



GESAMP

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

THE CHANGING ACIDITY OF THE GLOBAL ATMOSPHERE AND OCEAN AND ITS IMPACT ON AIR/SEA CHEMICAL EXCHANGE

GESAMP WORKING GROUP 38



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EXECUTIVE SUMMARY

Introduction

Human activity since the Industrial Revolution has resulted in profound socioeconomic changes for the population of the world. These changes are in turn driving major changes in many key Earth system parameters which profoundly affect the habitability of planet Earth. These drivers of change are accelerating as society continues to grow and use more energy for its needs — a process that has been characterized as the “great acceleration” (Steffen et al., 2015). These changes drive climate change, but also many other changes in the Earth system. They involve multiple drivers, and all have synergistic interactions with one another. The graphs illustrating the great acceleration by Steffen et al. (2015) show all the indicators considered increasing exponentially with time. However, the future of society and planet Earth does not have to involve a continuation of this trend, and indeed the proposed transition to “zero carbon” to regulate climate change requires a reversal of this exponential growth. This report concerns one process still subject to exponential growth (CO₂ emissions and resulting ocean acidification) and another where societal action has produced a reversal of the exponential trend (SO₂ and NO_x emissions from fossil fuel combustion and the resultant acidification of aerosols and rainfall), and we consider the response of components of the Earth system to these changes. This kind of analysis is important to identify the complex responses within the Earth system which arise from interconnections between these drivers of change and the resulting multiple biogeochemical responses to these drivers.

Since the Industrial Revolution, atmospheric CO₂ concentrations have increased to levels unprecedented in human history and have driven ocean acidification. Ocean pH (a logarithmic measure of ocean acidity) has decreased by 0.1 units and is projected to decrease by 0.3 units by the end of this century (Hopkins et al., 2020b). Marine ecosystems have evolved in a remarkably constant pH environment, so this acidification is predicted to have serious ecological consequences. The acidity of the atmosphere has similarly increased since industrial times, largely due to the release of SO₂ and NO_x as a result of fossil fuel combustion, offset in part by NH₃ emissions from agriculture, which partially neutralize the acidity. This acidification

has resulted in acid rain becoming a global phenomenon. However, controls on emissions of SO₂ and NO_x over the last few decades, alongside largely unconstrained emissions of NH₃, have led to a reversal of the acidification and a reduction of the extent of acid rain, and this is projected to continue (Baker et al., 2021). These contrasting trends in ocean and atmospheric acidity present interesting and potentially interlinked drivers of change in ocean biogeochemistry, as well as providing evidence of the ability of society to respond to scientific evidence of environmental impacts with successful emission control strategies. These trends provided the scientific background to this initiative by the Working Group on The Atmospheric Input of Chemicals to the Ocean (WG 38) of the Joint Group of Experts on the Scientific Aspects of Marine Environmental Protection (GESAMP) to investigate the impacts of these changes on some key aspects of ocean biogeochemistry associated with exchange across the air–sea interface. Specifically, WG 38 set out to investigate:

- How the changing ocean acidity might affect the emission of key climate-regulating gases from the ocean to the atmosphere;
- How the changing acidity in the atmosphere might affect the deposition of key nutrients delivered to the ocean through the atmosphere and the resultant impacts of this on ocean biogeochemistry.

Since these two challenges are interrelated and are both dependent on acid–base-driven environmental processes, it was decided to hold a single meeting involving two groups of experts meeting in parallel workshops to address each challenge but also allow the two groups to interact with each other. The joint meeting was held at the University of East Anglia in Norwich, United Kingdom of Great Britain and Northern Ireland, from 27 February through 2 March 2017. The scientists invited to participate in the workshops were selected to provide a diverse range of relevant expertise and experience. The workshops involved presentations by experts and extensive subsequent discussions. Six peer-reviewed publications have arisen from the workshops, and these are summarized in section 2 of this report. In this executive summary, we draw together and synthesize the results reported in these papers.

The effect of changing ocean acidity on the emission of key climate-regulating gases from the ocean to the atmosphere

The ocean is a major source of trace gases formed via biological processes and released to the atmosphere. In some cases, these trace gases are greenhouse gases in their own right (for example, N_2O); in other cases, such as dimethyl sulfide (DMS), they are released as gases and converted in the atmosphere into sulfate aerosols, which then directly influence climate. In the case of a final group of low molecular weight organohalogen and volatile organic hydrocarbon gases, reactions of these gases in the atmosphere yield radicals that affect atmospheric chemistry, and particularly ozone chemistry and climate. All these gases arise from microbial processes involving phytoplankton along with the rest of the microbial plankton community. While the biochemical processes involved are now better understood, these production processes and their cellular intensity are often very species-dependent, making it challenging to generalize about the fluxes in order to establish a global-scale estimate of their significance.

The WG 38 team reviewed how these trace gas production processes and magnitudes may be altered by ocean acidification, based on published experiments (Hopkins et al., 2020b). This review focused particularly on experiments that included not only a single phytoplankton species which produces the relevant gas, but also the wider plankton community which subsequently processes the gases before their release to the atmosphere. Such community-scale studies can be achieved using techniques such as enclosing and manipulating relatively large water samples with their associated plankton ecosystem.

The WG 38 review concludes that ocean acidification does have the potential to produce substantial changes in these trace gas fluxes, at a scale that could affect the wider Earth system, and modelling suggests that the scale of impact could be climatically important. This may be particularly the case in some key regions such as the polar regions, where ocean acidification is particularly rapid, and in upwelling regions, where sea-to-air fluxes of these gases may be particularly large. In the case of nitrogen gases such as N_2O , the mechanism by which ocean acidification affects the physiological process is, at least in part, driven by the fundamental physico-chemical impact of acidification on the pH-sensitive speciation of $\text{NH}_3/\text{NH}_4^+$ in seawater, and this means that acidification tends to result in a reduction of formation of N_2O . In the case of

the other trace gases, such as DMS and halogenated gases, the various published experiments conducted by the community have produced a wide range of results; in some experiments acidification enhanced the trace gas production rates, in others it reduced them, and in yet others it had little effect on them. This wide range of responses reflects the reality of different plankton communities responding differently, and hence makes it difficult to arrive at simple statements of the likely global-scale consequences. However, the experiments do suggest that the impacts of acidification may be sufficiently large that further experimental studies are needed, and these are recommended by the group. A particular issue recognized in the review is that ocean acidification will not operate as a single stressor on the plankton community, but rather will operate alongside other global change drivers, particularly increasing temperature. Developing experiments to understand the community responses to these multiple stressors is challenging but must be a priority.

A separate publication from the workshop (Kim et al., 2018) reviewed the experimental evidence regarding the impacts of ocean acidification on the production and composition of particulate and dissolved organic carbon by plankton communities. Changes in the amounts or composition of this biologically-produced carbon have the potential to profoundly alter ocean biogeochemical cycling. Although limited, the experimental evidence to date does not suggest such changes are likely. Notably, the C/N ratio of particulate organic matter produced during the experiments remained rather constant and similar to the Redfield ratio in all the experiments. This provides increased confidence in the current modelling approaches to predicting the responses of the ocean plankton community and wider ocean biogeochemistry to ocean acidification, at least in terms of the composition of organic matter.

The effects of changing acidity in the atmosphere on the deposition of key nutrients delivered to the ocean through the atmosphere and the resultant impacts of this on ocean biogeochemistry

The work of WG 38 and others has demonstrated that the atmosphere is an important route by which the key nutrients nitrogen, phosphorus and iron reach the ocean (Kanakidou et al., 2018). In the case of nitrogen, the flux to the ocean has increased considerably because of human activity. This flux involves reduced (ammonia/ammonium) nitrogen now derived predominantly from agriculture, oxidized nitrogen (nitrate/nitric

acid) now derived predominantly from combustion sources, and organic nitrogen of uncertain sources. The sources and bioavailability of this organic nitrogen merit further investigation. The emissions of NO_x from combustion sources have increased over the industrial era but are now declining due to emission control measures, while the emissions of ammonia from agriculture have risen throughout this period and continue to do so, leading to an evolving change in the atmospheric flux of nitrogen to the ocean (GESAMP, 2018). The changing acidity of the atmosphere, arising from the changing balance of combustion-derived emissions of SO₂ and NO_x and neutralizing emissions of ammonia, leads to changing speciation of nitrogen between gaseous (ammonia, nitric acid) and aerosol (ammonium, nitrate) forms in the atmosphere, which in turn leads to important changes in the atmospheric deposition of nitrogen to the ocean in terms of both the total flux and the spatial distribution pattern of that deposition flux (Baker et al., 2021; Kanakidou et al., 2018). These changes can now be modelled with some confidence and incorporated into Earth system models (ESMs).

The atmospheric deposition of iron and phosphorus also represents an important source of these key nutrients for the ocean, particularly in the case of iron. The total amounts of iron and phosphorus transported through the atmosphere to the ocean are dominated by material associated with soil dust and derived primarily from desert regions, and hence this supply is linked to climate (Kanakidou et al., 2018). However, most of this iron and phosphorus is relatively insoluble and hence of limited biological availability to marine plankton communities. The work of WG 38 involved comparisons of available models and data to better understand the controls on the supply of labile (and hence potentially biologically available) iron to the ocean. The available models can reproduce some but not all features of the available data. A notable conclusion from the WG 38 studies is that “pyrogenic iron”, which arises from both wildfires and industrial sources, is much more labile than iron from desert dust sources. This means that although pyrogenic iron is a much smaller source of total iron supply to the atmosphere and ocean, it is an important source of labile iron (Ito et al., 2019; Myriokefalitakis et al., 2018) and hence potentially an important driver of ocean biogeochemical change. Furthermore, it is clear from these studies that pH-dependent atmospheric processing, and related organic complexation, increases the lability of iron during atmospheric transport, and that such

processes must be incorporated into atmospheric iron transport models. A further conclusion of these studies is that including these pyrogenic sources in existing models along with representations of atmospheric processing of iron can improve the ability of models to reproduce the available data, but still not completely reproduce the data on the observed labile iron input to the ocean. This is particularly true over the Southern Ocean, which is a key area where iron supply limits ocean productivity.

The control of aerosol pH is a complex process dependent on both the supply of acidifying and neutralizing components and on the water content of aerosols (Baker et al., 2021). As a result of this, the pH of aerosols and their response to changing emissions of SO₂ and NO_x varies with their particle size. This means that the effects of changing atmospheric acidity will be different for dust-derived iron sources (predominantly coarse mode) and pyrogenic iron (finer mode). Model estimates suggest that overall, labile fluxes of iron and phosphorus to the ocean increased by about 30% from 1850 to the present day and may now decrease by the end of this century as a result of changes in atmospheric acidity, changes that models suggest can significantly affect ocean productivity.

The conclusions of these studies emphasize the need for further research to better understand aerosol pH, including more direct measurements, and the process controlling the lability of iron, phosphorus and other trace metals in atmospheric deposition, as well as the need for more direct measurements of the atmospheric deposition of these nutrients to the ocean, particularly in remote ocean regions such as the Southern Ocean.

