funnels kept in plastic bags between rain events. Just before sampling the contents of a collection bottle are used to rinse the inner surfaces of the funnel, and excess liquid shaken off the funnel. The bottle is then attached to the funnel and the funnel plus bottle assembly is deployed in the mount. Funnels are periodically blanked by collecting ~50 mL of rinse water in 125 mL low-density polyethylene bottles. Trace metal rain samples should be acidified as soon as possible after collection with 1 mL/L concentrated Aristar HNO₃. If sample volume permits and this can be done within a few hours of sample collection, an aliquot may be filtered (preferably 0.2 µm pore filter) before acidification. Both the filtered and unfiltered aliquots can then be acidified and stored as described above.

Since concentration of contaminants in rainwater collected in the first few minutes would be much higher than that in rainwater collected subsequently, concentration of contaminants in the rainwater sample would depend on total volume of sample collected. We suggest that a minimum volume of ~10-20 mL be collected. Recording the volume of water collected for each sample should be a core parameter for the dataset. The maximum regulatory/recommended storage times prior to analysis should be indicated, and in general details of the procedures used should be recorded as part of the metadata record describing the sample or dataset, conforming to the appropriate ISO standard, to facilitate later data exchange.

This meeting of GESAMP WG 38 was organized and supported by the Global Atmosphere Watch (GAW) and the World Weather Research Programme (WWRP) of the World Meteorological Organization (WMO), with additional support from the ICSU Scientific Committee on Oceanic Research (SCOR), the International Maritime Organization (IMO), the Swedish International Development Agency, and the University of Arizona.

B. Report of GESAMP Working Group 38 to the WMO Sand and Dust Storm Warning Advisory and Assessment System (SDS-WAS)

1. Introduction

GESAMP Working Group 38 (GESAMP WG 38) was established by GESAMP to assess the atmospheric input of chemicals to the ocean. One of the charges to GESAMP WG 38 was as follows:

“Work with the WMO Sand and Dust Storm Warning Advisory and Assessment System and with the WMO Precipitation Chemistry Data Synthesis and Community Project to evaluate the needs of the marine community and assist in clearly articulating them in the development of these WMO efforts.”

During its first meeting in Tucson, AZ, USA, from 11-14 December, 2008, GESAMP WG 38 members discussed a number of issues relevant to global atmospheric nutrient inputs and their effects on the oceans. GESAMP WG 38's effort has resulted in two advisory reports to WMO (one related to the WMO Sand and Dust Storm Warning Advisory and Assessment System [SDS-WAS] as indicated above, and a second to the WMO Precipitation Chemistry Data Synthesis and Community Project), as well as several targeted scientific papers. The charge related to the SDS-WAS was to advise that group on issues related to atmospheric dust transport over and into the ocean. This brief report addresses that charge.

The activities of the SDS-WAS and the ocean deposition research community as represented by GESAMP WG 38 are mutually supportive. The SDS-WAS can provide detailed information on sources, on specific dust events, and on the temporal-spatial distribution of dust and related chemical species. Such information is not readily available to the ocean deposition research community. Conversely, activities carried out by members of the ocean deposition research community can help SDS-WAS by providing data that can be used to test the SDS-WAS dust models. In this way the community can contribute to the improvement of the dust models, which in turn would improve dust transport, and deposition estimates.

2. Specific Recommendations

Cross-representation on regional steering groups or the scientific steering committee of the SDS-WAS and the ocean deposition research community should be arranged.

At the present time the ocean deposition research community has no formal organizational structure, but until that is developed GESAMP WG 38 can serve in that capacity. It is suggested that SOLAS (the Surface Ocean/Lower Atmosphere Study) of IGBP (International Geosphere/ Biosphere Programme) should be encouraged to formulate such a group. For planned ocean deposition field programmes, the ocean deposition research community should develop a convenient and efficient mechanism for notifying SDS-WAS of proposed field activities. Those SDS-WAS participants whose models cover the ocean deposition research community's field study domains could then interact with the field scientists: SDS-WAS would provide forecast data from their models during the field campaign phase and post-analysis products. The ocean deposition research community would use the forecasts as guidance and also provide verification of the forecasts and post-analyses to the SDS-WAS.

Model intercomparisons are needed to improve models. AeroCom (an international science initiative on aerosols and climate) is currently carrying out aerosol (including dust) model inter-comparisons. SDS-WAS and the ocean deposition research community should interact with AeroCom to emphasize the need to focus on emission scenarios and the improvement thereof along with improved wet and dry deposition parameterizations. Large and unusual dust events are of particular interest because they provide an opportunity to test modelling capabilities on a larger scale and because the movement of the dust is more readily detectable both by remote sensing and in situ instruments.

SDS-WAS should identify and catalog interesting dust events and related case studies and it should establish a mechanism whereby SDS-WAS can notify the ocean deposition research community and their global-scale modelling collaborators of these studies. The objective is to link the regional scale SDS-WAS models to the global scale, the scale of greatest interest of the ocean deposition community.

SDS-WAS is making an inventory of all types of measurements made in their community. SDS-WAS should make this information available to the ocean deposition research community. In return the ocean deposition research

community might be able to make suggestions for changes to the protocols that might improve the modelling products of both SDS-WAS and the ocean deposition research community.

It is desirable to have a uniform metric with which to assess dust model prediction skill. If SDS-WAS has a skill metric that they are using or plan to use, then the ocean deposition research community should interact with SDS-WAS to include in the metric those factors relevant to ocean deposition research community interests.

The Barcelona Center SDS-WAS group is carrying out a 45-year reanalysis of dust emissions along with estimates of transport to the North and Tropical Atlantic. The ocean deposition research community would like to be informed of progress with this activity and the availability of the products.

The ocean deposition research community should make an inventory of GAW (WMO Global Atmosphere Watch) station protocols in ocean and ocean-impacted environments to ascertain which measurements might be of use to the ocean deposition research community.

Of greatest interest are the measurements of aerosol concentration and composition and of precipitation chemistry. Particularly important here are GAW reports No. 153, Aerosol Measurements and No. 160, Precipitation Chemistry Measurements. Also important are ancillary measurements such as sun photometer data. Of particular interest are multispectral measurements such as those made in AERONET¹ LIDAR (LIght Detection And Ranging) data are also of great interest. It would be important to know where the LIDARS are located and what data are available. Of importance here are GAW Report No. 178, GAW LIDAR Observing Network, and Report No. 162, WMO/GAW Experts Workshop on a Global Surface-based Network for Long Term Observations of Column Aerosol Optical Properties.

The ocean deposition research community should identify a prioritized measurement protocol for ocean and remote coastal sites.

The minimum protocol would include the collection of bulk aerosol samples, which, at the very least would be analyzed for dust components and important associated N, Fe, and P species. The next highest priority would be the collection of precipitation. The ocean deposition research community should establish a priority system for sharing these samples with the wider community and work to conform with GAW Report No. 160 protocols.

The ocean deposition research community should contact oceanographic data centers (e.g., NODC (US National Oceanographic Data Center), ORSTOM (Office de la Recherche Scientifique et Technique d'Outre-Mer), etc.) to ascertain what data they have that are relevant to our ocean deposition interests.

This activity should become part of a greater effort to bridge the gap between the atmospheric chemistry community and the ocean chemistry community.

3. Conclusions

GESAMP WG 38 believes that if these recommendations are carried out it would strengthen the activities of the WMO SDS-WAS and greatly benefit the ongoing efforts to better understand the importance of the atmospheric deposition of chemicals, including mineral dust and its associated nutrients, to the ocean.

This meeting of GESAMP WG 38 was organized and supported by the Global Atmosphere Watch (GAW) and the World Weather Research Programme (WWRP) of the World Meteorological Organization (WMO), with additional support from the ICSU Scientific Committee on Oceanic Research (SCOR), the International Maritime Organization (IMO), the Swedish International Development Agency, and the University of Arizona.

¹ AERONET (AErosol RObotic NETwork) is an optical ground based aerosol monitoring network supported by NASA

IV. REPORT OF THE GESAMP/SDS-WAS WORKSHOP, MALTA, MARCH 2011

A. Introduction

Since 2007 GESAMP Working Group 38 has been studying the atmospheric input of chemicals to the ocean. These efforts have focused specifically on:

- Assessing the need for the development of new model and measurement products for improving our understanding of the impacts of the atmospheric deposition of nitrogen species and dust (iron) to the ocean;
- Reviewing the present information on the atmospheric deposition of phosphorus species to both the marine and terrestrial environments, considering both natural and anthropogenic sources, and evaluate the impact of atmospheric phosphorus deposition on marine and terrestrial ecosystems. To consider whether such a review of any other substance would be useful.
- Cooperating with the WMO Sand and Dust Storm Warning Advisory and Assessment System (SDS-WAS) and with the WMO Precipitation Chemistry Data Synthesis and Community Project to evaluate the needs of the marine community and assist in clearly articulating them in the development of these WMO efforts.

The earlier work and meetings of Working Group 38 took place at two meetings, as indicated earlier in this report. The first meeting was at the University of Arizona, Tucson, Arizona, USA from 10-14 December 2008. The second meeting was at IMO in London, England from 12-15 January 2010. In order to elaborate more specifically the role of minerals carried by dust that are involved in marine biological production, and to achieve more detailed and specific description of the atmospheric transport and deposition process of iron- and phosphorus-carried minerals, WMO proposed in 2010 that the above activities of Working Group 38 should be extended and that the Working Group meet jointly with the WMO SDS-WAS, with the overall objectives to:

- Identify test-bed regions for future studies (Central Atlantic; North Pacific; Indian Ocean; others);
- Employ dust/iron/phosphorus models with resolutions as high as possible;
- Improve quantitative estimates of the geographical distribution of mineral fractions;
- Assess, through long-term (re-analyses) and case-studies, the oceanic input of minerals and the marine response provided by dust/Fe/P, utilizing ocean modelling, remote-sensing and in-situ observations; and
- Elucidate environmental and climatic consequences.

A third meeting of Working Group 38 to address these issues was held in Malta from 7-9 March 2011, gathering together the SDS-WAS and GESAMP scientific communities working on these issues. An agenda and attendees at this meeting are presented in Annex 2. The three-day workshop focused on the three primary topics outlined below, and which are related to the objectives above. Individuals from GESAMP and SDS-WAS were asked to co-lead the discussions and report developments in each topic area. The goal was to provide advice as to how impacts of dust transport on marine productivity can most profitably be addressed in the future activities of WMO and GESAMP. The results of this workshop were incorporated in a paper submitted to *Environmental Science and Technology* and this paper was under review when the present report was published. The three topics discussed at the Malta meeting were:

Topic 1 Improving the quantitative estimates of the geographical distribution of the transport and deposition of mineral matter and its content to the ocean.

Topic 2 Long-term assessment of mineral dust/Fe/P input to the ocean: In-situ observations and marine response utilizing coupled atmospheric transport and ocean biogeochemical modelling and remote sensing

Topic 3 Specifying test-bed regions for joint studies of the transport and deposition of mineral matter to the ocean utilizing SDS-WAS transport modelling

Three reports were developed in these areas, and they are presented below. In places there is some overlap in the discussion in these reports, but in order to make each report complete, we have let such overlaps remain.

B. Report on Topic 1

Improving the quantitative estimates of the geographical distribution of the transport and deposition of mineral matter and its content to the ocean

Co-Discussion Chairs: F. Dentener (GESAMP), M. Schulz (WMO SDS-WAS)

Rapporteur: I. Tegen

1. Introduction

Emissions of mineral dust have impacts on the local and global environment, with implications for human health, ecosystems, visibility, and climate. One particular concern is the transport of mineral dust, containing macro- and micronutrients, to the ocean and the resulting influence on the biological productivity of the oceans. Dust deposition can be derived from measurements, but the dearth of data usually prevents a complete assessment based on measurements alone. Therefore models are often used to calculate deposition fluxes of dust on larger scales. Reliable dust deposition calculations require sound knowledge on all processes involved: 1) dust emission; 2) the composition of emitted dust; 3) chemical transformations in the atmosphere; 4) transport from the sources; and 5) size dependent removal by wet deposition (precipitation), sedimentation and dry deposition.

Several global and regional deposition estimates have been published. They generally reveal large inter-model deviations and large disagreement with measurements. The verification of model performance is impeded by a lack of benchmark data. The measurements are often discontinuous, obtained at different time periods, and have a limited representativity for larger scales. They are often obtained close to dust sources and therefore do not cover regions further away from the sources. Especially in the Southern Hemisphere, where oceanic nutrient limitation may be greatest, there is a severe lack of deposition measurements. In addition there are a variety of measurement techniques that are not easy to compare, and there is severe lack of reliable direct dry deposition measurements.

In this report we evaluate the state-of-art knowledge and uncertainties regarding the deposition of dust on the ocean and its mineralogical composition provided by models and measurement datasets. Global climate models were recently intercompared by Huneus et al. (2011) using results from the AeroCom model intercomparison. The deposition calculations from these global models are frequently used as input for biological productivity calculations. A model-measurement comparison (Huneus, 2011) shows that global models do reproduce the observed data over several orders of magnitude, although they in general greatly overestimate deposition to the southern oceans. However, the agreement with individual measurements is within a factor of three at best. To estimate the flux of mineral nutrients to the ocean, the mineralogical composition of dust deposited at the surface ocean must be known. Very few studies have been performed to assess mineralogical composition of dust over the ocean, and thus the associated uncertainties in the mineralogy are even larger than for dust alone.

Regional models have recently been used for dust forecasts, and some of the models are integrated in the newly established WMO SDS-WAS. These models include more detailed information on local dust source conditions and meteorological conditions, but are not necessarily optimized to provide reliable dust deposition calculations. This workshop report highlights possibilities for a more integrated approach to improve the dust deposition calculations to the ocean using the newest information available from regional and global models and measurements. It also identifies areas for further improvement and recommendations for science. In the following section we start by discussing the availability of benchmark data, including their mineralogical composition. We then identify the necessary steps regarding model development, model experiments and diagnostics. We finish with an evaluation of the state-of-knowledge regarding climate and anthropogenic influences on deposition of dust-related nutrients.

2. Measurement Benchmark Dataset

- a) *What is the current state of the art of measurements needed to estimate dust-related nutrient deposition fluxes?*

Various deposition observational datasets provide important information on the magnitude and temporal variability of dust deposition. However, the scarcity and the limited representativity of the data often preclude regional to global assessments of dust deposition. Therefore, observations are most essential to support the modelling of deposition fluxes of dust-related nutrients.

There are very few stations performing measurements of mineral dust deposition over the oceans. Both the AEROCE network containing a number of remote stations in the Atlantic and the SEAREX network in the Pacific were closed more than a decade ago. Fortunately, in the last years a few new sophisticatedly equipped monitoring stations have been established, often under the umbrella of the GAW programme (e.g., Malta and Izana). However, there is no recent systematic overview available of stations qualifying to monitor dust and dust deposition in the large monitoring networks (EBAS, EMEP, AENET). In addition, research programmes in Africa and in Asia (e.g., AMMA, ACE-ASIA), ship measurements (e.g., A. Baker) have provided additional shorter-term information. Nevertheless, as discussed in *Huneus et al (2011)*, these data are not sufficient to provide a complete overview of deposition to the world's oceans.

In addition to the measured dust concentration, spectral aerosol optical depths from ground based and satellite remote sensing are increasingly used to constrain models. However, these measurements are often associated with ambiguities due to a lack of understanding of the measurement errors, uncertainties regarding the vertical distribution of dust (for passive satellite sensors) and the degree of representation.

The quality of the experimental observations is often difficult to evaluate due to a lack of standardization of sampling and analytical methods, particularly concerning surface concentrations and deposition and particle solubility. Calculations of dust dry deposition will yield underestimates when dry deposition is inferred from size-segregated aerosol measurements that use too-low a cut-off diameter. In this approach the few large particles (>20µm) that are the major contributors to the mass flux get neglected, although these particles are in general only found very close to sources.

Furthermore, many datasets also integrate the contribution of sources other than dust. For instance the quantitative comparison of model output with spectral optical depth data from passive remote sensing, which integrates all aerosol components, might be ambiguous far away from source regions due to mixing of dust with concurrent contributors such as sea salt, anthropogenic pollution and biomass burning. A careful evaluation of the data is therefore necessary to separate these additional contributions. Ocean sediment trap mass fluxes could provide additional information on atmospheric dust deposition provided that the location is not strongly affected by coastal or upwelling sources of nutrients.

Iron (Fe) is one of the key-nutrients associated with mineral dust fertilizing the oceans. Measurement progress has been made towards linking the iron solubility to the dust mineralogy, particularly for African sources, and enhanced effort has focused on developing refined maps of the soil mineralogy. Sun photometers from the AERONET stations have also been used to derive the hematite/goetite content of dust. New field and laboratory data have been acquired pointing out the role of particle mixing and chemical processing during transport in increasing the solubility of iron-related dust.

b) What do we need to improve the estimate of dust-related nutrient deposition fluxes?

Long-term standardized observations are essential in order to constrain the temporal variability of dust-related nutrient deposition fluxes. Recommendations on this point are twofold:

- Existing stations in the northern hemisphere, some of which are historical (e.g., the Barbados station), should be maintained.
- New long-term observing programmes should be promoted downwind from dust source areas in the Southern Hemisphere (South America, Australia, South Africa), where observations are very sparse and the ocean ecosystem is expected to be most sensitive to Fe inputs.

The pertinence of existing and new monitoring stations with respect to their location and their ability in representing dust-unperturbed or perturbed conditions should be properly assessed, and this is addressed by the report on Topic 3.

The estimate of dust deposition fluxes and the assimilation of observations by models will benefit from the definition of commonly agreed standards with respect to sampling fractions and analytical protocols. This will allow harmonization of coordinated measurements of benchmark parameters such as size-dependent nutrient solubility, aerosol concentration, and chemical/mineralogical composition, concurrent to bulk dry and wet deposition measurements. This effort can benefit from working groups active in this area (SOLAS, EU projects EUSAAR/ACTRIS). Aerosol collection on both PM_{2.5} and TSP fractions should be pursued as much as possible. The comparison of direct dry deposition measurements with calculated values would enable improvements in estimates of the size-dependent dry deposition velocities for use in models.

The prediction of aerosol mineralogy is based on soil properties. However, the mineralogy of transported dust may be very different from the parent soil. The so-called fractionation or enrichment process should be urgently addressed to better understand the mineralogical composition. The size-segregated mineralogy and solubility should also be observed as a function of dust age in the atmosphere. These processes should be fully included into dust models. Dedicated intensive field observations and laboratory-based studies are required in order to evaluate the soil/aerosol size and mineral fractionation at emission and the physico-chemical processing (mixing, heterogeneous reactions, etc.) controlling their evolution during transport.

Finally, existing data from various measurements need to be re-assessed, and their consistency and uncertainties better characterized. Global benchmark data are made available in various contexts, but a continuously updated overview of such datasets in regional and global modelling is highly recommended. New data from lidar networks and space-borne lidars, as well as satellite aerosol products from desert regions (MODIS Deep Blue and MSG-DSAF) but also from PM₁₀ networks near dust source regions, should be exploited in an open manner to provide high resolution information on dust rise events.

3. Model Development, Experiments, Diagnostics and Documentation

a) Current status

Several model simulations exist today that provide a temporal and spatial distribution of dust deposition to the ocean. A multi-model ensemble mean such as from AeroCom is generally assumed to represent a best guess for the global distribution. Higher time and space resolved dust deposition is available from regional models, such as those currently employed and further improved in the framework of the WMO-SDS (Asia, Africa), ICAP, and the United States.

Recently, more vigorous attempts have been made to evaluate the model deposition with actual deposition measurements (e.g., *Huneus et al., 2011; Sugimoto et al., 2011; Uno et al., 2006*). A problematic factor in the evaluation of the models is the often unknown error of the deposition data. These studies show that the global distribution of a wide range of deposition flux values is relatively well reproduced. However, dust deposition is captured within at best a factor of 3 at single stations. The largest discrepancies appear for sites remote from dust sources with very low dust deposition, which seem to be overestimated by most models, most notably in the Southern Oceans. The limited data coverage is most critical in the Southern Ocean, where there are large HNLC areas that would be most sensitive to atmospheric dust and iron inputs

b) What is needed?

A general problem for dust modelling is the conditions in the source regions, which are not sufficiently well characterized. The influence of changing land management practices and variability of vegetation cover is recognized as an important factor driving dust emissions, but it is often not included in models. As mentioned earlier, mineralogical composition of soil and the fractionation of the dust emissions also need to be improved in the models. More sophisticated modelling of chemistry and aerosol coupling would be needed if it were ascertained that during atmospheric transport of mineral dust the solubility of iron, phosphorus and other micronutrients is controlled by photochemical and in-cloud processing of mineral aerosol.

More comparisons of models to observations of deposition are suggested to be crucial. High quality long-term measurements of surface concentration and wet deposition are needed. Model dry deposition is more problematic to validate mainly because of existing measurement problems. The recent decrease in such measurements and the missing commitment of funding agencies to ensure the continuation of selected long-term monitoring hinders our efforts to attain a better understanding of the evolution of dust levels in general and dust and climate interactions in particular.

Models and measurements often are interpreted in different ways. A particular problem is the dust particle size spectrum, which is often not covered to the same extent by models and measurements. Coarse particle fractions require additional attention to understand dust near source regions, in particular since those particles may deliver a considerable fraction of the dust mass flux into the oceans. Validation of deposition in models is important to help the dust model development in general, because it provides a check of the dust cycle and dust budget away from emissions sources. SDS dust models will thus profit from such evaluation work with co-benefits for the prediction of atmospheric dust in chemical weather forecasting.

Common model experiments using harmonized emission flux assumptions should be considered, especially by the SDS community, so as to compare the transport-deposition performance of models by taking away the large variability induced by differences in the source function. Significant value would be added to align those with periods and locations where more data are available. Both WMO-SDS nodes have proposed a model intercomparison. It would be useful to open these intercomparisons to other groups. Periods suggested for common reanalysis are the year 2006 and the spring of 2007. Common analysis among nodes could be useful to identify problems and provide input to global model. Furthermore, cooperation of initiatives such as AeroCom and ICAP is strongly recommended.

Assimilation of satellite-derived optical depth has been shown by several groups to lead to improved aerosol fields. For instance, the use of the ground-based lidar network data and CALIOP data with real-time distribution have shown recently its capability for improving model representation and forecast. In East Asia, there have been some efforts using the case study of the April 2007 dust event within the TEMM context (see the SOLA special issue). Horizontal and vertical transport pathways and subsequent ocean deposition of mineral dust and bio-available iron were also studied for two large dust outbreaks originating in the source regions of South America (Johnson et al., 2011). The associated model work is thus close to providing a more realistic dust reanalysis on global and regional scales. Because of the sensitivity of aerosol optical depth to primarily fine particles, additional validation is needed for the coarse dust aerosol fraction by surface in-situ concentration and deposition measurements. We note, however, that data assimilation, while improving our understanding of aerosol abundances, may not always lead to improvements in the estimated deposition rates.

Inter-annual and inter-decadal variability of regional dust sources is observed in many arid and semi-arid regions but not well understood. Such understanding would be needed to elucidate the long-term recent and future change in dust impact on ocean biogeochemistry. Possible research could involve the coordinated hindcast simulation of dust for periods where observations of dust in the atmosphere exist, such as the hindcast proposed in the framework of AeroCom for the period 1980-2008.

The requirements in terms of spatial and temporal coverage of dust deposition for a better understanding of the impact of dust on ocean biogeochemistry should be better defined. While daily deposition fields are needed for interpretation of short events, monthly global model results might be sufficient to study decadal and inter-annual trends in dust in the different parts of the global ocean. A further outstanding issue is what minimum model resolution is needed for assessment of the role of nutrient deposition in the oceans.

It was considered that the necessary documentation of model experiments (physics) is often incomplete and difficult to retrieve for those not directly involved in the experiments. The documentation of dust model simulations may be improved further by systematically making use of supplements in publications. This should be accompanied by making available model fields in the form of CF-compliant netCDF datasets via ftp sites or via common databases such as AeroCom, SDS, ICAP model intercomparisons. A publication should be accompanied by crucial model fields, such as monthly surface concentrations, emissions, dry and wet deposition fluxes, column loads and 3D mass mixing ratios of all individual dust tracers as well as dust aerosol optical depth.

4. *Climate and anthropogenic influences on deposition of dust-derived nutrients to the oceans*

Dust is the largest single source determining the global aerosol burden. As a consequence, anthropogenically or climate induced changes in atmospheric dust will have a large impact on climate in general, and deposition of nutrients to the ocean in particular. Model simulations of the current impact of dust on the ocean carbon cycle are highly uncertain. A few recent studies suggest that mineral dust input in the oceans suppresses CO₂ by 10-20 ppm, subject to large uncertainty. Changes in climate conditions and human influences on the environment can impact the delivery of nutrients to ocean surfaces by aeolian dust in different ways. Understanding those interactions are thus of importance for characterizing possible future changes in their oceanic impact.

The effect of climate on dust emission is complex. Climate directly affects wind erosivity by controlling windspeed, and more importantly, wind gustiness. Precipitation also impacts dust emission through delivery of wind-erodible and dust-sized particles. Years of high dust emission can follow years of especially high, or high intensity, precipitation that causes greater overland flow and sediment delivery to dust source regions. Climate also impacts vegetation, and large amounts of antecedent precipitation in drylands can sharply reduce wind erosion by the growth of plants in previously unvegetated areas. In addition, there are factors that control atmospheric dust, e.g., human activities that directly impact the erodibility and emissivity of the surface, and these are not yet well understood.

Dust emission occurs when the erosivity of the wind exceeds the erodibility of the soil in unvegetated bare gaps. Soil erodibility, characterized by the threshold wind speed for soils, is largely a function of the soil surface texture and the presence of biological or physical surface crusts. Dust emission efficiency, i.e., the amount of dust produced for a given amount of aeolian transport, also depends on the surface soil texture. Although human activities and climate have little impact on soil surface texture, they can have a major influence on the state of crusts that protect the soil from erosion and dust emission. Activities such as grazing, tillage, and vehicular movement destroy soil crusts and decrease the threshold wind speed. Activities that remove or reorganize vegetation, such as land clearing, deforestation, grass-to-shrub conversion, and overgrazing reduce the sheltering effect of vegetation and will also increase dust emission.

Nutrient delivery from dust deposition into the ocean depends on dust concentrations, nutrient concentration within the particles and solubility of the nutrients. Emissions of reactive gases and secondary aerosols from anthropogenic sources have increased since preindustrial times and are expected to have increased the solubility of micronutrients in dust particles, in particular downwind of industrialized regions (Solmon *et al.*, 2009). This depends on atmospheric processing of the particles and will change with changes in the anthropogenic concentration of reactive gases (e.g., SO₂, NO_x, etc.) that can mobilize the nutrients iron and phosphorus. The relevant timescale to look at is preindustrial to present. The longest ongoing measurement of dust concentrations at the surface is at Barbados, where measurements exist since the late 1960s (Prospero and Lamb, 2003). Trends in 20th century dust from visibility reduction measurements at meteorological stations have been inferred as a surrogate indicator for dust emissions (Mahowald *et al.* 2007). Such long-term observations indicate that there has been a strong increase in dust emission and transport over the tropical Atlantic in the beginning of the 1970s at the onset of severe drought conditions in the Sahel region. Other regionally significant dust increases have occurred, e.g., in the Aral Sea region or during the dust bowl years in the southwestern US in the 1930s and 1950s, but not much dust from these events may have reached the ocean.

5. Recommendations

The view that emerges from this analysis is that dust emission is highly dependent on changes in the climate as well as changes in source functions as a result of anthropogenic activities. This means that current dust parameterizations that necessarily simplify the processes that lead to dust emission, particularly in global models, may not work well under different climate regimes. As a result, parameterizations of desert dust emission may need to be made more process-specific before improved future predictions can be made. Furthermore, the impacts of human activities on vegetation and on soil crusts need to be included in models to understand the overall impact of humans on the dust cycle. At present, neither models nor observations of soil and vegetation disturbance by humans exist that can clearly guide our understanding of the impacts of humans on dust. Indeed, even the inclusion of so-called "natural" dynamic vegetation in global or regional climate models is in its infancy, and until these models can do a good job of predicting vegetation functional type, cover, and dynamics well, it will be very difficult to estimate the impact of climate on future dust emissions through its impact on the terrestrial biosphere.

Understanding what controls the interannual changes in dust on different timescales is a key factor for identifying the role of meteorology. What cannot be explained by climatology would indicate trends in anthropogenic sources and shifts in climate regimes. Particular focus should extend to understanding controls of dust sources and transport in the southern hemisphere, which are less well known than the major dust sources in the northern hemisphere.

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C. Report on Topic 2

Long-term assessment of mineral dust/Fe/P input to the ocean: In-situ observations and marine response utilizing coupled atmospheric transport and ocean biogeochemical modelling and remote sensing

Co-Discussion Chairs: Manmohan Sarin (GESAMP) and Slobodan Nickovic WMO SDS-WAS)

(Natalie Mahowald in absentia, GESAMP)

Rapporteur: Luisa Ickes

1. Introduction

The large-scale atmospheric transport and deposition of mineral dust from arid and semi-arid continental regions is believed to be a major, if not the dominant, source of iron (Fe) and phosphorus (P) to the remote ocean. However, the air-sea flux of mineral dust is highly episodic and variable in space and time. There are a limited number of case studies addressing the direct response of marine ecosystems to the atmospheric dust deposition. The conclusions drawn from these few case studies are often debatable and generally inconclusive. A detailed and specific description of the atmospheric transport and deposition processes of Fe- and P-carrying minerals to the open ocean requires systematic field measurements and satellite-based observations, together with improved model representations. Such an approach would help to improve our understanding of global scale climatic impacts of mineral dust deposition to the oceans.