Conclusion and recommendations for further research

In conclusion we are of the opinion that ocean acidification is unlikely to change the composition of marine organic matter. However, ocean acidification does have the potential to create major changes in the biogenic trace gas emissions from the ocean at a scale that can potentially have important impacts on atmospheric chemistry and climate, although the magnitude and even the direction of these changes is uncertain and requires more research.

The changing acidity of the atmosphere has altered the magnitude and distribution of atmospheric nitrogen fluxes to the ocean, at a scale that can impact ocean productivity. These

fluxes will change further and should be incorporated into ESMs of climate change. The changing acidity of the atmosphere along with the emission of pyrogenic iron has also altered the atmospheric flux of labile iron and phosphorus to the ocean. In the case of iron these changes are very likely to be large enough in scale to modify ocean biogeochemistry, and we recommend further studies of the controls of iron lability and further measurements of atmospheric iron fluxes to the remote ocean to improve atmospheric models and allow their appropriate incorporation into ESMs.

1. INTRODUCTION

1.1 Brief history of Working Group 38

In the 1980s, the Joint Group of Experts on the Scientific Aspects of Marine Environmental Protection (GESAMP) formed a working group sponsored by the WMO, the Intergovernmental Oceanographic Commission of the United Nations Educational, Scientific and Cultural Organization (IOC-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* in 1991 (Duce et al., 1991) that, for more than 15 years, was the state-of-the-art reference in this area, leading to ~2 000 citations in the literature. By 2008 that paper was quite out of date, and growing concern about the impact of atmospheric deposition of both natural and anthropogenic substances on ocean chemistry, biology and biogeochemistry as well as climate led to the formation of the GESAMP Working Group on The Atmospheric Input of Chemicals to the Ocean (WG 38).

Between its formation in 2008 and 2021, WG 38 held meetings and/or workshops at the University of Arizona in the United States of America in 2008, at the International Maritime Organization (IMO) in London in 2010, in Malta in 2011, and at the University of East Anglia in the United Kingdom of Great Britain and Northern Ireland in 2013 and 2017, and held a virtual workshop in 2020. Sponsors of those WG 38 efforts have included the Global Atmosphere Watch (GAW) programme of WMO, IMO, the International Science Council's Scientific Committee on Oceanic Research (SCOR), the Swedish International Development Agency (SIDA), the European Commission Joint Research Centre, the University of Arizona, the International Environment Institute (now the Institute of Earth Systems) at the University of Malta, and the United States National Science Foundation. Many of the above-mentioned meetings and workshops are described in detail in GESAMP Reports and Studies No. 84 (*The Atmospheric Input of Chemicals to the Ocean*) (GESAMP, 2012) and Reports and Studies No. 97 (*The Magnitude and Impacts of Anthropogenic Atmospheric Nitrogen Inputs to the Ocean*) (GESAMP, 2018). In addition, 21 peer-reviewed scientific papers on issues related to the air-sea exchange of chemicals and related impacts on climate and marine biogeochemical cycles

have been developed as a result of these WG 38 meetings and workshops.

1.2 The changing acidity study and its terms of reference

As a result of a number of human activities, the acid/base character of the ocean and the atmosphere has changed significantly in recent years. WG 38 developed two separate but simultaneous workshops to address the changing acidity of the global atmosphere and ocean and its impact on air-sea chemical exchange. These highly successful and productive workshops entitled "Impact of Ocean Acidification on Fluxes of Atmospheric non-CO₂ Climate-active Species" and "Changing Atmospheric Nutrient Oceanic Solubility" were held at the University of East Anglia in Norwich, the United Kingdom from 27 February through 2 March 2017. The invited scientists were selected for their expertise and interest in these areas, and also to provide a wide spectrum of expertise ranging from modelling to experimentation. Thirty-four scientists from 16 countries and from a wide range of career stages, from graduate students to senior scientists, participated in the workshops. The workshops took the form of informal presentations from experts followed by very lengthy discussion sessions exploring the multiple issues and feedbacks evident in these complex air-sea interaction issues. Six peer-reviewed scientific papers were published as a result of these workshops, and summaries of these papers are presented in section 2. The background for each workshop is given below.

Workshop on the Impact of Ocean Acidification on Fluxes of Atmospheric non-CO₂ Climate-active Species

Oceanic uptake of atmospheric CO₂ has increased over the past 200 years, driven by intensifying fossil fuel combustion and cement production. The resulting acidification of the world ocean, characterized by reductions in pH and increased *p*CO₂ of surface waters, has potentially significant consequences for marine ecosystem function, oceanic biogeochemical cycles, and ocean emissions of climatically- and chemically-active species (Royal Society, 2005).

Investigations of the impact of ocean acidification before this workshop had primarily focused on changes in oceanic uptake of anthropogenic CO₂ and shifts in carbonate equilibria, and on consequences for marine calcifying organisms (Royal Society, 2005; Williamson et al., 2013). Very little attention has been paid to the direct impacts of ocean

acidification on the ocean sources of a range of other gaseous and aerosol species that are influential in regulating radiative forcing, atmospheric oxidizing capacity (via OH radical and O₃ cycling) and atmospheric chemistry. These species include greenhouse gases such as nitrous oxide (N₂O) and methane (CH₄), atmospheric aerosol precursors such as dimethyl sulfide (DMS) and marine volatile organic compounds (VOCs), and a range of halocarbons important in tropospheric chemistry and particle formation (Gehlen et al., 2011; Hopkins et al., 2010).

The ecosystem composition and the oceanic processes governing emissions of these species are frequently sensitive to the changes in pH and ocean *p*CO₂ accompanying ocean acidification. The processes include, for example, metabolic rates of microbial activity, levels of surface primary production, and photochemical and microbially mediated production/loss pathways for individual species (Gehlen et al., 2011). The direct and indirect influences of these factors on oceanic fluxes of non-CO₂ trace gases and aerosols, and the subsequent feedbacks to climate, are not well understood (Gruber, 2011; Royal Society, 2005). Outlined below are some findings published before the workshop on potential impacts for key species, and highlights of critical research needs.

Nitrous oxide and the oceanic nitrogen cycle

Oceanic N₂O is produced by a combination of nitrification in the well-oxygenated ocean and denitrification in the sub-oxic ocean and in sediments (Frame and Casciotti, 2010, and references therein). These processes are mediated by marine bacteria and archaea during the remineralization of organic matter, and display sensitivity to ambient environmental factors (Löscher et al., 2012; Santoro et al., 2011). There have been very few evaluations of the impact of ocean acidification on the ocean's nitrogen cycle and on N₂O production. Studies by Beman et al. (2011) and Clark et al. (2014) are exceptions; however, both these studies are based on ocean measurements, and to our knowledge, no relevant laboratory-based process analyses have been published on this topic. The study by Beman et al., based on water samples from sites in the Atlantic and Pacific, suggests decreasing levels of marine nitrification accompanying ocean acidification; this has associated implications for oceanic N₂O fluxes. However, there has been little direct investigation of this (Clark et al., 2014; Rees, 2017). The impacts of ocean acidification on ocean N₂O are likely to be complex due to

interactions with other marine environmental changes, such as ocean deoxygenation and stratification, that could accompany ocean acidification (Codispoti, 2010). These interactions and impacts on oceanic N₂O remain unclear and unexplored.

Dimethyl sulfide

Marine emissions of DMS provide the largest source of natural sulfate aerosol to the atmosphere, and by contributing to cloud condensation nuclei, they play a fundamental role in cloud formation and climate (Carslaw et al., 2010). DMS in surface ocean waters is formed via enzymatic cleavage of the precursor dimethylsulfoniopropionate (DMSP); its concentration is regulated via a complex interaction of photochemical, microbial and phytoplankton/zooplankton processes (Archer et al., 2013). Ocean acidification (via changes in pH and *p*CO₂, and via indirect impacts on phytoplankton primary production) has the potential to shift this balance, and hence to influence ocean DMS levels and fluxes to the atmosphere (Archer et al., 2013, and references therein). Mesocosm studies in the Arctic and high latitudes provide some evidence for this dependence, indicating reduced DMS levels in response to high *p*CO₂ and high acidity environments (Archer et al., 2013; Hopkins et al., 2010). An ESM simulation incorporating processes representing this dependence suggests potential feedbacks to climate via increases in equilibrium surface temperature of 0.23–0.46 K by the year 2100 (Six et al., 2013). These findings are based on a handful of in situ and model studies; more process-based investigations, measurement campaigns and modelling studies are clearly needed to clarify these impacts of ocean acidification on DMS fluxes to the atmosphere.

Halocarbons

The potential impact of ocean acidification on marine halocarbons (for example, bromocarbons and iodocarbons, which are important in controlling oxidants such as O₃ and OH radical in the marine troposphere) has been investigated by a few studies analysing mesocosm experiments in the high northern latitudes (Hopkins et al., 2010, 2013; Wingenter, 2007). Initial analyses indicated possible decreases in marine halocarbon levels with increasing acidification (for example, Hopkins et al., 2010). However, a more recent study reports inconclusive findings on the net impact of ocean acidification on halocarbon levels, although it also demonstrates sensitivity of the marine ecosystem components to *p*CO₂ levels (Hopkins et al., 2013). As with the other

species considered here, information on the impacts of ocean acidification on halocarbons is sparse, and more investigation is clearly required.

In addition, ocean acidification is likely to influence several other species relevant to atmospheric chemistry and climate, such as non-methane hydrocarbons and oxygenated organics (Gattuso and Hansson, 2011). To our knowledge there are no published findings on these impacts.

The dearth of information on the direct influences of ocean acidification on marine fluxes of the climate- and chemistry-active species discussed above highlights the need for a comprehensive and coordinated set of laboratory studies, measurement campaigns and modelling investigations to identify and quantify these impacts.

Terms of reference for the workshop on the Impact of Ocean Acidification on Fluxes of Atmospheric non-CO₂ Climate-active Species

- Review and synthesize the current science on the direct impacts of ocean acidification on marine emissions to the atmosphere of key species important for climate and atmospheric chemistry.
- Identify the primary needs for new research to improve process understanding and to quantify the impact of ocean acidification on these marine fluxes (that is, provide recommendations on the specific laboratory process studies, field measurements and model analyses needed to support targeted research activities on this topic).
- Publish the results of this activity in the open peer-reviewed scientific literature.
- Provide input to and interact with national and international research programmes on ocean acidification (for example, the UK Ocean Acidification (UKOA) research programme, the US National Oceanic and Atmospheric Administration Ocean Acidification Program (NOAA-OAP)) and with relevant WMO programmes (for example, GAW) to build on their recent relevant activity in achieving the above objectives.

Workshop on Changing Atmospheric Nutrient Solubility

Atmospheric deposition of nutrients to the ocean is known to play a significant role in regulating marine productivity and biogeochemistry. This deposition therefore has potential impacts on the drawdown of CO₂ by surface seawater (and hence the global carbon cycle) as well as the production of other climate-active gases, such as N₂O and DMS (Boyd and Ellwood, 2010; Duce et al., 2008; Jickells et al., 2005). The specific impact of such deposition is dependent on the identity of the nutrient in question (e.g., N, P, Fe, Co, Zn, Ni, Cd), the location of the deposition (because atmospheric input probably has only a significant, immediate impact in waters where a particular nutrient is in short supply) and the bioavailability of the deposited nutrient (because non-available nutrients are not taken up by marine microorganisms and do not therefore influence the carbon cycle) (Moore et al., 2013). Bioavailability is largely governed by the chemical speciation of a nutrient; in general, insoluble species are not bioavailable. For iron and phosphorous (and perhaps the other nutrient trace metals), solubility increases during transport through the atmosphere. The causes of this increase are complex and not well understood, but interactions of aerosol particles with acids appear to play a significant role in the process (Baker and Croot, 2010; Baker et al., 2014; Kumar et al., 2010).

Emissions of acidic (SO₂ and NO_x) and alkaline (NH₃) gases have increased significantly since the Industrial Revolution, with a net increase in atmospheric acidity. This implies that iron and phosphorous solubility may also have increased over this time period, potentially resulting in increased marine productivity. More recently, pollution controls have decreased emissions of SO₂ from some regions, and further reductions in SO₂ and NO_x are likely in the future. Emissions of NH₃ are much more difficult to control, however, and are projected to stabilize or increase slightly by the end of this century. Future anthropogenic emissions are therefore likely to change the acidity of the atmosphere downwind of major urban/industrial centres, with potential consequences for the supply of soluble nutrients to the ocean (Dentener et al., 2006; Sanderson et al., 2006). Concurrent with this change in acidity, there are likely to be other changes (in the magnitude and species composition of atmospheric nitrogen supply to the ocean, and in the stoichiometric ratios of the nutrients — N:Fe, N:P, P:Fe), which may also impact marine productivity rates and

microbial species population composition (Moore et al., 2013).

The ability to predict such changes and their likely effects on marine productivity, atmospheric carbon drawdown into the ocean and climate depends on the availability of reliable numerical modelling tools. Several groups have now developed models of the atmospheric transport and chemistry of iron, nitrogen and phosphorous and, in a few cases, two or all of these (for example, Okin et al., 2011). However, there are some important weaknesses in these models, which limit their effectiveness as predictive tools:

- Poor validation of atmospheric chemistry model output against relevant observational data;
- Variety in computational algorithms used to simulate atmospheric processing of nutrients (algorithms in some cases are mutually exclusive).
- Reliance (for prediction of impacts) on ocean biogeochemistry models which, particularly in the case of iron, also suffer from major uncertainties in parameterization of iron biogeochemistry.

Terms of reference for the workshop on Changing Atmospheric Nutrient Solubility

- Review and synthesize the current scientific information on the solubility of key biogeochemical elements, their pH sensitivity and the biogeochemical controls on the pH sensitivity. Consider the likely changes in solubility of key species in the future and the potential biogeochemical consequences of such changes.
- Identify the key future research needs to reduce uncertainties in predictive capability in this area.
- Publish the results of this activity in the open peer-reviewed scientific literature.
- Interact with and provide information to leading relevant international groups including the Future Earth core projects SOLAS (Surface Ocean–Lower Atmosphere Study), IGAC (International Global Atmospheric Chemistry) and IMBER (Integrated Marine Biosphere Research); SCOR, particularly its GEOTRACES programme; and WMO programmes such as GAW.

2. SUMMARIES OF THE SIX PAPERS DEVELOPED BY WG 38

2.1 Summary of "Phytoplankton do not produce carbon-rich organic matter in high CO₂ oceans"

(Ja-Myung Kim, Kitack Lee, Young-Sang Suh and In-Seong Han)

This paper was published in *Geophysical Research Letters* **2018**, 45, 4189–4197.
<https://doi.org/10.1029/2017GL075865>
5.

Introduction

Photosynthesis by phytoplankton in the sunlit ocean transforms dissolved inorganic carbon (DIC) and nutrients into organic matter. Some of this organic matter is transported to the ocean interior by gravitational settlement, and a small proportion of this (~10% of the total organic matter vertically exported) is transported downward in a dissolved form, particularly in regions where winter overturning ventilates the deep ocean (Hansell, 2002). Together, these two processes (surface organic matter production and the vertical transport of a fraction of the organic matter produced), collectively referred to as the biological carbon pump, generate a vertical gradient of DIC (Volk and Hoffert, 1985). If all processes that influence the gravitational transport of organic matter (e.g., particle transformation into aggregates, vertical attenuation of sinking particle flux and degradation of sinking particles) remain unperturbed, the increase in surface organic C production resulting from an increase either in total organic production or in the C content of the organic matter produced would increase the amount of organic C removed from the surface. Such a change will directly influence $p\text{CO}_2$ levels in the surface ocean, and subsequently modify the oceanic uptake of atmospheric $p\text{CO}_2$. Moreover, the greater production of organic C may further lead to an expansion of the volume of suboxic water or an increase in the production of N_2O in the ocean interior (Oschlies et al., 2008; Tagliabue et al., 2011).

Given the growing concern about increasing anthropogenic CO_2 concentration in the global surface ocean, the excess production of organic C relative to organic N (corresponding to greater DIC consumption, that is, a C:N ratio >6.6) has been extensively examined under varying $p\text{CO}_2$ conditions. However, the experiments performed to date have not yielded consistent results regarding the effect

of $p\text{CO}_2$ on the elemental C:N ratio. Monoalgal culture and shipboard incubation experiments have been widely used to test the C:N ratio of organic matter produced. In these controlled experiments, the change in the ratio of particulate organic carbon to particulate organic nitrogen (POC:PON ratio) of target phytoplankton species with increasing $p\text{CO}_2$ levels showed mixed trends (Hutchins et al., 2009, and references therein). Another approach that has been used employs in situ $p\text{CO}_2$ perturbation experiments, which more closely mimic the natural environmental conditions and deal with natural phytoplankton communities. Such experiments enable evaluation of the C:N ratio, both in the dissolved inorganic species consumed and in organic matter (both particulate and dissolved forms) produced during photosynthesis. Notably, a few of these perturbation experiments showed excess DIC consumption relative to NO_3^- by phytoplankton during photosynthesis (Bellerby et al., 2008; Engel et al., 2005; Riebesell et al., 2007), whereas other experiments showed no excess DIC consumption (Silyakova et al., 2013) and total organic carbon (TOC) production (Kim et al., 2011).

Given the absence of consensus on the effect of $p\text{CO}_2$ on the elemental C:N ratio, there is a need for a thorough examination of C and N dynamics in both the consumption (dissolved inorganic components) and production (organic components) pools. In this study we therefore investigated the elemental C:N ratio of organic matter produced during phytoplankton blooms under proposed future $p\text{CO}_2$ scenarios. Our analysis was based on published data acquired from nine in situ $p\text{CO}_2$ perturbation experiments (Engel et al., 2005; Engel et al., 2008; Engel et al., 2014; Kim et al., 2006; Kim et al., 2011; Park et al., 2014; Riebesell et al., 2007; Schulz et al., 2017; Silyakova et al., 2013) carried out in diverse ocean regions. We also evaluated the excess DIC consumption relative to NO_3^- under high- $p\text{CO}_2$ conditions, and concurrently investigated whether the excess DIC consumed during photosynthesis was transformed exclusively into the production of excess organic C.

Methods

In situ $p\text{CO}_2$ perturbation experiments

Numerous in situ $p\text{CO}_2$ perturbation experiments have been performed across a wide range of geographical regions (e.g., Bach et al., 2016; Engel et al., 2014; Gazeau et al., 2017; Kim et al., 2010; Paul et al., 2015; Riebesell et al., 2008; Riebesell et al., 2013;

Taucher et al., 2017). From those experiments we chose nine to assess whether high $p\text{CO}_2$ levels led to greater DIC consumption relative to NO_3^- (that is, greater production of POC relative to PON). All nine of the selected experiments had the following characteristics: they were performed using pelagic mesocosm facilities; they tested only natural assemblages

of marine phytoplankton and produced at least organic C and N data for the particulate and dissolved forms; and they were performed with the deliberate addition of major nutrients. Table 1 shows the experimental conditions for the nine in situ $p\text{CO}_2$ perturbation experiments included in this study.

Table 1. Experimental conditions for in situ $p\text{CO}_2$ perturbation experiments used in this study

Year	Experimental site		ID	Target $p\text{CO}_2$ (μatm)	Dominant phytoplankton taxa during bloom phases
2001	Norwegian Sea	60.3°N, 5.2°E	A	190*, 410*, 710*	Prymnesiophytes
2003	Norwegian Sea	60.3°N, 5.2°E	B	190*, 370*, 700*	Prymnesiophytes
2004	East China Sea	34.6°N, 128.5°E	C	250*, 400*, 750*	Bacillariophytes
2005	Norwegian Sea	60.3°N, 5.2°E	D	350*, 700*, 1050*	Bacillariophytes, Prymnesiophytes
2008	East China Sea	34.6°N, 128.5°E	E	400*, 900*	Bacillariophytes, Picoplanktons, Autotrophic flagellates
2009	Baltic Sea	54.5°N, 10.0°E	F	355*, 482*, 626*, 760*, 862*	Cryptophytes, Bacillariophytes
2010	Arctic	78.6°N, 11.5°E	G	170, 185*, 270*, 375*, 480*, 685*, 820*, 1050*, 1420*	Prasinophytes, Dinoflagellates, Prymnesiophytes, Chlorophytes
2011	Norwegian Sea	60.3°N, 5.2°E	H	300, 310*, 390*, 590*, 890*, 1165*, 1425*, 2060, 3045	Bacillariophytes, Chlorophytes, Cryptophytes
2012	East China Sea	34.6°N, 128.5°E	I	260*, 330*, 540, 710*, 890*, 1040*	Bacillariophytes

Notes:

* $p\text{CO}_2$ conditions that were subject to analysis in this study

Datasets used in the present study and original papers are available from the World Data Center PANGAEA (experiment A: Engel et al. (2005) and PeECEI-team (2001); B: Engel et al. (2008) and PeECEII-team (2003); C: Kim et al. (2006) and Kim et al. (2006); D: PeECEIII-team (2005), Riebesell et al. (2007) and Schulz et al. (2008); E: Kim et al. (2011); F: Engel et al. (2014); G: Schulz et al. (2013), Silyakova et al. (2013) and Svalbard-team (2010); H: Schulz et al. (2017); I: Lee et al. (2016) and Park et al. (2014)).

Source: Kim et al. (2018).

Calculations

The C:N elemental ratios in the dissolved inorganic species consumed and the organic matter produced during photosynthesis were acquired during periods of ample nutrient concentrations. Our calculation was primarily focused on the bloom periods (that is, nutrient-replete conditions) of the chosen experiments because the majority of organic matter is produced during such periods.