In addition to global-scale effects, as indicated in the report on Topic 1, regional and temporal scale studies for physico-chemical properties of mineral dust and its geographical deposition to the ocean surface are also important for quantitative estimates of the supply of atmospherically derived Fe and P. Mineral dust particles vary over a wide size range, from ~0.1 to ~100 µm diameter. The coarser particles have shorter lifetime and are primarily deposited near the source regions, while fine particles (< 10 µm) can be involved in long-range transport and provide the surface area required for heterogeneous phase chemistry. Preferential accumulation of nitrate on calcium-rich dust compared to sulfate accumulation on aluminosilicate rich dust particles has been reported (Sullivan et al., 2007). The occurrence of Fe primarily associated with the highly insoluble mineral phase limits its solubility in seawater. The amount of water-soluble iron present in mineral dust aerosols continues to remain a major source of uncertainty in assessing the impact of the atmospheric supply of iron on marine biogeochemistry. Under present-day conditions of growing anthropogenic activities, the chemical processing of mineral dust particles during their long-range transport, mediated by acidic constituents (e.g., SO₂ and its oxidation products), organic acids and sunlight, is of growing importance for the enhanced solubility of aerosol iron. Likewise, it is essential to evaluate the impact of atmospheric deposition of phosphorus species, from both natural and anthropogenic sources, on the marine ecosystem.

In this context, long-term field observations and the development of atmospheric transport models with accurate chemical mechanism for the production of water-soluble Fe and P are of utmost importance for documenting dust emissions from source regions and assessing their effects on ocean ecosystem. Although global models have frequently been used to capture large-scale features of dust transport, the development of regional models is required for better resolution of the temporal variability of the emission and transport of dust. The use of high-resolution soil mineralogical maps would also be useful for modelling dust production and aid in simulating 3D transport and transformation of different minerals as a result of atmospheric processing (including the process of Fe- and P-solubility). Coupling atmospheric transport models with ocean thermodynamic and marine ecology models provides valuable information on marine primary production and nitrogen-fixation triggered by the atmospheric input of mineral dust and associated nutrients.

Satellite-based observations of chlorophyll-*a* and primary productivity in the surface ocean have been successfully used in specific case studies. However, establishing a causal relationship between atmospheric dust deposition and satellite-derived ocean productivity is necessary to understand and quantify the short-term variability in the marine surface primary productivity to dust deposition. Looking from a different perspective, it is also likely that the variability in the marine response to dust/Fe/P input is driven by large-scale ocean circulation. Atmospheric deposition of dust may drive primary productivity in most of the Fe-limited regions. Determining the mineral phases containing Fe and P, their bioavailability and differential uptake by the primary producers are also key issues. The size (eucariots versus procariots), shape and population of primary producers and/or nitrogen-fixing communities may be important in determining the impact of atmospheric Fe/P inputs. Finally, one of the pertinent questions that must be answered is - what are the spatial- and temporal-scales required for studying the short- and long-term responses of marine ecosystem to mineral dust deposition?

2. Observation parameters

We suggest a set of relevant and important measurements that should be considered in specific case studies. These are required for a better assessment of the atmospheric deposition vis-à-vis the marine response as well as for model validation:

- Atmospheric and size-dependent aerosol parameters: Total suspended particulates (TSP), PM_{2.5}, mineral dust and a suite of diagnostic tracers (Al, Ti, Si, K, PO₄, SO₄, NO₃, NH₄), heavy-metals (V, Pb, Cd, Ni, Cu), water-soluble fractions of Fe and P; wet- and dry-deposition fluxes of nutrient constituents (Fe as well as inorganic and organic P and N).
- Seawater parameters: Salinity, temperature, density, mixed layer depth, current fields at depth, sea level anomaly, chlorophyll-*a* biomass, pCO₂, POC, PON, DOC, CDOM, inorganic N and P, photosynthetically active radiation (PAR), DMS, N₂O and other biogenic trace gases, taxonomic composition of different species (cyanobacteria vs micro-algae), primary productivity and nitrogen-fixation, as well as carbon-based production models coupled with sediment trap data.

3. Major existing gaps and questions

We have identified some major existing gaps and questions related to our present-day understanding of the atmospheric transport of mineral dust and some model limitations for observing the impacts of dust deposition on marine productivity. These include:

- What particle-sizes and mineralogy of atmospheric mineral dust need to be measured for case-study assessment and deposition of dust-derived Fe and P?
- What processes control Fe- and P-solubility in mineral dust and is wet vis-à-vis dry-deposition most important in air-sea fluxes? The solubility of both Fe and P in the source regions of dust and during long-range transport (chemical processing) are major uncertainties. Is biomass-burning a significant source of soluble Fe and P in the area downwind of these source regions?
- How does the marine ecosystem respond to the atmospheric input of dust in Fe- and P-limited oceanic regions (in micro-nutrient eutrophic or oligotrophic waters)?
- What is the selective response of oceanic biomass and different phytoplankton communities (procariota vs eucariota) to dust input? How does dust affect the upper trophic levels?
- What is the impact of dust deposition on carbon sequestration and on the global carbon cycle and climate?

4. Action and recommendations

A list of publications has been compiled that addresses both the atmospheric transport and deposition of Fe and P to the marine environment and the associated oceanic response. This annotated publication list is presented in Annex 3. This list should be helpful in the development of subsequent case studies.

Prior to the meeting of WG 38 in Malta, the group addressing Topic 2 was asked to address the need for expanding the scope of case-studies in order to overcome the limited data set currently available with respect to spatial and temporal variability in the atmospheric deposition of mineral dust and the marine response on both short- and long-time scales. At the end of the Malta meeting the following recommendations were made:

- Identify new taxonomic and functional (nitrogen fixing and primary productivity) pico-planktonic and micro-planktonic groups to help understand surface ocean biogeochemical processes and model simulation in response to the atmospheric supply of iron in mineral dust.
- Develop atmospheric chemistry-transport models that include a complex Fe dissolution scheme that will allow better assessment of Fe-solubility as a function of dust load, mineralogical composition, ambient atmospheric temperature and relative humidity, abundances of trace species (in particular acidic species) and cloud-processing. It is further essential to understand the marine response to the supply of soluble-Fe during atmospheric processing of mineral dust vis-à-vis bio-available Fe produced by in-situ leaching of mineral dust by surface sea water.
- Utilize as much as possible deposition fluxes based on sediments trap measurements to provide additional evidence on the marine response to the air-sea deposition of mineral dust.
- Compile published evidence on the mineralogy of dust from source regions and promote in-situ observations of the size-resolved physical and mineralogical composition of soils. Although individual event-based studies provide critical information, long-term time-series observations away from dust source regions are most appropriate.
- Design and improve coupled models by incorporating complex atmospheric and marine biogeochemical processes.

D. Report on Topic 3

Specifying test-bed regions for joint studies of the transport and deposition of mineral matter to the ocean

*Co-Discussion Chairs: Alex Baker (GESAMP) and Carlos Pérez García-Pando (WMO SDS-WAS)
(Joseph Prospero in absentia - GESAMP))
Rapporteur: Sergio Rodriguez*

1. Introduction

As outlined in the reports on Topic 1 and Topic 2, there are several aspects of the transport and deposition of mineral dust to the ocean that are very poorly understood and require further study, both through observations and modelling. These include:

- Characterizing dust sources and transport pathways, especially those in the southern hemisphere;
- Quantifying changes in the solubility of dust components during transport through the atmosphere and identification of the factors responsible for those changes;
- Measurements and parameterisations of dry deposition fluxes of mineral dust and its chemical constituents; and
- Quantifying the impacts of dust deposition on marine primary production and nitrogen fixation.

In this report we briefly summarize the current state of knowledge for each of these aspects and recommend work that might be carried out to advance the science in each field.

2. Current Status

a) Dust sources and transport

The successful modelling of dust processes and an improved understanding of the iron cycle requires a better understanding of the factors that contribute to the uncertainties of the dust cycle in the models. Because of inter-model differences in simulated dust emission and deposition fluxes, estimates of the impact of dust on ocean CO₂ uptake in HNLC (high nutrient-low chlorophyll) regions are highly uncertain. The recent AeroCom dust model evaluation and inter-comparison has shown that models tend to greatly (10x) over estimate deposition to large areas of the Pacific, the Southern Ocean, and Antarctica. And yet from the standpoint of ocean impacts of dust-Fe on the oceans, these regions are critically important because large areas are characterized as HNLC and, consequently, would be most responsive to dust-Fe inputs. Many models reproduce reasonably well the seasonal variability of the Earth's most prolific dust source, North Africa. This performance is attributable to the fact that there are many more studies of African dust transport to remote regions than there are for dust from other regions. Consequently models are well tuned to this source. This tuning results in large model biases when applied to other source regions. Because of this, source emissions from other arid regions (e.g., Asia) have to be tuned to other measures such as aerosol optical depth (AOD). Another important problem in models is that in general they miss the winter transport of Saharan dust to South America. Also models show strong divergences in the southern hemisphere.

Models are almost completely dependent on the data set generated by the various University of Miami sites that were set up in the late 1970s and which continued into the mid-late 1990s, after which time only a few stations continued operations. Thus the models are working on data sets in which the oldest data are, for the most part, thirty years old and the youngest about 12-15 years old. The longest data set is from Barbados, which started in 1965 (with Parkin and Delany) and continues to this day, i.e. 45 years. The second longest set is from Miami, which started in 1974.

b) Solubility of dust components

There are many reports of studies on iron solubility in atmospheric aerosols, but rather few on the solubility of other potentially biogeochemically active elements. For iron, there are a number of different processes that might influence the overall amount of iron released into seawater after aerosol/dust deposition. Some proposed processes operate in the source region, some during atmospheric transport, and some after deposition into the ocean. Different processes are likely to be significant in different environments, and there is no consensus on which processes dominate. Baker and Croot (2010) recently reviewed the status of research into aerosol iron solubility. They noted that progress in this field was hindered by the lack of standardized methods and suitable reference materials. Probably as a consequence of the rather poor status of observational studies, there is a similar diversity of approaches to the treatment of iron solubility in modelling studies. It is encouraging that recent modelling work recognizes these problems, in

particular that it is unrealistic and inadequate to use a single, fixed value for the fraction of iron released into seawater from mineral dust.

c) *Dry deposition fluxes*

There are almost no direct measurements of dry deposition. Most estimates of dry deposition flux are based on concentrations measurements multiplied by a dry deposition velocity. Very often these dry deposition velocities are taken from the summary of *Duce et al. (1991)*, but in general the users of this procedure do not seem to be aware of the very high level of uncertainty associated with those values, even though those authors pointed this out. Models use rather crude dry deposition schemes because there is a lack of data to evaluate more detailed schemes. Consequently, as shown in the recent AeroCom intercomparison, models yield a wide range of estimates of dry deposition fluxes and also of the ratios of wet-to-dry deposition.

d) *Impacts on marine biogeochemistry*

Most of the more compelling evidence for links between atmospheric mineral dust inputs and marine biogeochemistry comes from broad-scale observations. Examples include: observations that nitrogen fixing organisms (*Trichodesmium*) are much more abundant in the tropical North Atlantic (where there is a strong dust input) than in the tropical South Atlantic (where dust inputs are low); the fact that (iron-limited) HNLC waters are generally located in areas far removed from the major dust source regions; and in the southern hemisphere that the dust supply is linked to glacial and interglacial cycles and seems to be related to changes in atmospheric CO₂ concentrations. Smaller scale experiments (e.g., bottle incubations of phytoplankton and meso-scale ocean fertilization experiments) have also provided firm evidence that the components of mineral dust (particularly Fe and P) can have significant impacts on marine biogeochemistry in some ocean regions. However in on-deck incubation studies where dust additions were conducted alongside element addition experiments, the results have often resulted in rather different responses in chlorophyll concentrations and productivity changes from those obtained by addition of Fe, P or Fe and P.

Recent sediment trap studies show an increased flux of biogenic particles that is apparently a response of primary producers to fertilization by mineral dust inputs. Enhanced biogenic particle fluxes recorded in traps at times of elevated mineral dust trap loadings indicate significant enhancement of primary production, even when this production is undetected by satellite chlorophyll-a retrievals. The lack of satellite detection of enhanced chlorophyll-a concentrations may in some cases be due to the presence of deep chlorophyll maxima at depths below those visible to satellite-borne instruments.

3. *Recommendations and proposed future work*

a) *Dust sources and transport - proposed sampling sites*

AeroCom Phase II will incorporate additional diagnostics that will allow more comprehensive assessments of models and lead to improvements in simulating the global dust cycle. The new model experiments will store detailed size distribution information, which will allow us to address issues such as the impact of the simulated size distribution in reproducing the dust deposition flux and surface concentration, which are crucial to understanding the iron cycle. However, we need additional observations mainly in the southern hemisphere to help constrain models. Ideally, model evaluation and improvement would benefit from combined measurements of dust surface concentration and column (sun-photometer and vertically resolved lidar) concentration together with rainfall (wet deposition). Below are presented recommendations for sites that could serve as long term monitoring stations:

* *North Atlantic*: Stations in the North Atlantic will play an important role by making measurements of aerosols and deposition which will serve as the critical test-bed data for the further development of dust transport models. Also they will generate the baseline data needed to track the response of North African dust sources, by far the largest in the world, as climate changes.

Barbados: Studies on Barbados and Miami have shown large changes in dust transport over the past decades. As for the future, the 2007 IPCC report suggests that large areas of northern North Africa will become drier; but, critically, the models could not agree on the future direction of a large area of North Africa in the Sahara and the Sahel that is known to be a major source of present-day dust. In this context Barbados is a vitally important station to monitor this source and the transport to the Atlantic. Logistics are excellent and local technical support is available through scientific institutions on the island.

Bermuda, Miami and Izaña: Although a lesser priority, these stations would provide data on the latitudinal distribution of dust transport. These data are important for assessing nutrient inputs to the central Atlantic. Bermuda will also serve to characterize the transport of dust and "industrial" iron to the central Atlantic; although very little soil dust emerges from North America, "industrial" iron could have a significant impact on ocean biogeochemistry because it is much more soluble than dust-Fe. Both Miami and Bermuda will also provide test data for models which all seem to have difficulties in resolving transport in the transition regions between major wind systems (i.e., in the Atlantic, between the trade winds and the westerlies). Local support is available through the University of Miami in Miami, on Bermuda by the Bermuda Institute of Ocean Sciences (BIOS) and at Izaña by the Izaña Atmospheric Research Centre.