Prior to evaluating the elemental C:N ratio, data on DIC change were corrected for changes resulting from variations in salinity, CaCO_3 production and air-sea CO_2 gas exchange, using the equations below. The remaining

changes in DIC were attributed to changes solely related to organic matter production ($\Delta\text{DIC}_{\text{org}}$):

$$\Delta\text{DIC}_{\text{org}} = \Delta n\text{DIC} - \Delta\text{DIC}_{\text{inorg}} - F \quad (1)$$

To account for evaporation or precipitation, the decrease in DIC was normalized to the mean salinity (S) during the entire period of the experiment ($n\text{DIC} = \text{DIC}_{\text{meas}} \times (S_{\text{mean}}/S_{\text{meas}})$, $\Delta n\text{DIC} = n\text{DIC}_{\text{ref}} - n\text{DIC}_{\text{d-n}}$). The decrease in DIC resulting from calcification ($\Delta\text{DIC}_{\text{inorg}} = 0.5 \times \Delta\text{TA}_{\text{inorg}}$) was estimated from the decrease in concurrently varying total alkalinity (TA). Because TA increases proportionally with the utilization of nutrients by phytoplankton during biosynthesis, the

change in TA was corrected for the drawdown of NO_3^- ($\Delta\text{TA}_{\text{inorg}} = \Delta\text{TA}_{\text{meas}} + \Delta\text{NO}_3^-_{\text{meas}}$). Finally, $\Delta\text{DIC}_{\text{org}}$ was corrected for air-sea CO_2 exchange ($F = k K_0 (p\text{CO}_2^{\text{water}} - p\text{CO}_2^{\text{air}})$; where F ($\text{mol m}^{-2} \text{s}^{-1}$) is the flux of CO_2 across the air-water interface; k (m s^{-1}) is the gas transfer velocity (Czerny et al., 2013); K_0 ($\text{mol m}^{-3} \mu\text{atm}^{-1}$) is the solubility of CO_2 ; and the $p\text{CO}_2^{\text{water}}$ (μatm) and $p\text{CO}_2^{\text{air}}$ (μatm) terms are the partial pressure of CO_2 in water and air, respectively).

Results

Dissolved inorganic C:N elemental ratio consumed during photosynthesis

The ratio of DIC to NO_3^- consumed by phytoplankton ($\Delta\text{DIC}_{\text{org}}:\Delta\text{NO}_3^-$ ratio) during the bloom periods in all nine $p\text{CO}_2$ perturbation experiments was evaluated. Experiments A, B, and D, which were performed in a Norwegian fjord, showed that there was an excess of DIC consumption relative to NO_3^- at high $p\text{CO}_2$ levels (Figure 1(a)). The $\Delta\text{DIC}_{\text{org}}:\Delta\text{NO}_3^-$ ratio associated with the production of organic matter increased by ~ 0.46 for every increase of 100 μatm $p\text{CO}_2$ within the $p\text{CO}_2$ range tested (190–1050 μatm). In contrast, experiments E, G, and I, which were carried out in the temperate Pacific Ocean and the Arctic Ocean, did not show this trend of increase (Figure 1(b)).

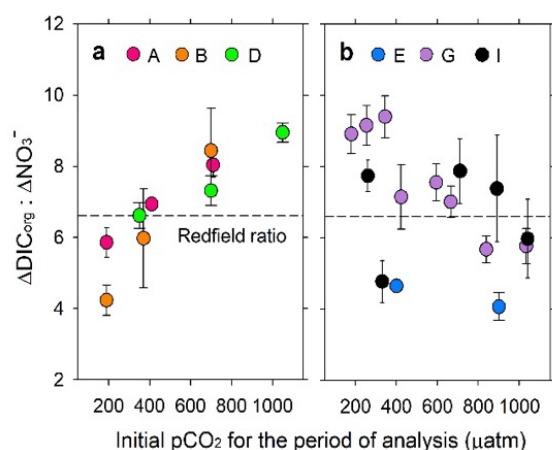


Figure 1. The dissolved inorganic C:N elemental ratio associated with consumption for organic matter formation. (a) The mean $\Delta\text{DIC}_{\text{org}}:\Delta\text{NO}_3^-$ ratio plotted as a function of initial $p\text{CO}_2$ conditions for experiments A, B, and D; and (b) experiments E, G, and I. The dashed lines represent the Redfield C:N ratio (6.6).

Source: Kim et al. (2018).

Among the nine experiments, the $\Delta\text{DIC}_{\text{org}}:\Delta\text{NO}_3^-$ ratio during the bloom periods at a given $p\text{CO}_2$ level was found to vary. No explicit explanation for this variation is available, but one might speculate that the species-specific regulation of C acquisition could change the $\Delta\text{DIC}_{\text{org}}:\Delta\text{NO}_3^-$ ratio in response to CO_2 availability. For example, the prymnesiophyte alga *Emiliania huxleyi* – the dominant plankton species in experiments A, B, and D – has been reported to operate carbon concentrating mechanisms inefficiently, in contrast to the bloom forming diatoms (such as *Skeletonema costatum*) that dominated in experiments E and G. In the succession of major taxa over the multiple bloom phases of experiment G, the $\Delta\text{DIC}_{\text{org}}:\Delta\text{NO}_3^-$ ratio varied considerably, indicating that fluctuations in this ratio may be controlled by physiological differences in the phytoplankton tested and the complexity of responses of phytoplankton communities to varying $p\text{CO}_2$. The absence of a consistent $\Delta\text{DIC}_{\text{org}}:\Delta\text{NO}_3^-$ ratio indicates that the prediction of overconsumption of DIC by phytoplankton relative to NO_3^- in a future high- $p\text{CO}_2$ ocean may not be conclusive. More importantly, for C overconsumption to truly enhance the biological carbon pump, all of the excess DIC would need to be exclusively transformed into organic matter having an elevated C:N ratio.

Organic C:N elemental ratio in particulate and dissolved forms

In contrast to the absence of consistency in the $\Delta\text{DIC}_{\text{org}}:\Delta\text{NO}_3^-$ ratio observed during phytoplankton bloom periods, the C:N ratio of particulate organic matter produced was not sensitive to $p\text{CO}_2$ conditions (Figure 2). The POC:PON ratio in all experimental data examined neither increased nor decreased significantly in response to increasing $p\text{CO}_2$. All regression slopes for POC versus PON converged to a value of 6.58 ± 0.05 ($r^2 = 0.98$), which is close to the Redfield ratio of 6.6 (Redfield et al., 1963) (Figure 2 inset). Regardless of the $p\text{CO}_2$ levels, the resulting POC:PON ratio found in nutrient replete conditions was also observed in experiments performed under low-nutrient conditions, as shown in experiments in the Baltic Sea and Mediterranean Sea without nutrient addition (Figure 2) (Bourdin et al., 2017; Gazeau et al., 2017; Paul et al., 2015).

The excess consumption of DIC during photosynthesis, as seen intermittently, did not lead to the accumulation of dissolved organic carbon (DOC) in any of the nine experiments. The DOC produced (accounting for <20% of

TOC production) remained well below the amount of excess DIC consumed. In all experiments, neither the production of DOC (Engel et al., 2004; Kim et al., 2006; Kim et al., 2011; Lee et al., 2016) nor the DOC:DON ratio (Engel et al., 2014; Schulz et al., 2008; Schulz et al., 2017) increased under the high- $p\text{CO}_2$ conditions that prevailed during the bloom periods before nutrient exhaustion. Consequently, there was no increase in the C:N ratio in total organic matter production (TOC:TON) with increasing $p\text{CO}_2$.

One remaining enigma in our results is the apparent mismatch between the $\Delta\text{DIC}_{\text{org}}:\Delta\text{NO}_3^-$ ratio associated with consumption, and the TOC:TON ratio associated with production. One explanation for this mismatch is the possible inclusion of heterotrophic organisms in the measurements of POC and PON. Such inclusion may lower the C:N ratio associated with phytoplanktonic production of organic matter, because the C:N ratios of major zooplankton (~5.7) (Kjørboe, 2013) have been reported to be slightly lower than the phytoplanktonic value of 6.6. The biomass of zooplankton during periods of phytoplankton blooms accounted for <10% of the total POC in experiments D, G and I (Aberle et al., 2013; Park et al., 2014; Suffrian et al., 2008). As a result, the reduction in the POC:PON ratio due to the presence of zooplankton was estimated to be ~0.1, which is considerably smaller than the discrepancy between the C:N ratios measured in the inorganic and organic pools.

Another possible explanation is the production and vertical settlement of C-rich (C:N > 14 (Mari et al., 2017)) transparent exopolymer particles (TEPs), which are proposed to be released as a result of the cellular C overflow after the onset of nutrient depletion (Passow, 2002). According to this proposed mechanism, excess DIC consumed during photosynthesis is transferred to TEPs, which rapidly escape through the bottom of high- $p\text{CO}_2$ enclosures, possibly via aggregation with particulate organic matter. The positive correlation between TEP production and $p\text{CO}_2$ observed in bioassays appears to be in line with this TEP production mechanism (Engel, 2002). However, we did not find concrete evidence suggestive of greater amounts of TEPs in either suspended or ballasted matter produced in the experiments from which the proposed “C overconsumption” mechanism was derived. In experiments A and D, the total concentration of TEPs and their C content did not differ across $p\text{CO}_2$ treatments (Egge et al., 2009; Engel et al., 2004). In experiment D, the POC:PON ratio of organic matter collected on traps installed in the

bottom of the high- $p\text{CO}_2$ enclosures did not differ from the Redfield ratio (Schulz et al., 2008).

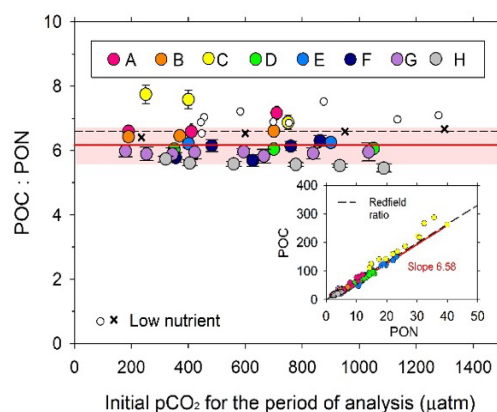


Figure 2. The C:N elemental ratio for particulate organic matter plotted as a function of initial $p\text{CO}_2$ conditions. Inset: the mean POC:PON ratio for experiments A–H. The dashed black line and the solid red line represent the Redfield C:N ratio and average value for the POC:PON ratio, respectively. The shaded area represents the standard deviation ($1\sigma = 0.6$) from the average value of 6.2. Open circles and crosses show the mean ratio obtained from the experiments performed under low-nutrient conditions without enrichment (Gazeau et al., 2017 and Paul et al., 2015).

Source: Kim et al. (2018).

Conclusions

Analysis of datasets obtained from the nine in situ $p\text{CO}_2$ perturbation experiments showed that natural phytoplankton communities did not produce excess POC relative to PON under high- $p\text{CO}_2$ conditions during bloom phases. Excess DIC consumed by phytoplankton may be converted into TEPs that subsequently aggregate with organic particles. Direct verification of this transformation is not straightforward. Moreover, our understanding of the effects of $p\text{CO}_2$ on particle transformation and regulation of the sinking particle flux (both of which contribute to the vertical transport of organic C) are currently incomplete. Therefore, we cautiously propose that the feedbacks (for example, low O_2 zone expansion and greater N_2O production) that are predicted to arise from the production of disproportionately C-rich organic matter are unlikely to occur in future high- $p\text{CO}_2$ oceans.

2.2 Summary of “Aerosols in atmospheric chemistry and biogeochemical cycles of nutrients”

(Maria Kanakidou, Stelios Myriokefalitakis and Kostas Tsigaridis)

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<https://doi.org/10.1088/1748-9326/aabcbd>.

Introduction

Nutrient equilibria of both land and marine ecosystems have been disturbed during the Anthropocene period. This paper integrates knowledge on the impact of multiphase chemistry on atmospheric water acidity, atmospheric composition and solubility of nutrients (which determines their bioavailability), focusing on the biogeochemical cycles of N, P and Fe, including their organic fractions and impact on marine ecosystems (Figure 3). The human-driven contribution to atmospheric deposition of these nutrients, modelled by global simulations using past and future anthropogenic emissions of pollutants, is put in perspective with regard to potential changes in nutrient limitations and biodiversity.

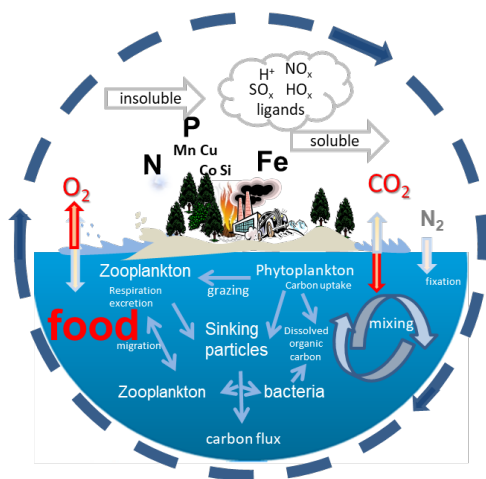


Figure 3. Terrestrial vegetation and marine phytoplankton are responsible for the O₂ in the atmosphere of our planet and most removal of CO₂ from the atmosphere.

Source: Kanakidou et al. (2018).

Nutrients in the atmosphere

Humans have significantly modified the composition of atmospheric aerosols due to emissions of aerosols and of their precursor gases. Both natural and anthropogenic sources

emit into the atmosphere various aerosol components (carbonaceous aerosols that include black, brown and organic carbon) or their precursor molecules, such as SO₂, NO_x, NH₃ and VOCs, as well as other trace elements attached to the aerosol phase like P and metals. Nitrogen, P, as well as many metals (e.g., Fe, Cu, Ni, Co, Cd, Zn) are essential micronutrients for marine phytoplankton, while at high levels they can be toxic (Paytan et al., 2009). Nitrogen, P and Fe are known to control primary productivity in vast areas of the open ocean (Moore et al., 2013; Okin et al., 2011).

Multiphase chemistry reactions produce oxygenated organics and form organic ligands like oxalic acid that are important components of water-soluble organic carbon, affecting the water associated with aerosols and the aerosol pH. They contribute to the fixation of nutrients like N onto aerosols, and to the conversion of insoluble forms of trace elements like Fe and P into soluble material that can be easily assimilated by the terrestrial or oceanic organisms affecting the ecosystems. Atmospheric reactions of inorganic N (NO_x and NH₃) with organic compounds in the gas and the aqueous/aerosol phases can form organic nitrogen (ON) compounds and transfer inorganic N to the aerosol phase. A significant amount of ON is attached to secondary organic aerosols (Ito et al., 2014; Kanakidou et al., 2012, 2016). The secondary production of ON can be of similar magnitude to ON primary emissions from specific sources as has been estimated for biomass burning (Ito et al., 2015).

Aerosol processing: solubilization of nutrients and role of acidity

Desert dust contains a large variety of minerals and metals, most of them in insoluble forms (Nickovic et al., 2012). However, to be bioavailable, elements must be in the soluble forms (or in nanoparticles of diameter smaller than 0.2 μm). Conversion of nutrients from insoluble to soluble forms (solubilization) requires acidic conditions and for metals can be followed by chelation (reversible complexation of a ligand to a metal ion), which further increases solubilization. Such conditions may be produced by soil microorganisms (Mackey and Paytan, 2009) or by abiotic chemical reactions in the atmosphere (Stockdale et al., 2016). Both these biotic and abiotic mechanisms proceed initially by the production of inorganic or organic acids with a simultaneous pH decrease, and of ligands needed to react with minerals and release nutrients to the solution.

The reduced acidity of coarse compared to fine aerosols significantly suppresses Fe and P dissolution, while it favours the partitioning of nitrate to the aerosol phase. It also partially explains the observed inverse relationship between Fe solubility and particle size (Baker and Jickells, 2006). Atmospheric acidity also affects nutrient deposition through its control on the partitioning of $\text{HNO}_3/\text{NO}_3^-$ to the aerosol phase. An aerosol pH higher than 2 is required for NO_3^- to start being transferred the aerosol phase, and at a pH of about 4 or higher it is mostly present in the aerosol phase, due to the semi-volatile character of NH_4NO_3 . Such pH constraints can be fulfilled by coarse dust aerosols where non-volatile cations like Ca_2^+ keep pH levels relatively high, or by biomass burning aerosol where K^+ cations play a similar role. On the other hand, anthropogenic or acid-coated fine aerosols suppress $\text{HNO}_3/\text{NO}_3^-$ partitioning to the aerosol phase. Because of the different removal rates of HNO_3 and NO_3^- through deposition and thus lifetimes against

removal, aerosol acidity – through its impact on the $\text{HNO}_3/\text{NO}_3^-$ partitioning – will also affect the $\text{HNO}_3/\text{NO}_3^-$ deposition distribution.

Organics as carriers of nutrients

Organics are key players in biosphere–atmosphere–climate interactions, and their role as carriers of nutrients has only recently been recognized. They have a significant human-driven component due to primary anthropogenic emissions or interactions of natural emissions with pollution (Kanakidou et al., 2000). Element ratios have been used to construct the ON and organic P atmospheric cycles based on the relatively better understood organic carbon cycle (Kanakidou et al., 2012). During the last decade, attention has been paid to biological material that is widely found as part of organic aerosols directly emitted by vegetation, as well as to the amounts of organics present in soils and potentially carried by soil dust aerosol (Schlesinger, 1977).

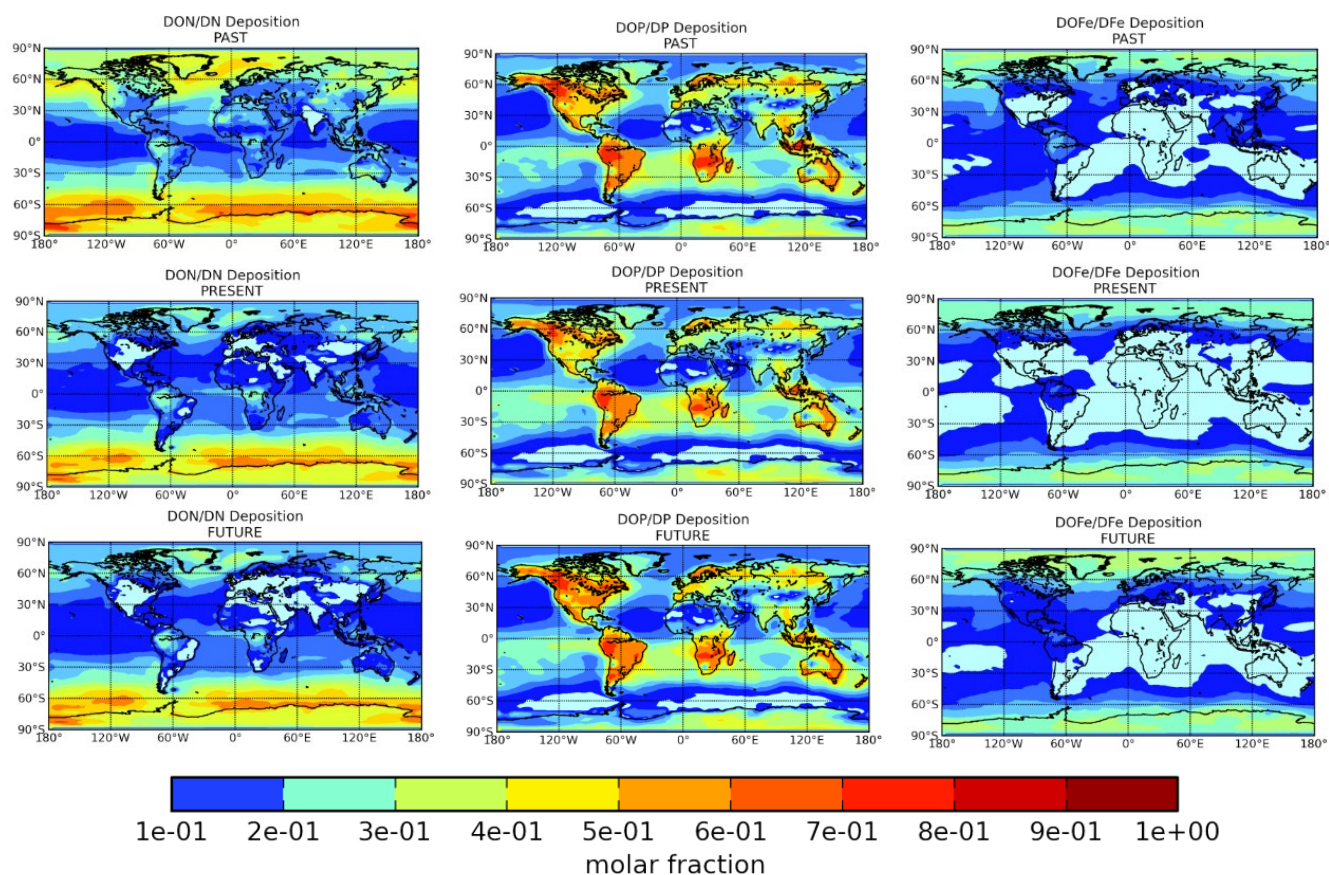


Figure 4. Fractions of soluble organic N (DON) to total soluble N (DN) deposition (left panels); of soluble organic P (DOP) to total soluble P deposition (middle panels); and of Fe-oxalate complexes to total soluble Fe deposition (note that only cloud water chemistry is considered as a source of Fe-oxalate for these simulations) (right panels) with emissions. Top: past (emission year 1850); middle: present (year 2005 for N and year 2008 for P and Fe); bottom: future (emission year 2050 for N, emission year 2100 for P and Fe).