French Guiana: There is a great need for a station in French Guiana to characterize low-latitude dust transport. A study carried out 30 years ago in Cayenne by the University of Miami showed that in late winter and spring, the transport of African dust to South America was as great as that taking place in the summer months at Barbados. The dust-phosphorous carried in this transport is believed to play an important role in the nutrient balance of the Amazon basin. This transport is prominent in satellite products. It is notable that in the recent AeroCom model intercomparison, the models missed or greatly underestimated this transport. French Guiana has good infrastructure and can provide high-quality scientific support.

Iceland: A station in Iceland would play an important role in characterizing the response of high-latitude deserts to climate change. Studies on Heimaey, Iceland, that began in 1991 with the University of Miami show that there is considerable dust activity on Iceland, much of it linked to periglacial deposits. These sources are expected to become more active with time as the glaciers retreat. A recent study in the Gulf of Alaska shows that outbreaks of glacial dust along the coast are an important source of iron over a large region of the eastern Gulf. Thus, glacial sources can be expected to become increasingly important as an iron source in the coming decades. In Iceland logistics and scientific support are excellent.

* South Atlantic: The central South Atlantic is heavily impacted by emissions, especially biomass burning products, transported from central and southern Africa. Unfortunately there are no suitably-located islands in the region that could be used to characterize this transport. The southern South Atlantic is most strongly affected by transport from sources, including dust and pollutants, in southern South America.

Falkland Islands: The Falklands are ideally located to measure the activity of dust sources in southern South America, which is believed to have been a major dust source during glacial periods (as reflected by great increases in dust concentrations in Antarctic ice cores at those times). The University of Miami operated a station in the Falklands beginning in the 1980s. Because of logistics and infrastructure limitations the sampler was not well sited. Consequently samples were heavily impacted by local sources, primarily peat burning. However, the infrastructure should have improved since the mid-1990s when sampling was stopped there. The University of East Anglia has recently established a new site in the western Falklands with a clean air sector directly exposed to southern South America. No results are yet available from the site, but it is hoped that it will provide a much-needed record of dust concentrations in the region.

* North Pacific: Emissions from Asia dominate the aerosol composition over a huge area of the North Pacific

Midway: Midway is ideally situated to monitor the transport of dust from Asian sources; a station on this island should have a very high priority. Measurements made by the University of Miami starting in 1981 and ending in 2001 clearly show the strong spring cycle of Asian dust transport along with the transport of high concentrations of pollutants. The presence of both dust and pollutants in the same air mass could have a great affect on Fe solubility in contrast to African dust, which is usually associated with relatively low concentrations of pollutants. Also we might expect to measure high concentrations of "industrial" iron that is known to be highly soluble. In 2001 NASA established an AERONET site on Midway; these measurements clearly document the strong impact of the spring dust/pollution transport on the yearly cycle of AOD. Midway is now a wildlife refuge under the US Department of the Interior. Regular flights to the island have resumed recently. Consequently logistics and local technical support should be good.

* South Pacific: Australia is believed to be the major source of dust for the South Pacific and the Southern Ocean.

Norfolk and Chatham Islands: These islands are ideally suited to monitor this source. Norfolk would capture dust transport out of Australia to the northeast and Chatham Island the transport to the Southeast. The University of Miami had operated long-term sites on these islands in the past. The logistics are quite good, as is local support for operations.

* Indian Ocean: Sources in the Indian subcontinent, Southeast Asia and North Africa provide the major inputs to the northern Indian Ocean, the Bay of Bengal and the Arabian Sea.

The Maldives Islands: As a follow-up on the INDOEX programme and under the leadership of V. Ramanathan (Scripps/UCSD), a Climate Observatory was established at Hanimadhoo Island in the northern part of the Republic of the Maldives. The site is strongly impacted by the annual monsoon cycle. With the Northeast Monsoon it receives great quantities of dust and pollution largely transported from the Indian subcontinent, the Middle East, and North Africa. During the Southwest Monsoon the air is extremely clean. This would be an ideal region to study the effects of pollution on dust Fe solubility and the seasonal variability of impact of dust on local water biogeochemistry.

* The Southern Ocean: Southern South America, southern Africa and western Australia are believed to be the major sources to the southern regions. There are not many good options in this region. Logistics are difficult and there is very little dust.

Cape Grim: The Cape Grim Baseline Air Pollution Station, located in remote northwestern Tasmania, would be ideal from the standpoint of its location with respect to Australia and the presence of a highly capable staff. But for the study of dust there are concerns about strong upslope winds that could carry local dust to the site.

Reunion Island: Reunion is well located and there is good local support. But there is not much dust in this region and sampling could be exacerbated by local impacts.

Marion Island and Prince Edward Island: These would be excellent except for very bad logistics (which may have improved since the mid-90s). Because of its location in the "roaring forties", weather is frequently rainy and often severe; consequently the air is very clean.

b) *Solubility of dust components*

There are many issues we need to understand concerning the solubility of iron. For example, what transformations affect iron solubility in the atmosphere? Can we distinguish and quantify the relative importance of mineralogy, size and atmospheric chemical processing? What are the relative contributions of desert dust and combustion/anthropogenic aerosol to the soluble iron budget? Are there anthropogenic contributions to other key elements (e.g., contributions to the load of phosphorus observed in dust events due to the use and production of fertilizers have been observed over the Indian and North Atlantic Oceans)? In this regard, we suggest specific atmospheric experiments including detailed observations and modelling (including dust and atmospheric iron processing) downwind of the two main source regions (North Africa and East Asia).

For example downwind of North Africa, four sites (Izaña, Cape Verde, Barbados and Bermuda) could be used for a coordinated experiment. Ideally, measurements would include:

- Aerosol physics: size, number, surface area and mass distributions, altitude resolved aerosol properties (lidar measurements), aerosol optical depth (sun photometer) [All of the above sites currently house AERONET sun photometers, and three (Izaña, Barbados, Bermuda) also have lidar instruments].
- Size resolved aerosol chemistry and rainfall chemistry: Total iron (and Al, Mn, Ti, P, Ca, Si, Na, micronutrient and potentially toxic trace metals) and soluble iron (and Al, Mn, Ti, P, Ca, Si, Na, micronutrient and potentially toxic trace metals) – probably by more than one method, nitrate, sulfate, oxalate, other organic acids, black carbon, organic carbon, V, K, ammonium, organic N, organic P.
- Mineralogy: Clays, iron oxides (hematite, goethite, amorphous iron oxides)
- Aerosol Mass Spectrometry: mixing state of dust, nitrate, sulfate
- Deposition fluxes: Wet deposition and direct measurements of bulk or dry flux

c) *Dry deposition fluxes*

There is an urgent need to improve estimates of dry deposition fluxes of mineral matter to the ocean, both in terms of observational and modelling work. This field does not appear to have advanced significantly in the last ~30 years, and the use of inadequate and highly uncertain parameterizations of dry deposition velocity is commonplace. The GESAMP/SDS-WAS group is unaware of any workers currently making progress in this field.

d) *Impacts on marine biogeochemistry*

Natural dust inputs may affect primary productivity and nitrogen fixation in certain ocean regions. Experiments designed to demonstrate the impact of such events on marine ecosystems pose some significant challenges. In situ experiments will be logistically difficult, requiring access to the study site by a relatively large number of researchers, potentially for many weeks at a time. Thus a large research vessel and/or easy access to a well-equipped marine laboratory will be required.

The choice of study site will also be problematic. Areas which are frequently subject to dust inputs may already have sufficient supplies of dust-borne trace elements, and thus would not show a strong response to a given deposition event, whether natural or deliberately introduced. The response of areas with less frequent (and possibly weak) dust inputs may be dependent on seasonality in dust inputs and community composition. In some circumstances it may be desirable to study the first deposition of dust to waters after a prolonged absence of dust. Perhaps the most dramatic results might be expected from studying the deposition of dust to a region that very rarely receives dust. In practice such an experiment would be very difficult to plan and conduct for a natural dust event because we are not able to reliably predict individual dust outbreak events on relevant timescales, particularly with regard to the availability of research vessels. One potential solution to this problem would be to perform “deliberate dust release” experiments, of the type already conducted for meso-scale iron enrichment experiments in the remote ocean. Such experiments would also pose significant technical problems, but a preliminary scoping study carried out by the University of East Anglia indicated that none of these problems was insurmountable.

Experiments aimed at investigating the influence of dust on primary productivity would be conducted chiefly in HNLC areas (as have iron enrichment experiments), while studies of dust/nitrogen-fixation interactions would be carried out in tropical and sub-tropical waters. A summary of the atmospheric and marine measurements that might be made during such experiments is given in the table below. The marine measurements proposed recognize the central role of iron as a micronutrient in the oceans, but also highlights the need to study other dust components, particularly the other micronutrient trace elements (e.g. Zn, Co, Cu, Cd, Ni), whose behavior will become better known in the coming years as a result of the recently started international GEOTRACES Programme.

Atmospheric Measurements	Marine Measurements
Wet deposition and direct measurements of bulk or dry flux, aerosol and rainfall composition (total and soluble trace elements, inorganic and organic N and P, atmospheric N isotopes*	Dissolved Fe & Fe-binding ligands, nitrogen fixation rate*, marine N isotopes*, macronutrients, trace elements/micronutrients, photosynthetic efficiency, algal and bacterial productivity, carbon export, ocean physics

* indicates parameters of particular importance for nitrogen-fixation studies

Any such experiments would benefit from longer-term monitoring of atmospheric dust inputs to the study region (perhaps from nearby island monitoring sites), remote sensing of dust and ocean parameters, integrated modelling support, and ocean surveys in the study region conducted using robotic ocean gliders.

Sediment traps attached to deep-sea moorings at different depth levels are a good tool to observe changes in particle flux (lithogenic and biogenic particles) continuously. Factors controlling the particle transport in the ocean such as displacements by currents and biological processes (e.g., aggregation, disaggregation), which also affect trap efficiency, must be taken into account. At the least, the lithogenic flux in open ocean regions can be used as an estimate for aerosol deposition to the oceans. Long-term sediment trap study sites have been established at different oceanic sites, which are influenced by dust outbreaks (e.g. Kiel 276 at 33°N and 22°W, Tropical Eastern North Atlantic Time-Series Observatory at 17.59°N and 24.25°E, Bermuda Atlantic Time Series Study at 31.67°N and 64.17°W). Those study sites are often associated with atmospheric observatories. Ocean and atmospheric observatories together with satellite and modeled dust occurrence and deposition data will help to reveal and understand the biogeochemical response to dust input.

4. **References**

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E. Potential importance of volcanic emissions on marine biogeochemical cycles and clouds*Mitsuo Uematsu (GESAMP)***1. Introduction**

Large volcanic eruptions have been observed and their impacts have been reported on land and they have affected peoples' lives during the past several decades. Included are such eruptions as Mt. St. Helens (USA) in 1980, Pinatubo (The Philippines) in 1991, and Mt. Eyjafjallajökull (Iceland) in 2010. Volcanoes emit a number of gases (H_2O , CO_2 , H_2S , SO_2 , HCl , HF , H_2 , N_2 , Ar , CH_4 , CO , NH_3) and ash particles that contain Si, Al, Fe, Ca, and P, both through sporadic explosions and continuous eruptions. It is well known that those gases and particles affect the composition of the atmosphere and, through this, global climate. However, there is very little knowledge of their impact on the marine environment, although many volcanic activities have been reported in oceanic regions. In this brief report three case studies addressing different marine-related processes are introduced, and the importance of sporadic volcanic emission on biogeochemical cycles and climate, especially over the Pacific Ocean, are discussed.

2. Case 1: Supply of nitrogen compounds

The eruption of the Miyake-jima Volcano (34.08°N , 139.53°E) in the Izu Islands, Japan, 180 km south southwest of Tokyo, began on 8 July 2000. A substantial amount of NH_3 gas was found to be emitted from the Miyake-jima Volcano together with SO_2 gas, and geochemically significant quantities of aerosol particles composed of ammonium sulfate formed in that volcanic plume. Through the use of satellite images, the additional atmospheric deposition of ammonium sulfate to the ocean caused an increase of phytoplankton in the nutrient deficient region south of the Kuroshio Current. The emission of volcanic gases from Miyake-jima has likely been modifying marine air quality as well as the open ocean ecosystem over parts of the western North Pacific for the past several years (Uematsu et al., 2004).

3. Case 2: Supply of Iron

The horizontal distribution of dissolved iron in surface waters of the North Pacific Ocean have been investigated along with basic biogeochemical parameters between $40\text{--}49^\circ\text{N}$ and $160\text{--}175^\circ\text{E}$ in the western subarctic North Pacific during the July–August 2008. A total of 101 surface samples (depth about 1 meter) were collected using a towed fish and Teflon pumping system. Analysis of these samples produced high-resolution maps of dissolved iron, macronutrients and chlorophyll-a in this region. Dissolved iron in the surface waters was variable, ranging from 0.01 nM to 0.18 nM. Phytoplankton blooms ($\sim 2.2 \mu\text{g Chl a L}^{-1}$) were dominated by large centric diatoms, and they were observed in a low salinity (33.0–33.2) water mass at $41\text{--}42.5^\circ\text{N}$ along 160°E . Dissolved iron in the low salinity water ranged from 0.01–0.16 nM, with minimum values found where the chlorophyll-a concentration was highest. Another small phytoplankton bloom dominated by *prymnesiophytes* was observed near the southern boundary of a high nutrient/low chlorophyll (HNLC) region around 44.7°N along 160°E , where dissolved iron was in the 0.03–0.05 nM range. Although most of the surface water samples collected from the high nitrate (8–17 μM) subarctic gyre region showed low phytoplankton standing stocks (0.4–1.0 $\mu\text{g Chl a L}^{-1}$), a sharp increase in chlorophyll a concentration up to $2.4 \mu\text{g L}^{-1}$ was observed over the Emperor Seamount Chain ($48.6\text{--}48.8^\circ\text{N}$; $168\text{--}170^\circ\text{E}$). This phytoplankton community was primarily composed of pennate diatoms, *prymnesiophytes* and *cryptophytes*. Relatively high salinity values of the surface water over the seamount indicate that uplift of the iron-rich subsurface water stimulated phytoplankton growth over the seamount. However, surface dissolved iron concentrations were consistently low at 0.03–0.05 nM over the seamount, probably due to rapid uptake of the supplied iron by the plankton assemblage. On the other hand, atmospheric deposition of volcanic ash from Karymsky volcano, Kamchatka, Russia, was detected at 48.8°N ; 168°E during the cruise. The deposition occurred 4 days before the observation of high chlorophyll waters in the same region, and the surface chlorophyll-a concentration was $\sim 0.7 \mu\text{g L}^{-1}$ before the deposition event. Bottle incubation experiments conducted during the cruise confirmed that phytoplankton could increase their chlorophyll a biomass from $0.4 \mu\text{g L}^{-1}$ to $>2 \mu\text{g L}^{-1}$ within 3 days if sufficient iron ($\sim 2 \text{ nM}$) was added. These results suggest that iron released from volcanic ash could also play an important role in phytoplankton production in these HNLC waters (Takeda et al., 2010).

4. Case 3: Effect on marine clouds

Kilauea Volcano on Hawaii Island in the Hawaiian Islands experienced an active eruption from 19 March until the end of December 2008. The eruption released approximately 1.8×10^6 tons of SO_2 , which was oxidized to sulfate aerosol during transport to the northwest Pacific Ocean. The volcanic sulfate aerosol layer covered a large area ($\sim 6.5 \times 10^6 \text{ km}^2$) of the lower troposphere over the North Pacific for several months. The sulfate aerosol affected the

formation of cumulus water clouds by reducing the typical cloud droplet effective radius by ~25% and increasing the cloud fractional coverage over the ocean from 9.9% to 13.4% (over the region 170°E-160°W, 10°N-20°N). The affected cumulus clouds appeared whiter than normal and thus reflected more solar radiation. Consequently, satellite observations revealed an approximately 1% increase in albedo at the top of the atmosphere to the west of the Island of Hawaii (over the region 170°W-155°W, 18°N-20°N), which induced a ~ -5 W m⁻² change in the shortwave radiation budget. Modelled daily average incoming surface shortwave radiation for the same region was also diminished by ~ 5 W m⁻² and the sea surface cooled by ~ 0.1 K month⁻¹. This large impact of the Kilauea eruption may also have affected the oceanic environment (Eguchi *et al.*, 2011).

5. References

- Eguchi, K., I. Uno, K. Yumimoto, T. Takemura, T.Y. Nakajima, M. Uematsu, and Z. Liu, "Modulation of Cloud Droplets and Radiation over the North Pacific by Sulfate Aerosol Erupted from Mount Kilauea" SOLA, 2011, submitted.
- Takeda, S., A. Okubo, I. Tanita, H. Obata, T. Kodama, K. Suzuki B33J-04 "Observation of natural phytoplankton blooms in the western subarctic North Pacific: Is there relation to atmospheric iron supply?" AGU Fall Meeting, San Francisco, p 292, 2010.
- Uematsu, M., M. Toratani, M. Kajino, Y. Narita, Y. Senga, and T. Kimoto. "Enhancement of primary productivity in the western North Pacific caused by the eruption of the Miyake-jima Volcano" *Geophys. Res. Lett.*, 31, L06106, doi:10.1029/2003GL018790 (2004).

F. Policy considerations

Atmospheric mineral dust originates from very specific source areas and is then transported over long distances, influencing the climate and chemistry of the atmosphere on local, regional, and global scales. It has implications for human health, visibility, and climate. It also provides essential components for ocean fertility, primarily the micronutrient iron. Policy-makers must be aware of the importance of atmospheric mineral dust and its wide range of environmental impacts.

Continued support for research on mineral dust has multiple benefits ranging from improving short-term forecasting to improved understanding of the role of mineral dust in supplying nutrients to the world's oceans. Recently, supplying iron to iron-depleted regions was proposed as a form of *geo-engineering* to remove carbon dioxide from the atmosphere. While a discussion of the pros and cons of this approach is beyond the scope of this document, clearly an improved understanding of the role of mineral dust and related processes will inform a balanced decision-making.

Measurements on various times scales have suggested strong correlations of dust emissions, transport and deposition with climate change. Models have severe difficulties in reproducing these relationships, possibly due to anthropogenic activities unrelated to climate not being sufficiently included in these models. Therefore, despite reasonable performance under current conditions, the predictive capacity of models for future conditions is highly uncertain. Given the importance of dust in the earth system, including deposition to the oceans, it is one of the primary uncertainties in future climate change conditions.

The increased supply of dissolved phosphorus from atmospheric anthropogenic sources (through large-scale use in fertilizers) may also have a significant impact on ocean surface biogeochemistry. Model simulation studies for future scenarios are highly uncertain due to the extreme variability on the regional scale. We emphasize the need for the development of chemistry-driven atmospheric transport models and measurement parameters for improving our understanding of the impacts of the atmospheric deposition of dust/Fe/P to the ocean.

The lack of high quality, harmonized deposition measurements available for model verification is a serious issue. It is recommended to use the existing WMO GAW sites for extended measurements pertaining to dust deposition and the related ocean biological and physical parameters. Additional atmospheric sampling sites, especially in the Southern Hemisphere, are necessary. Therefore continuing long-term observations remains of highest priority, both for improving models and monitoring future changes.

Finally, institutional support for assessment activities, intercomparisons, and appropriate identification and documentation of models and measurements, remains a high priority. This is necessary to ensure an improved understanding of the role of dust on longer time scales.

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Agendas for and Attendees at each of the Three Meetings of the Working Group

FIRST MEETING, GESAMP WORKING GROUP 38

THE ATMOSPHERIC INPUT OF CHEMICALS TO THE OCEAN

**The University of Arizona, Tucson, Arizona, USA
(10-14 December 2008)**

Agenda

Wednesday, 10 December 2008

1830: Informal dinner for those who have arrived by this time - meet near the hotel check-in desk

Thursday, 11 December 2008 (Room location at the university)

0830-0900: Introductions and logistical information

0900-1030: Individual 5-10 minute presentations (not more than 4 slides) on priority issues and approaches that should be addressed by the group relative to one or more of the workshop goals outlined below

1030-1045: Coffee Break

1045-1215: Continuation of individual presentations

1215-1330: Lunch

1330-1530: Plenary discussion of the first 2 goals of the workshop outlined below

1530-1545: Coffee break

1545-1745: Plenary discussion of the last 3 goals of the workshop outlined below

1900: Group Dinner

Friday, 12 December 2008

0830-0930: Continuation of plenary discussions of workshop goals

0930-1030: Break up into 5 subgroups to address each goal in more detail.

1030-1100: Coffee Break

1100-1215: Continuation of sub-group meetings

1215-1330: Lunch

1330-1730: Continuation of sub-group meetings, with a coffee break when necessary

Evening free

Saturday, 13 December 2008

- 0830-1030: Plenary meeting, with reports from each sub-group
- 1030-1045: Coffee break
- 1045-1215: Sub-groups meet again
- 1215-1330: Lunch
- 1330-1730: Continuation of sub-group meetings, with a coffee break when necessary
- Evening: Possible group dinner

Sunday, 14 December 2008

- 0830-0930: Plenary session - final reports from sub-groups as to their activities between meetings
- 0930-1200: Discussion about the date and location of the next meeting as well as intersessional activities. For example, if it is believed that a detailed review (or reviews) is/are required, outline(s) should be drawn up and intersessional tasks assigned for the preparation of preliminary draft papers on critical issues that would be addressed by the review(s).
- 1200: Meeting adjourned

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Joseph M. Prospero
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Peking University

Natalie Mahowald
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SECOND MEETING, GESAMP WORKING GROUP 38

THE ATMOSPHERIC INPUT OF CHEMICALS TO THE OCEAN

**International Maritime Organization
4, Albert Embankment, London SE1 7SR, United Kingdom
(12-15 January 2010)**

Overall Goal: To complete the three papers being worked on by the Working Group such that by the end of the meeting they are essentially ready for submission to journals for publication.

Agenda

(Meeting in Committee Room 5 at IMO in plenary, with Committee Rooms 3 and 4 available for breakout sessions)

Tuesday, 12 January 2010

PLENARY SESSION

0830-0840: Brief introduction by Bob Duce and Peter Liss

0840-0850: Welcome remarks by Rene Coenen, IMO Technical Secretary for GESAMP

0850-0900: Introductory remarks by Dr Liisa Jalkanen, Chief, Atmospheric Environment Research Division, Research Department, World Meteorological Organization

0900-1045: Presentation and discussion of the draft of the paper The Shifting Importance of Limiting Nutrients in the Surface Oceans - led by Greg Okin

1045-1100: Coffee Break

1100-1300: Presentation and discussion of the draft of the paper SO₂, NO_x and their Impact on Ocean Acidification - led by Keith Hunter

1300-1400: Lunch

1400-1600: Presentation and discussion of the draft of the paper Atmospheric Organic Material and the Nutrients it Carries to the Ocean - led by Maria Kanakidou

1600-1615: Coffee break

1615-1800: Plenary discussion of the three papers - areas on which to focus in the individual group discussions

Evening Free

Wednesday, 13 January 2010

BREAKOUT SESSIONS

0900-1300: Three breakout sessions working in detail on the three papers - coffee break as appropriate

1300-1400: Lunch

1400-1600: Continuation of breakout sessions

1600-1630: Coffee Break

PLENARY SESSION

1630-1800: Plenary discussion of progress on the three papers

1900: Group dinner - location to be announced

Thursday, 14 January 2010

BREAKOUT SESSIONS

0900-1300: Three breakout sessions continue, working in detail on the three papers - coffee break as appropriate

1300-1400: Lunch

1400-1800: Continuation of breakout sessions, coffee break as appropriate

1900: Possible group dinner and entertainment - location to be announced

Friday, 15 January 2010

BREAKOUT SESSIONS

0900-1000: Wrap-up of the three papers in individual sessions

1000-1030: Coffee Break

PLENARY SESSION

1030-1130: Final presentation and discussion of the paper The Shifting Importance of Limiting Nutrients in the Surface Oceans - led by Greg Okin

1130-1230: Final presentation and discussion of the paper SO₂, NO_x and their Impact on Ocean Acidification - led by Keith Hunter

1230-1330: Lunch

1330-1430: Final presentation and discussion of the paper Atmospheric Organic Material and the Nutrients it Carries to the Ocean - led by Maria Kanakidou

1430-1600: Discussion of any future activities of the Working Group

1600: Close of the second meeting of GESAMP WG 38

Attendees at the Second Meeting

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Alex Baker
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Tim Bowmer
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Rene Coenen
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Robert Duce, Co-Chair
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Tong Zhu

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THIRD MEETING, GESAMP WORKING GROUP 38, JOINTLY WITH THE WMO SDS-WAS

THE ATMOSPHERIC INPUT OF CHEMICALS TO THE OCEAN

SDS-WAS/GESAMP Expert Workshop on Modelling and Observing the Impacts of Dust Transport and Deposition on Marine Productivity

Hotel Victoria, Sliema, Malta
(7-9 March 2011)

(Bob Duce, Peter Liss, and Michael Schulz, Co-Chairs)

Agenda

Monday, 7 March 2011

0830-0900: Workshop logistics, introductions and goals - Slobodan Nickovic (WMO) and Anton Micallef (U of Malta)

The workshop will address three primary topics outlined below. One individual from GESAMP and one from SDS-WAS have been asked to co-lead the discussions in each topic area. The goal will be to provide advice as to how impacts of dust transport on marine productivity via these topics can most profitably be addressed in the future activities of WMO and GESAMP. Particular attention should be paid not only to the scientific approaches that should be taken, but also advice that should be given to policymakers related to potential consequences on climate and the environment

0900-1030: **Topic 1** - Plenary discussion led by Frank Dentener (GESAMP) and Michael Schulz (SDS-WAS) on improving the quantitative estimates of the geographical distribution of the transport and deposition of mineral matter and its content to the ocean

1030-1050: Coffee break

1050-1230: Continuation of the plenary discussion of Topic-1

1230-1345: Lunch

1345-1530: Continuation of the plenary discussion of Topic 1

1530-1550: Coffee break

1550-1800: **Topic 2** - Plenary discussion led by Monmohan Sarin (GESAMP) and Slobodan Nickovic (SDS-WAS) on the development of case-studies of dust/Fe/P input to the ocean and the resultant marine response remote-sensing, in-situ observations, and ocean biogeochemical modelling

1800: Adjourn for dinner

1930-2130: GESAMP members reconvene for a discussion of the status of the three papers currently being produced for publication and what needs to be done to complete them - led by Peter Liss (for Keith Hunter, pH paper) Maria Kanakidou (Organic P,N, and C paper), and Greg Okin (cocktail paper)

Tuesday, 8 March 2011

0800-1030: Continuation of the plenary discussion of Topic 2

1030-1050: Coffee break

- 1050-1230: Continuation of the plenary discussion of Topic 2
- 1230-1345: Lunch
- 1345-1530: **Topic 3** - Plenary discussion led by Alex Baker (GESAMP) and Carlos Perez (SDS-WAS) on specifying test-bed regions for joint studies of the transport and deposition to the ocean of mineral matter (Central Atlantic; North Pacific; Indian Ocean; Mediterranean; others), utilizing SDS-WAS transport modelling
- 1530-1550: Coffee break
- 1550-1800: Continuation of the plenary discussion of Topic 3
- 1800: Adjourn
- 1900: Workshop dinner

Wednesday, 9 March 2011

- 0800-1100: Topic groups 1, 2, and 3 meet separately and develop their reports and conclusions/recommendations
- 1100-1120: Coffee break
- 1120-1230: Discussion led by Mitsuo Uematsu (GESAMP) on the potential importance of volcanic emissions on marine biogeochemical cycles
- 1230-1345: Lunch
- 1345-1545: Each Topic group presents its report and primary recommendations/conclusions in plenary
- 1545-1600: Coffee break
- 1600: End of Workshop

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ANNEX 3

List of Representative Papers that Address the Impact of Dust Deposition on Marine Biogeochemistry

Abbreviations:

AOD: aerosol optical depth

CCN: cloud condensation nuclei

DMS: Dimethyl sulfide

HNLC: high nitrate low chlorophyll

SIZ: sea-ice zone

SOA: South Atlantic Ocean/ SO: Southern Ocean

Note: References of relevance for ocean response, although not directly demonstrating the ocean response, are given in italics.