Source: Kanakidou et al. (2018).

Global simulations with the TM4-ECPL model show that organic forms of N, P and Fe contribute to the atmospheric deposition of nutrients by 20%–40%, 35%–45% and 7%–18%, respectively (Figure 4). Bioaerosols have been found to make an important contribution to the atmospheric sources of N and P (Table 1), indicating potentially significant interactions between the terrestrial and marine ecosystems. These results deserve further experimental and modelling studies to reduce uncertainties and improve understanding of the feedbacks induced by atmospheric deposition of nutrients to the ecosystems.

Importance of humans in changing atmospheric acidity and nutrient biogeochemical cycles

Anthropogenic emissions of atmospheric acid precursors (NO_x and SO_2) had been increasing from the pre-industrial period until the last 30 years, when they started to decline due to measures taken for air pollution mitigation. In parallel, emissions of NH_3 , the main neutralizing agent in the atmosphere, have also changed, but at different rates compared to NO_x emissions (Lamarque et al., 2010). This is because of the absence of direct regulations on NH_3 emissions, which have been indirectly affected – at least in Europe – by changes in agricultural practices since 1990 (EEA, 2010). These emission changes have also modified the acidity of the various atmospheric compartments (gases, aerosols, clouds, rain), which responded differently to these changes (Weber et al., 2016). They thus led to changes in all three nutrients here discussed, namely N, P and Fe. Changes in the stoichiometry N:P:Fe of the deposition fluxes have been calculated using the global TM4-ECPL model (Kanakidou et al., 2016; Myriokefalitakis et al., 2015, 2016) that reflect not only the chemistry-driven modifications of the deposition fluxes but also those due to changes in the primary anthropogenic emissions of these nutrients.

Nitrogen deposition, and in particular nitrate deposition, is also affected by aerosol acidity since the partitioning of gaseous HNO_3 to the aerosol phase (NO_3^-) does not occur under very acidic conditions. Kanakidou et al. (2016) have shown that at present a larger fraction of the total NO_3^- is in the gas phase (as HNO_3) than had been in the 'past' (year 1850) and will be in the 'future' (year 2100). As a consequence, calculations show that the lifetime of the total NO_3^- due to atmospheric deposition has decreased by 35% from 'past' to present-day and will increase by about 20% in the 'future'. These changes in the partitioning between gas

and aerosol phases are modulated by acidity changes with key roles played by SO_2 and NH_3 emissions and lead to changes in the geographical pattern of the deposition. Similarly, the deposited soluble fluxes of Fe (and P) carried by dust alone calculated as the sum of the initially emitted soluble dust-nutrients and the amounts solubilized during chemical processing (ageing) in the atmosphere were found to be at present higher by 12% and 24% for Fe and P, respectively, compared to when anthropogenic and biomass burning emissions of the year 1850 ('past') are used in the model (Myriokefalitakis et al., 2015, 2016). An almost equivalent change is predicted by the model using predicted 2100 emissions ('future') based on the representative concentration pathways – RCP 6.0 (van Vuuren et al., 2011). These are driven by much larger changes in the amounts solubilized during atmospheric ageing and are entirely due to the modification of the atmospheric acidity and ligand content of aerosol and cloud water induced by changes in anthropogenic and biomass burning emissions.

Summary and recommendations

- Atmospheric processing via multiphase chemistry is important for the formation of nutrients or their transformation to readily bioavailable forms. This process needs to be further understood and considered when modelling atmospheric deposition of nutrients.
- There is a clear consensus on the importance of the organic fractions of N, P and Fe as an integral part of their atmospheric cycles and that atmospheric aerosols are the key carriers of these components. Interestingly, model simulations show that bioaerosols contribute significantly to the atmospheric sources of N and P, indicating potentially significant interactions between the terrestrial and marine ecosystems.
- Further experimental and modelling studies are needed to provide accurate quantification of organic nutrient sources and impacts on the ecosystems. In particular, measurements in remote locations are logistically difficult but invaluable for the documentation and understanding of atmospheric processing of aerosols. There is also need for better characterization of organic nutrients present in atmospheric aerosols and their association with the presence of organic matter in the ocean, and of the ecosystem response to their atmospheric inputs.

- Little is also known on the bioavailability of the atmospheric organic material deposited to the ecosystems, although it is expected that when inorganic nutrients are in short supply, some organisms will adapt and search for other forms of nutrients (organics) even if they might be less easy to assimilate.
- It has been suggested that changes in the relative composition of nutrients subject to atmospheric deposition are driving human-induced limitations of specific nutrients in ecosystems, like P limitation in the eastern Mediterranean and in alpine lakes induced by atmospheric inputs of N. These modifications are also favouring the development of certain species compared to others and impacting the overall functioning of the ecosystems.
- Microbes play a dual role in the atmosphere: they contribute to bioaerosols as carriers of nutrients (mainly N and P) but also act as mediators increasing or reducing the bioavailability of nutrients in the environment. The presence of microbes in the soils has attracted attention to explain the occurrence of bioavailable Fe and P, and because of their potential use for sustainable agricultural development. However, no attention – to our knowledge – has been given to the presence of such microbes in atmospheric aerosols and their potential contribution to biotic solubilization of nutrients present in aerosols during atmospheric transport.
- Finally, it has been seen that although Redfield stoichiometry (the assumed constant nutrient ratio in phytoplankton) is commonly used for a first identification of the limiting nutrient for development of an ecosystem, several organisms deviate from Redfield stoichiometry, in particular those able to adapt to nutrient stress conditions. Therefore, there is a close link between the community structure and the average relative nutrient proportions of suspended and sinking particles in the ocean that deserves deeper study, by applying a new 'non-Redfield' approach in biogeochemistry modelling (Moore et al., 2013).

2.3 **Summary of “Reviews and syntheses: the GESAMP atmospheric iron deposition model intercomparison study”**

(Stelios Myriokefalitakis, Akinori Ito, Maria Kanakidou, Athanasios Nenes, Maarten C. Krol, Natalie M. Mahowald, Rachel A. Scanza, Douglas S. Hamilton, Matthew S. Johnson, Nicholas Meskhidze, Jasper F. Kok, Cecile Guieu, Alex R. Baker, Timothy D. Jickells, Manmohan M. Sarin, Srinivas Bikkina, Rachel Shelley, Andrew Bowie, Morgane M. G. Perron and Robert A. Duce)

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<https://doi.org/10.5194/bg-15-6659-2018>.

Introduction

Understanding the impact of the micronutrient Fe on global marine primary productivity requires adequate knowledge of the rates and the location of Fe supply to the ocean, as well as of the physico-chemical forms of Fe that can be utilized by marine biota (those that are bioavailable). The atmospheric modelling community is mostly focused on the soluble fraction of Fe deposited to the ocean; for this study, the general term “labile Fe” (LFe) was used to represent the overall bioavailable Fe in simulated atmospheric aerosols. However, modelling the atmospheric supply of LFe to the global ocean is challenging, due to the multitude of forms under which Fe can be present in aerosols (Meskhidze et al., 2017), as well as the variety and complexity of processes that alter the solubility of Fe during its transport through the atmosphere (Baker and Croot, 2010). Iron in soils, mostly occurring as iron oxides, includes a small fraction of soluble Fe (roughly 0.1%) (see, for example, Ito and Shi (2016), while the Fe in fly ash has also been observed to be mainly present as ferric sulfate salts or nanoparticulate Fe, and thus is highly soluble (Fu et al., 2012; Schroth et al., 2009). However, LFe can also be formed in the atmosphere by the chemical processing of mineral dust and combustion aerosols (Ito, 2012; Ito and Feng, 2010; Johnson and Meskhidze, 2013; Meskhidze et al., 2005; Myriokefalitakis et al., 2015). We use the general term “solubilization” to describe the process that converts part of the insoluble Fe in aerosols to LFe during atmospheric transport. Indeed, there is clear experimental evidence that atmospheric acidity – mainly driven by air pollution over highly populated or industrialized regions – increases the mineral Fe solubility.

Proton concentration in aerosols plays an important role in mineral Fe solubilization; however, this solubilization also depends on the presence of organic ligands (such as oxalate) in the atmosphere, sunlight and the ambient temperature (see, for example, Hamer et al. (2003), Lanzl et al. (2012), Lasaga et al. (1994), Zhu et al. (1993)).

To develop a global picture of the impact of present-day atmospheric composition on the Fe supply to the ocean, we performed a systematic comparison between state-of-the-art global models containing dedicated Fe aerosol schemes and evaluated model outputs using field observations. Overall, the goals of the present study were:

- (i) To quantify the magnitude of atmospheric total Fe (TFe) and LFe fluxes to the global ocean;
- (ii) To explain the differences in simulated LFe between the models compared;
- (iii) To provide multi-model ensemble TFe and LFe atmospheric Fe deposition fluxes for the next generation of ocean biogeochemistry modelling studies.

Results and discussion

The global models used in this study (CAM4, GEOS-Chem, IMPACT and TM4-ECPL (Ito and Kok, 2017; Johnson and Meskhidze, 2013; Myriokefalitakis et al., 2015, 2016; Scanza et al., 2018)) differ in spatial resolution, meteorology, emissions used for gas and aerosol species, and aerosol microphysics (size distribution and refractive properties).

Figure 5 presents the global LFe sources and deposition fluxes to the global ocean for all models compared and their ensemble mean, for the four seasons, that is, December, January and February (DJF); March, April and May (MAM); June, July and August (JJA); and September, October and November (SON). Despite the different assumptions applied in the models, maximum LFe sources and deposition fluxes are mainly calculated for MAM and JJA due to the relatively more intense emissions from dust and biomass burning. Models with the highest LFe sources also exhibit the highest deposition fluxes to the ocean. However, a significant difference in the magnitude of the deposition fluxes is found between models (Figure 5).