Authors	Title	Contents	Publication
O. Aumont L. Bopp M. Schulz	What does temporal variability in aeolian dust deposition contribute to sea-surface iron and chlorophyll distributions?	- global model of ocean biogeochemistry forced with daily fields of dust deposition to investigate impact of variability of dust deposition (1996-2001) - dust deposition explains a large part of the temporal variability of surface iron in the tropical regions and in part of the subarctic Pacific - while dust deposition is dominated by daily events, its impact on surface iron is maximal on interannual timescales - largest fluctuations of surface iron produced by dust occur in oligotrophic regions where phytoplankton growth is not primarily controlled by iron availability → variability of surface chlorophyll induced by aerosol iron is predicted to be very small everywhere	Geophysical Research Letters, Vol. 35, L07607; 2008 doi: 10.1029/2007GL031131
A.R. Baker P.L. Croot	Atmospheric and marine controls on aerosol iron solubility in seawater	- fraction of atmospheric deposited iron plays a keyrole for the productivity in many open ocean regions - basic idea and interactions of solubility of iron in seawater is presented - experimental methods for the determination of iron solubility is discussed	Marine Chemistry, Vol. 120, Issues 1-4, pp. 4-13; 2008 doi: 10.1016/j.marchem.2008.09.003
J.K.B. Bishop R.E. Davis J.T. Sherman	Robotic Observations of Dust Storm Enhancement of Carbon Biomass in the North Pacific	- investigations with two autonomous robotic profiling floats (subarctic North Pacific, 10 April 2001, 8 months) → records of carbon biomass variability from surface to 1000 meters below surface - marine biological response to dust event (passage of Gobi desert dust cloud) → near doubling of biomass in the mixed layer over a 2-week period → temporal evolution of particulate organic carbon enhancement and an increase in chlorophyll use efficiency ↔ natural iron fertilization by the dust	Science, Vol. 298, no. 5594, pp. 817-821; 2002 doi: 10.1126/science.1074961

N. Cassar M.L. Bender B.A. Barnett S. Fan W.J. Moxim H. Levy II B. Tilbrook	The Southern Ocean Biological Response to Aeolian Iron Deposition	- gross primary production and net community production (comparable to export production) are compared with model estimates of dissolved iron over large areas of the Southern Ocean → export production is proportional to modeled input of soluble iron in aerosols (fertilization due to addition of aerosol iron) - aerosol iron input particularly enhances gross primary production over the large area of the Southern Ocean downwind of dry continental areas → sequestration of carbon dioxide → may have been a major cause of the reduction of atmospheric CO₂ during the ice ages	Science, Vol. 317, no. 5841, pp. 1067-1070; 2007 doi: 10.1126/science.1144602
F. Chai M.-S. Jiang Y. Chao R.C. Dugdale F. Chavez R.T. Barber	Modelling responses of diatom productivity and biogenic silica export to iron enrichment in the equatorial Pacific Ocean	- Diatoms contribute to the initial increase of the total phytoplankton biomass due to iron enhancement, but decrease sharply after 10 days because of mesozooplankton grazing (grazing pressure prevents significant phytoplankton biomass accumulation) - increasing mesozooplankton grazing rate, the diatom increase due to iron addition stays at minimum level, but small phytoplankton tend to increase - larger size of the iron patch tends to produce a broader extent and longer-lasting phytoplankton blooms - modeled depth-time distribution of sinking biogenic silica (BSi) indicates that it would take more than 30 days after iron injection to detect any significant BSi export out of the euphotic zone	Global Biogeochemical Cycles, Vol. 21, GB3S90; 2007 doi: 10.1029/2006GB002804
S.C.Doney I. Lima R.A. Feely D.M. Glover K. Lindsay N. Mahowald J.K. Moore R. Wanninkhof	Mechanisms governing interannual variability in upper-ocean inorganic carbon system and air-sea CO ₂ fluxes: Physical climate and atmospheric dust	- presentation of a systematic global analysis of the magnitude and processes governing carbon system variability on subannual to decadal time-scales - mechanisms governing interannual variability in the upper-ocean carbon system and air-sea CO₂ flux differ with region (major regions: Southern Ocean, tropical Indo-Pacific, and Northern Hemisphere temperate and subpolar latitudes) - Ocean circulation is the dominant underlying factor driving biogeochemical variability over most of the ocean - Variations in atmospheric iron deposition downwind of dust source regions generate substantial variability in ocean export production and air-sea CO₂ flux in HNLC in the Southern Ocean, equatorial Pacific and subpolar North Pacific - reduced global dust deposition (beginning in the mid 1990s) generates increased air-sea CO₂ outgassing in the Southern Ocean	Deep-Sea Research II, 56, pp. 640-655; 2009 doi: 10.1016/j.dsr2.2008.12.006
R.A. Duce	The impact of atmospheric nitrogen, phosphorus, and iron species on marine biological productivity	- first attempt to evaluate the potential importance of atmospheric Fe, P, and N on marine biological productivity - compared modeled nutrient atmospheric deposition to upward nutrient fluxes via advection and diffusion in the Sargasso Sea and central Pacific gyre - general conclusion that in these areas atmospheric deposition is important for Fe, unimportant for P, and of intermediate importance for N	in <u>The Role of Air-Sea Exchange in Geochemical Cycling</u> , P. Buat-Menard, ed., Reidel, Dordrecht, 497-529 (1986)
D.J. Erickson III J.L. Hernandez P. Ginoux W.W. Gregg C. McClain	Atmospheric iron delivery and surface ocean biological activity in the Southern Ocean and Patagonian region	- iron is a limiting nutrient for biologic activity in many parts of the world ocean - correlation analysis to clarify the spatial response of chlorophyll concentrations to iron flux in oceanic biogeochemistry → several regions between 40°S and 60°S show correlations from 0.6 to 0.95 (significant at the 0.05 level), particularly the Patagonian region	Geophysical Research Letters, Vol. 30, no. 12, pp. 1609-1613; 2003 doi: 10.1029/2003GL017241

J. Christian		- surface chlorophyll and iron flux follow similar patterns (chlorophyll may be displaced to different latitudes due to meridional ocean transport) - dust deposition of Fe may occur in one region and then ocean circulation moves the fertilized water mass away from the area of highest Fe flux → non-co-location of high CHL and high dust flux	
S. Fan W.J. Moxim H. Levy II	Aeolian input of bioavailable iron to the ocean	- soluble Fe fraction increases with transport time from the source region and with the corresponding decrease in dust concentration → small Fe solubility and large dust deposition near the sources → large Fe solubility corresponding to smaller dust deposition distant from source regions - anthropogenic emissions of SO₂ and NO should have caused a significant increase in hematite dissolution and soluble Fe input to the North Atlantic and North Pacific Oceans since the industrial revolution - re-mineralization of organic matter in the mixed layer does not lead to significant iron recycling	Geophysical Research Letters, Vol. 33, L07602; 2006 doi: 10.1029/2005GL024852
A.J. Gabric R.A. Cropp G.H. McTainsh B.M. Johnston H. Butler B. Tilbrook M. Keywood	Australian dust storms in 2002–2003 and their impact on Southern Ocean biogeochemistry	- 2002–2003 most active dust storm seasons in the last 40 years in Australia → large dust plumes advected over the adjacent SO → large scale natural dust fertilization in the Australian sector of the SO ↔ importance of dust derived nutrients in the marine carbon cycle of the SO - dust storm events that were advected south in late October, early November and January had a clear affect on AOD values in the 40°–45°S and 45°–50°S bands → strong coherence between the optical characteristics of the SO atmosphere and dust loading - satellite and field data on surface chlorophyll indicate a significant biological response (unusually strong south of 50°S), associated with a strong CO₂ drawdown	Global Biogeochemical Cycles, Vol. 24, GB2005; 2010 doi:10.1029/2009GB003541
A.J. Gabric J.M. Shephard J.M. Knight G. Jones A.J. Trevena	Correlations between the satellite-derived seasonal cycles of phytoplankton biomass and aerosol optical depth in the Southern Ocean: Evidence for the influence of sea ice	- the production of DMS is related to atmospheric sulfate aerosols in the upper ocean (confirmed through shipboard measurements, global modelling) - correlation between surface chlorophyll (CHL) and AOD is analysed - mean CHL and AOD time series (1997–2004) are strongly coherent in the band between 50°S and 60°S (with absence in the SIZ south of 60°S) - interannual variability in CHL occurs in the SIZ related to the variability in sea-ice production during the previous winter - clear latitudinal difference in the cross correlation between CHL and AOD, with the AOD peak preceding the CHL bloom by up to 6 weeks in the SIZ → substantial trace gas emissions (aerosol precursors) are being produced over the SIZ in spring (October–December) as sea ice melts	Global Biogeochemical Cycles, Vol. 19, GB4018, pp. 10; 2005 doi: 10.1029/2005GB002546
A.J. Gabric R. Simó R.A. Cropp A.C. Hirst J. Dachs	Modelling estimates of the global emission of dimethylsulfide under enhanced greenhouse conditions	- presentation of a modelling analysis of the global DMS response to simulate climate change (marine food-web model, an atmosphere-ocean general circulation model (GCM), and an empirical dimethylsulfide (DMS) algorithm used) - predict the DMS seawater concentration and the DMS sea-to-air flux in 10° latitude bands from 70°N to 70°S under contemporary and enhanced greenhouse conditions (changes to nutrients not explicitly included) - strong regional variability in the simulated DMS flux response, with little change in the tropics and major increases predicted at high latitudes → future increases in stratification in	Global Biogeochemical Cycles, Vol. 18, GB2014; 2004 doi: 10.1029/2003GB002183

		the polar oceans will play a critical role in the DMS cycle and climate change - ecological data indicate that planktonic populations can respond extremely sensitively and quickly to ocean variability	
A.J. Gabric R. Cropp G.P. Ayers G. McTainsh R. Braddock	Coupling between cycles of phytoplankton biomass and aerosol optical depth as derived from SeaWiFS time series in the Subantarctic Southern Ocean	- the Subantarctic Southern Ocean is a high-nutrient low-chlorophyll region → primary production is limited by deep mixing and the availability of iron (can be transported by Australian dust, particularly during the austral spring and summer) - coupling between satellite-derived (SeaWiFS) aerosol optical thickness and chlorophyll concentration in the upper ocean at monthly, weekly and daily timescales → episodic atmospheric delivery of iron is stimulating phytoplankton growth	Geophysical Research Letters, Vol. 29, pp. 1112-1116; 2002 doi: 10.1029/2001GL013545
S. Gassó A.F. Stein	Does dust from Patagonia reach the sub-Antarctic Atlantic Ocean?	- difficult to determine Patagonian dust by satellite measurements (clear sky condition needed, no black background (sea-ice), dust emission short lived) → combined approach of different satellite detectors aided by an aerosol transport model - observations confirm that dust advects through the SW Atlantic Ocean and can reach the area around the biological rich sub-Antarctic Ocean within 30 hours of emission	Geophysical Research Letters, Vol. 34, L01801; 2007 doi: 10.1029/2006GL027693
H.R. Gordon	Atmospheric correction of ocean color imagery in the Earth Observing System era	- to realize an improvement in the retrieval of biologically important ocean parameters, e.g., the concentration of the photosynthetic pigment chlorophyll a, from this increased sensitivity, significantly better atmospheric correction than was applied to CZCS (coastal zone color scanner) is required - inclusion of the effects of multiple scattering, which are strongly dependent on the aerosol size distribution, concentration, and absorption properties are necessary - SeaWiFS, MODIS, and MISR algorithms are predentes - related issues such as the influence of aerosol vertical structure in the troposphere, polarization of the light field, sea surface roughness, and oceanic whitecaps on the sea surface are evaluated and plans for their inclusion in the algorithm are described	Journal of Geophysical Research, Vol. 102, no. D14, pp. 17,081-17,106; 1997 doi: 10.1029/96JD02443
C.O. Jo J.-Y. Lee K.-A. Park Y.H. Kim K.-R. Kim	Asian dust initiated early spring bloom in the northern East/ Japan Sea	- data for the TOMS aerosol index and SeaWiFS chlorophyll indicate that an early spring bloom in the northern East/Japan Sea can be initiated during the Asian dust event in association with precipitation (one month earlier than the bloom during non-dust event years) - normally initiated in this area as the surface mixed layer becomes shallower than critical depth, earlier bloom coincided with deepening of critical depth → supply of bio-available nutrients such as iron through wet deposition induces deepening of the critical depth, which results in an early initiation of the bloom	Geophysical Research Letters, Vol. 34, L05602; 2007 doi: 10.1029/2006GL027395
M.S. Johnson N. Meskhidze V.P. Kiliyanpilakkil S. Gassó	Understanding the transport of Patagonian dust and its influence on marine biological activity in the South Atlantic Ocean	- simulations (2009) indicate that the synoptic meteorological patterns of high and low pressure systems are largely accountable for dust transport trajectories over the SAO → South American dust plumes are elevated above the marine boundary layer → bulk concentration of mineral dust can quickly reach the HNLC waters of the SAO and Antarctica in ~3–4 days after emission from the source regions of Northern Patagonia - the effect of iron-laden mineral dust supply on surface ocean biomass is investigated by comparing predicted surface chlorophyll-a concentration ([Chl-a]) to remotely-sensed data - this study suggests that: (1) atmospheric fluxes of mineral dust from Patagonia are not likely to be the major source of bioavailable iron to ocean regions characterized by high primary productivity (2) Patagonian dust plumes could still influence background [Chl-a] in the South Atlantic	Atmospheric Chemistry and Physics, Vol. 11, pp. 2487-2502; 2011 doi: 10.5194/acp-11-2487-2011

		sector of the SO	
M.S. Johnson N. Meskhidze F. Solmon S. Gassó P.Y. Chuang D.M. Gaiero R.M. Yantosca S. Wu Y. Wang C. Carouge	Modelling dust and soluble iron deposition to the South Atlantic Ocean	- the global chemical transport model GEOS-Chem (+ dust-iron dissolution scheme) was used - dissolved iron fraction of mineral dust over the SAO was small (on average only accounting for 0.57% of total iron) ↔ low ambient concentrations of acidic trace gases available for mixing with dust plumes, not enough to overcome the alkalinity buffer of Patagonian dust and initiate considerable acid dissolution of mineral-iron - sol-Fe deposited to the SAO was largely controlled by the initial amount of sol-Fe at the source region → Patagonian dust should have a minor effect on biological productivity in the SAO	Journal of Geophysical Research, Vol. 115, D15202, pp. 13; 2010 doi: 10.1029/2009JD013311
Y. Iwamoto K. Yumimoto M. Toratani A. Tsuda K. Miura I. Uno M. Uematsu	Biogeochemical implications of increased mineral particle concentrations in surface waters of the northwestern North Pacific during an Asian dust event	- mineral dust aerosols were scavenged by sea fog, and their deposition to the ocean increased the particle concentration in surface seawater - a general relationship for the solubility of iron from dust particles led to an estimate of 20 to 330 $\mu\text{g m}^{-2}$ for the amount of bio-available iron delivered during the dust event (comparable to total dissolved iron added during an iron fertilization experiment in the northwestern North Pacific)	Geophysical Research Letters, Vol. 38, L01604, pp. 5; 2011 doi:10.1029/2010GL0459062011
A. Kumar M.M. Sarin	Aerosol iron solubility in a semi-arid region: Temporal trend and impact of anthropogenic sources	- 1-yr chemical data for the fine mode ($\text{PM}_{2.5}$) air-borne particulate matter in a semi-arid region of western India - inverse relationship between aerosol Fe and fractional Fe solubility (range: 0.06–16.1%) - increase in the solubility of iron, during wintertime, is marked by a uniform decrease in the mass fraction of mineral dust → advective transport of pollutants and Fe derived from combustion sources is one of the possible causes for the enhanced solubility of iron over a semi-arid region in western India	Tellus-B 62B, pp. 125-132 ; 2010 doi: 10.1111/j.1600-0889.2009.00448
A. Kumar M.M. Sarin	Atmospheric water-soluble constituents in fine and coarse aerosols from high-altitude site in western India: Long-range transport and seasonal variability	- one-year data set on water-soluble ionic species in $\text{PM}_{2.5}$ (fine) and $\text{PM}_{10-2.5}$ (coarse) aerosols from a high-altitude site in high-dust region of western India - the water-soluble ionic composition varied from 1.0 to 19.5 $\mu\text{g m}^{-3}$ in the fine mode and constitutes 50, 39 and 31% of the aerosol mass during winter, summer and monsoon respectively, with dominant contribution from SO_4^{2-}, NH_4^+ and HCO_3^- - twofold increase (relative to high-dust conditions in summer) in the abundances of nss-SO_4^{2-} and NH_4^+ and their co-variability during wintertime → dominance of anthropogenic sources and long-range transport of combustion products - the water-soluble ionic composition varied from 0.1 to 24.8 $\mu\text{g m}^{-3}$ in the coarse mode and constitutes 21% of the aerosol mass at annual average, with dominant contribution from Ca^{2+} and HCO_3^- - nss-$\text{SO}_4^{2-}/\text{NO}_3^-$ mass ratio extreme variable during winter - high abundance of nitrate in the coarse mode, during all seasons → association with mineral dust - near quantitative neutralization of acidic species (NO_3^- and SO_4^{2-}) by NH_4^+ in $\text{PM}_{2.5}$ and mineral dust in $\text{PM}_{10-2.5}$, representing a dominant atmospheric chemical transformation process occurring in the high-dust semi-arid region	Atmospheric Environment, Vol. 44, pp. 1245-1254; 2010 doi: 10.1016/j.atmosenv.2009.12.035