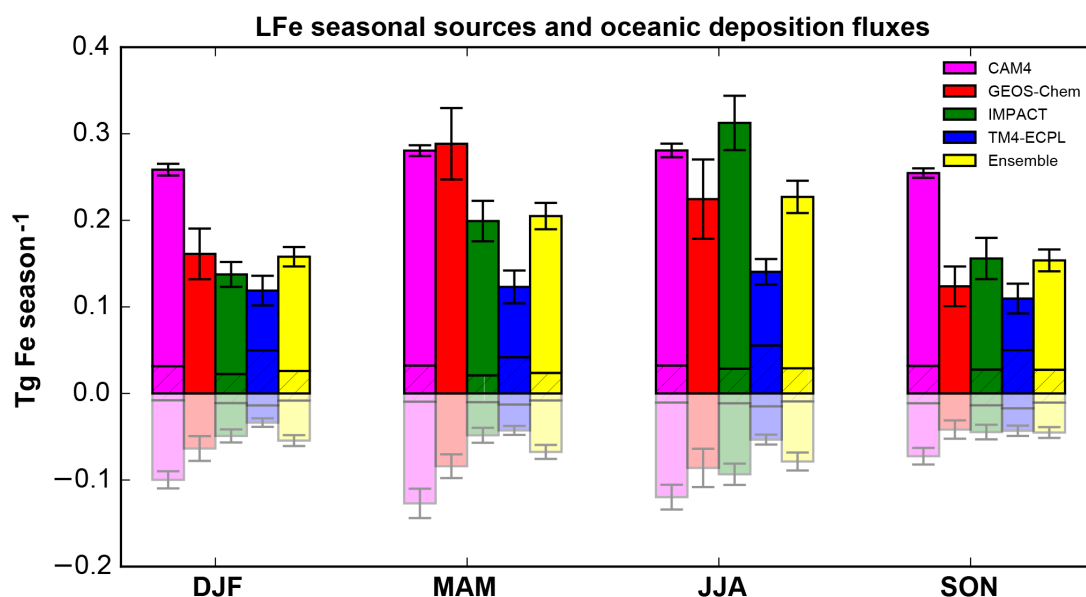


Figure 5. Seasonal LFe sources (positive bars) and oceanic deposition fluxes (negative bars/pale colours) in Tg Fe per season for DJF, MAM, JJA and SON, as calculated by each model (CAM4: magenta; GEOS-Chem: red; IMPACT: green and TM4-ECPL: blue), as well as the ensemble model (yellow). The hatched areas correspond to the combustion aerosols and the error bars correspond to the standard deviation for the season.

Source: Myriokefalitakis, et al. (2018).

Average model calculations indicate that about $72 (\pm 43)$ Tg y^{-1} of TFe from mineral dust are deposited on the Earth's surface. The respective TFe annual mean global deposition

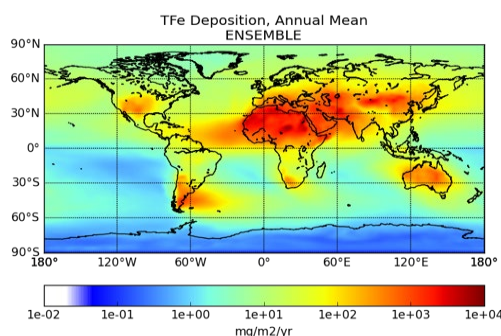
flux from combustion sources is estimated at $\sim 2.2 (\pm 0.5)$ Tg Fe y^{-1} , with two main types of region where the TFe fluxes exceed $2\,500 \text{ mg Fe m}^{-2} \text{ y}^{-1}$. These are in the vicinity

of major biomass burning regions (e.g., southern Africa, South America and Southeast Asia), where fluxes range up to $\sim 3\,000\text{ mg Fe m}^{-2}\text{ y}^{-1}$ and in the vicinity of highly populated regions where Fe is being released from coal and oil combustion processes (India and China), with fluxes up to $\sim 3\,500\text{ mg Fe m}^{-2}\text{ y}^{-1}$ (Figures 6(a) and (b)).

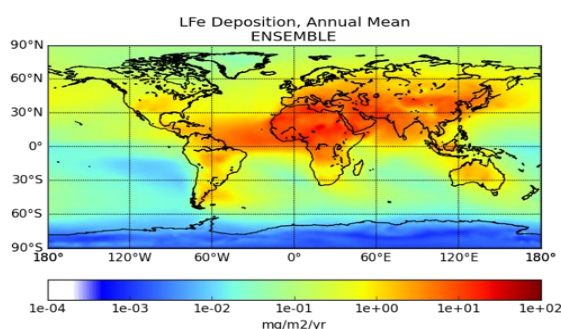
A global mean LFe deposition flux of $0.7 (\pm 0.2)\text{ Tg Fe y}^{-1}$ is derived from all models, with about $0.2\text{--}0.4\text{ Tg Fe y}^{-1}$ deposited into the global ocean. The highest annual mean LFe deposition fluxes (up to $36\text{ mg Fe m}^{-2}\text{ y}^{-1}$) are simulated near dust source regions (Figure 6(c)), owing mainly to primary emissions. The global mean LFe deposition flux from combustion sources is estimated at about $0.2 (\pm 0.04)\text{ Tg Fe y}^{-1}$, with maximum global deposition rates of $4\text{--}5\text{ mg Fe m}^{-2}\text{ y}^{-1}$ (Figure 6(d)) simulated in the outflow of tropical biomass burning regions (South

America, southern Africa and Southeast Asia). Focusing on the marine environment, an annual mean LFe deposition flux of $15\text{ mg Fe m}^{-2}\text{ y}^{-1}$ is calculated for both the tropical Atlantic Ocean and the Indian Ocean (up to $16\text{ mg Fe m}^{-2}\text{ y}^{-1}$), under the influence of the Arabian and Indian peninsulas, whereas a mean flux as high as $\sim 29\text{ mg Fe m}^{-2}\text{ y}^{-1}$ is estimated for the Mediterranean Sea downwind of the Sahara Desert. Deposition rates around $1\text{ mg Fe m}^{-2}\text{ y}^{-1}$ are calculated over the Northern Pacific in the outflow of East Asian dust source regions, such as the Taklamakan and Gobi Deserts. There are also plumes downwind of Patagonia and Australia. The LFe deposition rates to the Southern Ocean are associated mainly with the Patagonian, southern African and Australian deserts, with a nevertheless significant contribution from combustion sources (up to $\sim 40\%\text{--}50\%$ regionally; Figure 6(d)).

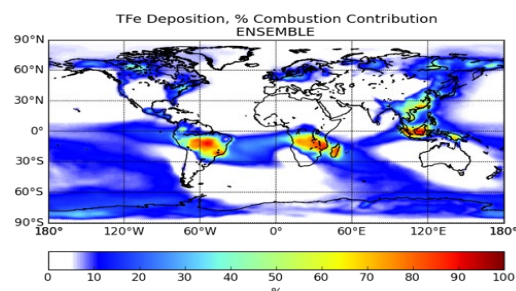
(a)



(c)



(b)



(d)

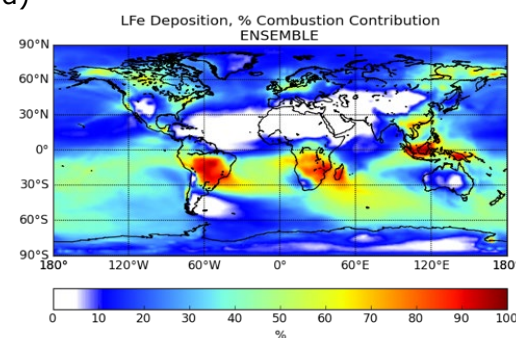


Figure 6. Ensemble model results for annual deposition fluxes ($\text{mg Fe m}^{-2}\text{ y}^{-1}$) for (a) TFe and for (c) LFe and their respective percentage contribution of combustion aerosols (b, d)

Source: Myriokefalitakis, et al. (2018).

All models capture well the tendency for higher Fe concentrations near and downwind of the major dust source regions. However, the models tend to overestimate the TFe surface mass concentrations in the northern hemisphere, especially near the dust source regions (Figure 7). On the other hand, models tend to underestimate the lowest concentrations observed over

remote ocean areas (Figure 7). The derived correlation coefficients indicate that the models have, nevertheless, similar behaviour for the key processes that affect Fe deposition. All in all, our analysis indicates that the models miss – or do not accurately represent – important processes that could drive the variability in field observations. It should be noted, however,

that the comparison of monthly mean model results with the shorter-term (for example, daily) observations during different sampling periods is inherently biased by the episodic nature of atmospheric emissions.

Summary and conclusions

Summary of results

- This study reviewed and synthesized state-of-the-art global models that represent the solubility and atmospheric deposition of Fe-containing aerosols from mineral dust and combustion.
- The study reveals two critical questions in atmospheric Fe-cycle simulations that require further exploration: (i) the size distribution of Fe-containing aerosol and (ii) the relative contribution of dust and combustion atmospheric aerosols to labile Fe (LFe) inputs to remote oceanic regions, especially the Southern Ocean.

Conclusions

This study presents the first comparison of models of the atmospheric component of the Fe-cycle by assessing aerosol simulations of TFe and LFe from four state-of-the-art global aerosol models. This work indicates that the representation of atmospheric Fe may vary significantly between models, both in terms of the magnitude of soil and combustion Fe emissions and the complexity of parameterizations of aerosol Fe atmospheric processing. Our analysis indicates that large differences exist between these models in the representation of processes such as emissions, transport and deposition. In particular, a large diversity is documented between models in terms of the primary sources of LFe (emissions) and the secondary processes (solubilization through atmospheric processing), which may introduce uncertainties in the estimated oceanic deposition. There are many intrinsic reasons for this diversity; in addition to the uncertainty related to the emitted Fe mass in the atmosphere from dust aerosols and the strength of combustion aerosol sources from anthropogenic and biomass burning processes, the parameterizations used to calculate aerosol acidity and the production

of oxalate in the aqueous phase of the atmosphere are large sources of uncertainty. The diversity of model results over the remote ocean also reflects uncertainties in the Fe content of dust and combustion aerosols (for example, soil mineralogy and the initial Fe soluble content in primary sources), and/or in the parameterizations applied for the size distribution of the transported Fe-containing aerosols. Aerosol size and solubility are suggested here to be important factors driving the atmospheric cycle of Fe since they both control Fe removal processes from the atmosphere via dry deposition (including gravitational settling) and wet scavenging. In this respect, new field observations and laboratory studies are needed to improve our understanding of Fe solubilization processes in the atmosphere, and how these processes change in the presence of anthropogenic pollution. All in all, the development of novel modelling tools and their evaluation based on a greater number of atmospheric observations, especially over the remote ocean, are deemed necessary to reduce the uncertainty associated with the simulation of the atmospheric Fe deposition.

2.4 Summary of “Pyrogenic iron: the missing link to high iron solubility in aerosols”

(Akinori Ito, Stelios Myriokefalitakis, Maria Kanakidou, Natalie M. Mahowald, Rachel A. Scanza, Douglas S. Hamilton, Alex R. Baker, Timothy Jickells, Manmohan Sarin, Srinivas Bikkina, Yuan Gao, Rachel U. Shelley, Clifton S. Buck, William M. Landing, Andrew R. Bowie, Morgane M. G. Perron, Cécile Guieu, Nicholas Meskhidze, Matthew S. Johnson, Yan Feng, Jasper F. Kok, Athanasios Nenes and Robert A. Duce)

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<https://doi.org/10.1126/sciadv.aau7671>

Introduction

Iron is an essential nutrient for marine phytoplankton; in high-nutrient-low-chlorophyll regions of the ocean where Fe is scarce, dissolved Fe supplied via airborne aerosols becomes especially important.