A. Kumar M.M. Sarin	Mineral aerosols from western India: Temporal variability of coarse and fine atmospheric dust and elemental characteristics	- $PM_{2.5}$ and PM_{10} samples collected in India (Jan–Dec-2007) - dominant and uniform contribution of mineral dust (60–80%) in the coarse mode relative to large temporal variability (11–75%) observed in the fine mode - coarse mass fraction: characteristic increase with the wind speed during summer months (Mar to Jun) - fine aerosol mass: temporal pattern associated with north-easterlies during wintertime (Oct–Feb) - relative enrichment of Fe in fine mode Fe/Al weight ratio during winter months due to the down-wind advective transport of combustion products derived from large-scale biomass burning, industrial and automobile emission sources (northern India) - relative enrichment of Ca and Mg in the coarse mode Ca/Al and Mg/Al weight ratios shows dominant contribution from carbonate minerals	Atmospheric Environment, Vol. 43, pp. 4005-4013; 2009 doi:10.1016/j.atmosenv.2009.05.014
A. Kumar M.M. Sarin A.K. Sudheer	Mineral and anthropogenic aerosols in Arabian Sea-atmospheric boundary layer: Sources and spatial variability	- chemical characteristics of aerosols in the Arabian Sea–atmospheric boundary layer (AABL) have been studied during the spring inter-monsoon (April and May 2006) based on the analysis of water-soluble constituents (Na^+, NH_4^+, K^+, Mg^{2+}, Ca^{2+}, Cl^-, NO_3^-, SO_4^{2-}), crustal elements (Al, Fe, Ca), and carbonaceous species (EC, OC) - the water-soluble species account for 35% of the total suspended particulate (TSP); with dominant contribution of Ca^{2+} and SO_4^{2-} followed by Na^+ and minor contributions of K^+, Mg^{2+}, Cl^-, and NO_3^- (22 days cruise covering a latitudinal transect from 9°N to 22°N) - the abundances of Ca^{2+} and SO_4^{2-} do not exhibit any noticeable latitudinal distribution pattern but the non-sea-salt (nss) component constitutes ~ 85–90% of their total concentration, indicating dominant transport from continental sources - a significant linear positive correlation among nss-Ca^{2+} and nss-SO_4^{2-}, and nss-Ca^{2+}/nss-SO_4^{2-} molar ratio averaging around 0.61 (range: 0.20–1.16) suggests uptake of anthropogenic SO_4^{2-} by mineral dust ($CaCO_3$) - on average, mineral dust accounts for 44% of the TSP (relatively high abundance occurring over the south Arabian Sea) and Fe/Al weight-ratio exhibit characteristic narrow range: 0.40–0.59 - the impact of carbonaceous species (EC and OC) is nowhere pronounced in the AABL	Atmospheric Environment, Vol. 42, pp. 5169-5181; 2008 doi: 10.1016/j.atmosenv.2008.03.004
A. Kumar M.M. Sarin B. Srinivas	Aerosol iron solubility over Bay of Bengal: Role of anthropogenic sources and chemical processing	- chemical composition (involving water-soluble inorganic constituents, crustal elements and carbonaceous species) of size-segregated aerosols (PM_{10} and $PM_{2.5}$), collected from the marine atmospheric boundary layer (MABL) of the Bay of Bengal (BoB) has been studied (27th Dec 08–28th Jan 09) → factors controlling the spatio-temporal variability in the fractional solubility of aerosol iron - significant linear relationship among fractional Fe solubility [WS-Fe (%)] and nss-SO_4^{2-} over N-BoB (characterized by higher abundance of aerosol iron (Fe_A) and SO_4^{2-}) provides evidence for the acid processing of mineral dust during atmospheric transport from Indo-Gangetic Plain - temporal shift in the winds exhibit enhanced fractional solubility of aerosol Fe associated with the lower abundance of dust and nss-SO_4^{2-} - observations suggest the dominance of combustion sources (biomass burning and fossil-fuel) in dictating the aerosol iron solubility over south Bay of Bengal → impact of the anthropogenic sources is also ascertained based on the covariance of WS-Fe with K^+ and	Marine Chemistry, Vol. 121, pp. 167-175; 2010 doi: 10.1016/j.marchem.2010.04.005

		<i>OC (organic carbon); as well as enrichment factor of heavy metals (Pb and Cd) associated with the outflow from south-east Asia</i>	
P.J. Lam J.K.B. Bishop	The continental margin is a key source of iron to the HNLC North Pacific Ocean	- FeP = tracer for the delivery of total Fe, also retains the memory of its source through its chemical speciation - calculations show that subsurface Fe delivery from the shelf is likely as important a source of bioavailable iron to the HNLC WSP gyre than dust - this subsurface supply of iron is shallow enough to be accessible to the surface through winter upwelling and vertical mixing (key source of bioavailable Fe to the HNLC North Pacific) - strong lateral advection of labile Mn and Fe from redox-mobilized labile sources at the continental shelf supplemented by a more variable source of Fe from the upper continental slope	Geophysical Research Letters, Vol. 35, L07608; 2008 doi: 10.1029/2008GL033294
P.J. Lam J.K.B. Bishop C.C. Henning M.A. Marcus G.A. Waychunas I.Y. Fung	Wintertime phytoplankton bloom in the subarctic Pacific supported by continental margin iron	- first evidence of the delivery and importance of iron from the continental margin and its arrival at OSP in the open HNLC subarctic Pacific - the entire continental shelf from California to the Aleutian Islands may be a source of additional iron in winter to the North Pacific → degree of iron limitation in the subarctic Pacific is not constant through the year and productivity can be boosted by different natural iron sources in different seasons - the wintertime delivery of bioavailable iron to the subarctic Pacific may address the paradox of why wintertime chlorophyll levels in subpolar HNLC regions are so high despite light limitation - the effects of shelf were found to be limited to coastal regions because the sedimentary iron was quickly scavenged out of the water column → the sensitivity of global ocean primary production to the shelf iron source was low - iron from shelf and continental sources is affecting the productivity of open ocean HNLC regions far (hundreds of kilometers) downstream	Global Biogeochemical Cycles, Vol. 20, GB1006; 2006 doi:10.1029/2005GB002557
C. Mahaffey R.G. Williams G.A. Wolff N. Mahowald W. Anderson M. Woodward	Biogeochemical signatures of nitrogen fixation in the eastern North Atlantic	- isotopic signal (low natural abundance of ¹⁵N relative to ¹⁴N) over the eastern North Atlantic (between 26°N and 32°N along 20°W) in spring 2000 leads together with phytopigment data and nitrate to phosphate ratios in the upper thermocline to the suggestion that nitrogen fixation provides a local dominant supply of nitrogen to phytoplankton over part of the eastern North Atlantic - biogeochemical proxies are coincident with enhanced atmospheric dust deposition → atmospheric dust events may spatially and temporally constrain the distribution of N₂ fixers	Geophysical Research Letters, Vol. 30, no. 6, 1300; 2003 doi: 10.1029/2002GL016542
N.M. Mahowald S. Kloster S. Engelstaedter J.K. Moore S. Mukhopadhyay J.R. McConnell S. Albani S.C. Doney A. Bhattacharya M.A.J. Curran	Observed 20 th century desert dust variability: impact on climate and biogeochemistry	- reconstruction of desert dust variability over the 20th century based on observational and model synthesis - most important: North African, East Asian and Middle East/Central Asian sources - the results suggest that desert dust roughly doubled over the 20th century over much, but not all the globe - largest estimated differences: between the dusty 1980–1989 period compared to the relatively dust-free 1955–1964 period - including desert dust fluctuations in climate model simulations improves our ability to simulate decadal scale variability in global surface temperature, regional changes in temperature and precipitation and possibly explains the residual global carbon flux	Atmospheric Chemistry and Physics, Vol. 10, pp. 10875–10893; 2010 doi: 10.5194/acp-10-10875-2010

M.G. Flanner F.M. Hoffman D.M. Lawrence K. Lindsay P.A. Mayewski J. Neff D. Rothenberg E. Thomas P.E. Thornton C.S. Zender		<i>unexplained by other mechanisms</i>	
N. Mahowald K. Lindsay D. Rothenberg S.C. Doney J.K. Moore P. Thornton J.T. Randerson C.D. Jones	<i>Desert dust and anthropogenic aerosol interactions in the Community Climate System Model coupled-carbon-climate model</i>	- the globally averaged climate and carbon is not significantly perturbed - the CCSM3.1 model has a slightly negative sensitivity to climate (i.e., more climate change means more carbon is taken up), due partly to the N-limitation in the land model, and partly due to a slow uptake by the oceans - the impact of aerosols onto the coupled-climate-carbon cycle may be largely explained by the globally averaged cooling from the aerosols, and is proportional to the climate impact on the carbon cycle - there are globally significant changes in carbon which are likely to be due to changes in regional climate driven by aerosols, or by changes in diffuse and direct radiation - inclusion of realistic desert dust cycling does significantly impact the ocean biogeochemistry in our simulations, in terms of the nitrogen fixation and the ocean productivity - having interactive dust and anthropogenic aerosols is as important or more important as changes in carbon dioxide and the resulting climate changes to the nitrogen cycle and productivity in our model - many changes to ocean biogeochemistry seem to occur due to physical forcing of climate by aerosols instead of purely from the addition of iron	<i>Biogeosciences, Vol. 8, pp. 387–414; 2011</i> doi: 10.5194/bg-8-387-2011
E. Marañón A. Fernández B. Mouríño-Carballido S. Martínez-García E. Teira P. Cermeño P. Chouciño M. Huete-Ortega E. Fernández A. Calvo-Díaz X.A.G. Morán A. Bode E. Moreno-Ostos M.M. Varela	<i>Degree of oligotrophy controls the response of microbial plankton to Saharan dust</i>	- oligotrophy: lack of nutrients - different groups of phytoplankton and bacterioplankton responded differently to Saharan dust addition, although bulk abundance and biomass tended to remain unchanged - the relative increase in bacterial production, which was the dominant response to dust addition in ultraoligotrophic environments, became larger with increasing oligotrophy. In contrast, primary production, which was stimulated only in the least oligotrophic waters, became less responsive to dust as the ecosystem's degree of oligotrophy increased → given the divergent consequences of a predominantly bacterial vs. phytoplanktonic response, dust inputs can, depending on the ecosystem's degree of oligotrophy, stimulate or weaken biological CO₂ drawdown	<i>Limnology and Oceanography, Vol. 55(6), pp. 2339–2352; 2010</i> doi: 10.4319/lo.2010.55.6.2339

M.D. Patey E.P. Achterberg			
N. Meskhidze W.L. Chameides A. Nenes	Dust and pollution: A recipe for enhanced ocean fertilization?	- Fe solubilization in deliquesced mineral dust aerosols emanating from East Asia during the springtime outflow conditions is investigated with a Lagrangian box model of the gas and aqueous-phase chemistry (simulates scavenging, chemical reactions and dissolution of Fe-III oxides due to acid mobilization) - SO₂ pollutant emissions are a potential source of acidity to advecting dust from East Asia - only plumes with relatively high initial SO₂-to-dust ratios are capable of delivering significant amounts of bioavailable Fe to the NPO - large dust advection episodes should have insignificant dissolved iron fraction (DIF) as the amount of SO₂ required to acidify such dust plumes is about an order of magnitude higher than what can typically be entrained in the plume during its advection - smaller dust plumes will generally have higher DIFs because they require lower amounts of SO₂ and, even if such small plumes may not cause algae blooms, they could still be important sources of dissolved Fe to the NPO → future changes in SO₂-pollutant emissions from East Asia may affect the productivity of the NPO	Journal of Geophysical Research, Vol. 110, D03301; 2005 doi:10.1029/2004JD005082
N. Meskhidze A. Nenes W.L. Chameides C. Luo N. Mahowald	Atlantic Southern Ocean productivity: Fertilization from above or below?	- two sources of Fe for the surface waters of the SO have been proposed: (1) oceanic input (upwelling of nutrient-rich water, lateral flows from continental margins) (2) atmospheric input - upwelling of nutrient-rich water is the predominant source of bioavailable Fe in the surface waters of the south Atlantic Ocean - acidification of aeolian dust may be required to solubilize the large fraction of mineral-iron and make it bioavailable	Global Biogeochemical Cycles, Vol. 21, GB2006; 2007 doi:10.1029/2006GB002711
J.K. Moore O. Braucher	Sedimentary and mineral dust sources of dissolved iron to the world ocean	- fluxes from continental margins and mineral dust deposition are key sources of dissolved iron to the oceans ↔ primary production, biological carbon export and nitrogen fixation (global scale) - calculation of the relative importance of dust deposition vs. sedimentation (on an annual basis)	Biogeosciences, Vol. 5, pp. 631–656; 2008 doi: 10.5194/bg-5-631-2008
A. Nenes M.D. Krom N. Mihalopoulos P. Van Cappellen Z. Shi A. Bougiatioti P. Zampas B. Herut	Atmospheric acidification of mineral aerosols: a source of bioavailable phosphorus for the oceans	- deposition of atmospheric aerosols provides the major external source of phosphorus to surface waters ↔ primary productivity - but only a fraction of deposited aerosol phosphorus is watersoluble and available for uptake by phytoplankton - atmospheric acidification of aerosols is a prime mechanism producing soluble phosphorus from soil-derived minerals (expected where polluted and dust-laden air masses mix) → anthropogenic and natural acidic gas emissions may be a key regulator of ocean biogeochemistry	Atmospheric Chemistry and Physics Discussion, Vol. 11, pp. 6163-6185 ; 2011 doi: 10.5194/acpd-11-6163-2011
P. Parekh M.J. Follows E. Boyle	Modelling the global ocean iron cycle	- simplest model representing a net scavenging of iron from the water column, and not attempting to explicitly represent the detailed processes, if the lifetime of dissolved iron with respect to scavenging is of the order of 100 years; broadly consistent with the observed data - a more detailed model, including rapid scavenging and complexation with an organic ligand, of uniform total concentration can also fit the data over a range of parameter values - based on this model it is argued, that a weaker ligand and greater total ligand concentration	Global Biogeochemical Cycles, Vol. 18, GB1002; 2004 doi:10.1029/2003GB002061

		<i>are more appropriate choices</i> - strong contrast between the scavenging-based models, in which the deep iron concentration and upwelling iron supply to the surface SO increase in concert with enhanced aeolian supply → phosphate can be completely drawn down - in the case where deep iron concentrations are controlled by complexation with an organic ligand, the drawdown of phosphate asymptotes toward a non-zero value which reflects the upper limit of deep dissolved iron imposed by the available ligand	
L. Patara N. Pinardi C. Corselli E. Malinverno M. Tonani R. Santoleri S. Masina	Particle fluxes in the deep Eastern Mediterranean basins: the role of ocean vertical velocities	- the relationship between deep sedimentary fluxes and ocean current vertical velocities in an offshore area of the Ionian Sea (deepest basin of the Eastern Mediterranean Sea) is analysed (1999-May 2001) - tight coupling is observed between the upper and deep traps and the estimated particle sinking rates are more than 200mday^{-1} → direct effect of downward velocities in determining high sedimentation rates is excluded but upward velocities in the subsurface layers of the water column are positively correlated with deep particle fluxes → upwelling would produce an increase in upper ocean nutrient levels (stimulating primary production and grazing) a few weeks before an enhanced vertical flux is found in the sediment traps - tight coupling between surface and deep layers through particle aggregation mechanisms → fast sinking rates of organic material in the deep ocean are connected to both lithogenic and biological aggregation mechanisms that transfer particles rapidly in the deep water column - two emerging fast sinking mechanisms have been captured: 1. Pulses of primary production, triggered by upward current vertical velocities, followed by grazing and macrozooplankton-related biogenic flux that rapidly conveys the material in the deep ocean 2. Large Saharan dust events that fertilize the upper ocean and possibly contribute to aggregation of organic material, thus producing high sedimentation fluxes	Biogeosciences, Vol. 6, pp. 333-348; 2009 doi: 10.5194/bg-6-333-2009
A.G. Ramos A. Martel G.A. Codd E. Soler J. Coca A. Redondo L.F. Morrison J.S. Metcalf A. Ojeda S. Suárez M. Petit	Bloom of the marine diazotrophic cyanobacterium <i>Trichodesmium erythraeum</i> in the Northwest African Upwelling	- A <i>T. erythraeum</i> bloom such as that observed in August 2004 in the NW African Upwelling does not appear to have been recorded for the area previously → development due to the exceptionally warm weather and/or to the massive dust storms from the Sahara Desert observed in the NE Atlantic in August 2004	Marine Ecology Progress Series, Vol. 301, pp. 303-305; 2005 doi: 10.3354/meps301303
N. Rastogi M.M. Sarin	<i>Chemistry of aerosols over a semi-arid region: Evidence for acid neutralization by mineral</i>	- evidence for quantitative neutralization of acidic constituents by mineral aerosols - ubiquitous alkaline-nature of rainfall events over this high dust region further attests to chemical data → regional-scale atmospheric transformation processes suggest the over estimation of negative radiative forcing (climate cooling) due to sulphate aerosols in the	Geophysical Research Letters, Vol. 33, L23815 GL027708; 2006 doi: 10.1029/2006GL027708

	<i>dust</i>	<i>global climate models</i>	
M.M. Sarin	Atmospheric dry deposition of N, P and Fe to the tropical Bay of Bengal	- N, P, Fe and their dry-deposition fluxes show significant spatio-temporal variability over north and south Bay of Bengal (N-BoB & S-BoB) - the aerosol N_{inorg} (Av. 185 nmol m^{-3}) is dominated by NH_4^+ (Av. 170 nmol m^{-3}) $\rightarrow$ aerosol-NH_4^+ concentration over Bay of Bengal has increased by a factor of three over the past one decade - the water-soluble organic nitrogen (N_{org}) accounts for no more than 15% of the total nitrogen ($N_{Tot} = N_{inorg} + N_{org}$) and occurs mainly in the fine mode ($PM_{2.5}$) - the wet-deposition fluxes of N, P and Fe are not significant during the late NE-monsoon (Jan-March) when continental outflow dominates the widespread dispersal of pollutants over Bay of Bengal	unpublished, in progress
M.M. Sarin	Impact of Anthropogenic Sources on Aerosol Iron Solubility: Comparative Study from Tropical Bay of Bengal and Arabian Sea	- characteristic differences in the nature of mineral dust and chemical processing of alluvial dust by atmospheric acidic constituents (H_2SO_4, HNO_3) enhances the fractional solubility of Fe $\rightarrow$ comparison of the aerosol-Fe over Bay of Bengal and Arabian Sea - furthermore impact of biomass and fossil-fuel combustion sources $\rightarrow$ higher solubility	unpublished, in progress
F. Solmon P.Y. Chuang N. Meskhidze Y. Chen	Acidic processing of mineral dust iron by anthropogenic compounds over the north Pacific Ocean	- Atmospheric processing of mineral aerosol by anthropogenic pollutants may be an important process by which insoluble iron can be transformed into soluble forms (= available to oceanic biota) - production of soluble iron varies temporally and regionally depending on pollution-to-dust ratio (due to strong buffering by calcite) - ~30% to 70% of particulate soluble iron over the North Pacific Ocean basin can be attributed to atmospheric processing (especially chemical processing) - sensitivity tests suggest that doubling SO_2 emissions can induce a significant increase (13% on average, up to 40% during specific events) in dissolved iron production and deposition to the remote Pacific - half of the primary productivity induced by iron deposition in a north Pacific high-nutrient low-chlorophyll region is estimated to be due to soluble iron derived from anthropogenic chemical processing of Asian aerosol	Journal of Geophysical Research, Vol. 114, D02305; 2009 doi:10.1029/2008JD010417
A. Tagliabue L. Bopp O. Aumont	Ocean biogeochemistry exhibits contrasting responses to a large scale reduction in dust deposition	- despite enforcing a climatically realistic dramatic reduction in the ocean deposition of aerosol Fe, we find that global NPP and FCO_2 only decline by around 3% $\leftrightarrow$ spatial redistribution of NPP that accompanies a decline in aeolian Fe input, as well as the lesser importance of aeolian Fe sources relative to continental shelf supply in the Pelagic Integration Scheme for Carbon and Ecosystem studies - dust deposition plays locally a role in sustaining diatom biomass in the ASO and could therefore be important in controlling the relative utilization of NO_3 and $Si(OH)_4$ and the associated marine food web; concomitant declines in denitrification stabilize the ocean DIN inventory (especially in the Pacific Ocean) and the excess NO_3 that arises from reduced bacterial consumption can act as a negative feedback on N_2 fixation - the denitrification- N_2 fixation feedback is controlled by changes in nutrients and NPP/carbon export, and its efficiency depends on the degree and timescales of deep-water ventilation above denitrification sites $\leftrightarrow$ compensating for any dust mediated decline	Biogeosciences, Vol. 5, pp. 11-24; 2008 doi: 10.5194/bg-5-11-2008

		- change in air-sea CO ₂ exchange between 1860 and 2100 is predominantly controlled by the change in atmospheric pCO ₂ and the decline in dust deposition reduces cumulative uptake by only 4%	
C. Theodosi Z. Markaki N. Mihalopoulos	Iron speciation, solubility and temporal variability in wet and dry deposition in the Eastern Mediterranean	- Iron solubility ranged from 27.2% for pH between 4 and 5 (polluted rainwater) to 0.5% for pH close to 8 (Sahara dust episodes), indicating that Fe solubility, and therefore Fe bioavailability to ecosystems, is enhanced in the presence of acidic species - Dissolved Reactive Iron (DSRFe) levels deposited in the Eastern Mediterranean Sea were sufficient to account for the dissolved iron levels in seawater → dissolved iron in the Mediterranean Sea could be exclusively attributed to atmospheric deposition - during summer and autumn less than 5% of the deposited dissolved Fe is required for phytoplankton growth	Marine Chemistry, Vol. 120, pp. 100-107; 2010 doi: 10.1016/j.marchem.2008.05.004
C. Theodosi Z. Markaki A. Tselepidis N. Mihalopoulos	The significance of atmospheric inputs of soluble and particulate major and trace metals to the eastern Mediterranean seawater	- V, Cr, Fe and Pb were mainly associated with the particulate form (64–98%), whilst for Mn, Zn, Cu and Cd the soluble fraction represents 60–70% of the total input → significance of atmospheric inputs to the biogeochemical cycling of trace elements - the solubility of all studied metals was found to decrease with increasing pH values and increasing dust mass - Cr, Mn and Cu fluxes were higher during the dry season compared to those measured during the wet season (other metals: opposite trend; Fe and Zn are removed almost equally by wet and dry deposition)	Marine Chemistry, Vol. 120, pp. 154-163; 2010 doi: 10.1016/j.marchem.2010.02.003
R. Young K. Carder P. Betzer D. Costello R. Duce J. Ditullio N. Tindale E. Laws M. Uematsu J. Merrill R. Feely	Atmospheric iron inputs and primary productivity: phytoplankton responses in the North Pacific	- major pulses of dust from Asia was followed by major increases in primary production → chemical analyses of the atmospheric particles showed that they were iron-rich (10-15%) and, further, that if only a small proportion (e.g. 10%) of this iron dissolved in the euphotic zone - at all depths, systematic decreases in production followed the initial surge in production, indicating that the phytoplankton may have evolved from being iron-limited to being nitrogen-limited - mineral particles with settling velocities equivalent to those of 14 to 18-μm-diameter spherical quartz particles were the most likely source for the iron stimulating the increases in primary production	Global Biogeochemical Cycles, Vol. 5, pp. 119-134; 1991 doi: 10.1029/91GB00927
W. Yuan J. Zhang	High correlations between Asian dust events and biological productivity in the western North Pacific	- investigation of dust events at 11 meteorological stations in China and sediment-trap fluxes at KNOT (the Kyodo North Pacific Ocean Time-series station) (12.1997-04.2000) - Al flux has significant correlations (0.66–0.78) with dust events at a water depth of 924 m → Badain Juran Desert region is a primary source of eolian dust to the western North Pacific - high correlations between the dust events and opal flux, and PD (pennate diatoms) → dust events stimulate biological productivity, providing nutrients via processes such as particle floating, adsorption and coprecipitation - evident correlation between opal flux at 924 m and GHA (geopotential height anomalies) at 850 hPa level with about a 10-day time lag → atmospheric cyclone activities might also contribute to ocean productivity	Geophysical Research Letters, Vol. 33, L07603; 2006 doi: 10.1029/2005GL025174

Acronyms and Abbreviations

ACE-ASIA	Asian Pacific Regional Aerosols Characterization Experiment
AENET	Acid Deposition Monitoring Network in East Asia
AEROCE	AIR/Ocean Experiment
AeroCom	Aerosol Comparisons between Observations and Models
AERONET	AErosol RObotic NETwork
AMMA	African Monsoon Multidisciplinary Analyses
AOD	Aerosol Optical Depth
BIOS	Bermuda Institute of Ocean Sciences
CALIOP	Cloud-Aerosol Lidar with Orthogonal Polarisation
CDOM	Colored Dissolved Organic Matter
CF-compliant netCDF -	Climate and Forecast (CF) Metadata Convention for Network Common Data Form
DIC	Dissolved Inorganic Carbon
DMS	DiMethyl Sulfide
DON	Dissolved Organic Nitrogen
DOP	Dissolved Organic Phosphorus
Acronyms	
EAENET	Acid Deposition Monitoring Network in East Asia
EBAS	Data base system operated by NILU/Kjeller/Norway to archive ground-based in-situ observations
EMEP	European Monitoring and Evaluation Programme
EUSAAR/ACTRIS-	EUropean Supersites for Atmospheric Aerosol Research / Aerosols, Clouds and Trace gases Research InfraStructure Network
GAW	Global Atmosphere Watch
GEOTRACES	An international research programme on trace elements in the ocean
GESAMP	Group of Experts on the Scientific Aspects of Marine Environmental Protection
HNLC	High Nutrient/Low Chlorophyll
ICAP	International Cooperative for Aerosol Prediction
ICSU	International Council for Science
IGBP	International Geosphere Biosphere Programme
IMO	International Maritime Organization
IN	Inorganic Nitrogen
INDOEX	INDian Ocean Experiment
LIDAR	LIght Detection And Ranging
MODIS	MODerate resolution Imaging Spectrometer
MSA	Methane Sulfonic Acid
MSG-DSAF	Meteosat Second Generation Dust Source Activation Frequency
NADP	National Atmospheric Deposition Programme (US)
NASA	National Aeronautics and Space Administration (US)
NMOC	Non-Methane Organic Carbon
NODC	(National Oceanographic Data Center (US)
NPP	Net Primary Productivity
OA	Ocean acidification
OC	Organic Carbon
ON	Organic Nitrogen
OP	Organic Phosphorus
ORSTOM	Office de la Recherche Scientifique et Technique d'Outre-Mer (France)
PAR	Photosynthetically Active Radiation
PM ₁₀	Particulate Matter less than 10 micrometers in diameter
PM _{2.5}	Particulate Matter less than 2.5 micrometers in diameter
POPs	Persistent Organic Pollutants
SCOR	Scientific Committee for Oceanic Research
SDS	Sand and Dust Storm
SDS-WAS	Sand and Dust Storm Warning Advisory and Assessment System

SEAREX	SEa/AiR Experiment
SIDA	Swedish International Development Agency
SOLA	Scientific Online Letters of the Atmosphere, Meteorological Society of Japan
SOLAS	Surface Ocean Lower Atmosphere Study
TSP	Total Soluble Phosphorus or Total Suspended Particulates
UCSD	University of California San Diego
UNEP	United Nations Environment Programme
UNESCO	United Nations Educational, Scientific, and Cultural Organization
WG	Working Group
WMO	World Meteorological Organization
WWRP	World Weather Research Programme

GESAMP REPORTS AND STUDIES

The following reports and studies have been published so far. They are available from the GESAMP website:
www.gesamp.org

1. Report of the seventh session, London, 24-30 April 1975. (1975). Rep. Stud. GESAMP, (1):pag.var. Available also in French, Spanish and Russian
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