Previously, only those iron oxides contained in mineral dust, which have demonstrated low solubilities (<0.5% near source regions), were considered as atmospheric sources of Fe to the ocean (Jickells et al., 2005). However, in recent years, observations have indicated that aerosols impacted by airborne pollutants have higher Fe solubilities (>10%) (Sholkovitz et al., 2012). Nonetheless, the observational data alone do not provide clarity with respect to why aerosols demonstrate such high Fe solubility over remote open ocean regions (Meskhidze et al., 2019). Additionally, Fe solubility estimates resulting from numerical models have shown a large degree of scattering against the observational data, so conclusions

regarding the causes of high aerosol Fe solubility differ according to the methods employed in their prediction (Myriokefalitakis et al., 2018). Thus, the explanation for high Fe solubility in some field data compared to that measured in soil particles remains loosely constrained, and several hypotheses have been proposed to explain this puzzling observation (Mahowald et al., 2018). Here, a statistical analysis of Fe solubility from four models and observations compiled from multiple field campaigns reveals that pyrogenic aerosols are the main sources of the high Fe solubility from the shipborne measurements.

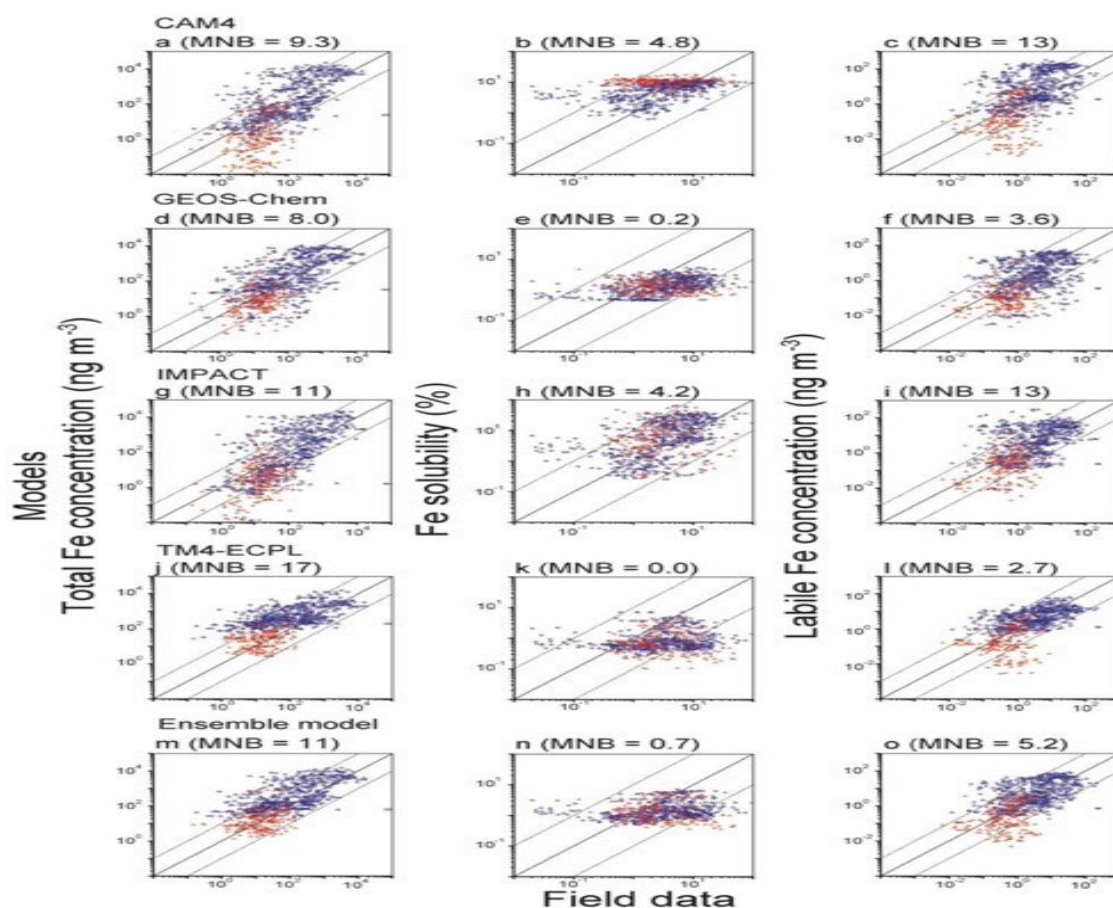


Figure 7. Comparison of simulated and observed TFe concentrations (ng m^{-3}), Fe solubility (%) and LFe concentrations (ng m^{-3}) in the northern (blue circles) and southern (red squares) hemispheres. (a), (b) and (c): CAM4; (d), (e) and (f): GEOS-Chem; (g), (h) and (i): IMPACT; (j), (k) and (l): TM4-ECPL; (m), (n) and (o): ensemble model. The mean normalized biases (MNB) between the models and observations are presented in parentheses. The solid line represents a 1:1 correspondence and the dashed lines show the 10:1 and 1:10 relationships, respectively. The bias correction in the mineral dust size distribution is applied for the comparison with field data (Kok et al., 2017).

Source: Myriokefalitakis et al. (2018).

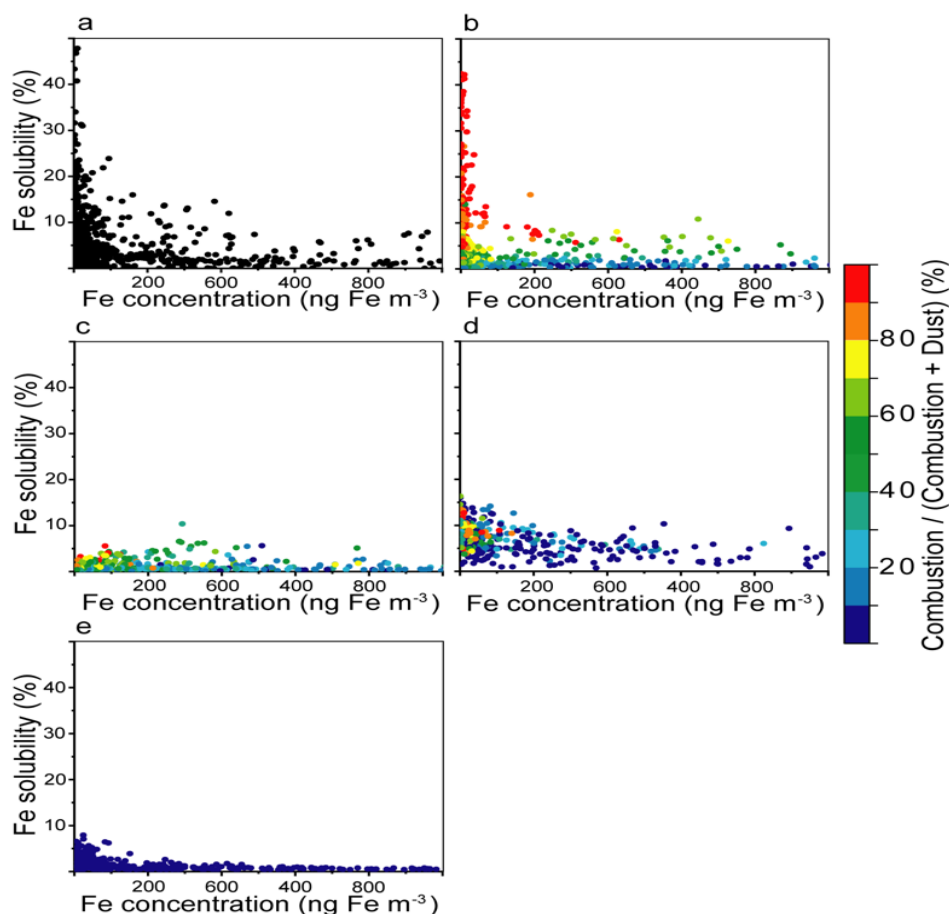


Figure 8. Relationship between aerosol Fe concentration (ng m^{-3}) and Fe solubility (%) for the (a) field data and (b) IMPACT, (c) TM4-ECPL, (d) CAM4, and (e) GEOS-Chem models. The colour of the predicted results for each mathematical model represents the proportion of dissolved pyrogenic Fe to all dissolved Fe present in the aerosols, with warm colours indicating higher proportions.

Source: Ito et al. (2019).

Results and discussion

This study combined results from multiple numerical models with observational data to statistically clarify the cause of the high Fe solubility observed in the marine atmosphere compared to the low solubility of Fe in soils. It was found that the degree of and changes in solubility were most faithfully reproduced in models that predicted an increase in pyrogenic Fe solubility under high atmospheric acidity during atmospheric transport (Figure 8), with more details provided below using the case study of the North Atlantic (Shelley et al., 2018). These results, as well as those from other regions such as the northern Indian Ocean (Srinivas et al., 2012), the equatorial Atlantic Ocean (Baker et al., 2006) and the Southern Ocean (Sholkovitz et al., 2012; Gao et al., 2013; Bowie et al., 2009), suggest that agreement with field data depends not only on the chemical

composition of the aeolian source, but also on the degree of atmospheric processing occurring during transport.

The extensive number of observations of aerosol Fe over the North Atlantic offer a useful shipborne measurement with which to compare four models: IMPACT (Ito et al., 2018), TM4-ECPL (Myriokefalitakis et al., 2015), CAM4 (Scanza et al., 2018) and GEOS-Chem (Johnson and Meskhidze, 2013). In Figure 9, the aerosol samples are simply classified using air-mass back trajectories as originating from either North Africa or other air-mass regimes (Shelley et al., 2018). The “degree of atmospheric processing” for the field data can be derived from the ratio of Fe solubility obtained from two different leaching methods. All models calculate that mineral dust is a major source of LFe at high total Fe concentrations (those samples largely influenced by North African air masses) and

reproduced the low solubility of $0.4\% \pm 0.1\%$ reported in the field data. The internal mixing of alkaline components with Fe-containing minerals in mineral dust can lead to higher pH and inhibit the Fe acid dissolution process. In North African mineral dust, the ratio of LFe to the sum of labile and less labile Fe concentrations indicates a weak degree of Fe processing in aerosols ($5.6\% \pm 2.2\%$ on average). By contrast, non-North African air masses correspond with a greater extent of aerosol Fe solubilization ($36\% \pm 15\%$ on average). At the same time, three models (IMPACT, TM4-ECPL and CAM4) estimate a large contribution from combustion aerosols to the labile aerosol Fe at higher Fe solubility and lower concentrations (Figure 9). Moreover, the IMPACT model reproduced the sporadically high Fe solubility observed in aerosols from the other air-mass regimes, specifically marine and high-latitude air masses.

The results further demonstrate that when combined with air pollutants, pyrogenic Fe becomes highly water-soluble in very acidic solutions due to photochemical reactions. (Figure 10). Three models (IMPACT, TM4-ECPL and CAM4) can calculate the contribution from combustion aerosols to total Fe and to LFe deposition fluxes. The models agree that mineral dust is the major source of Fe deposited to the North Atlantic, Arabian Sea and South Atlantic downwind from the arid and semi-arid regions of North Africa, the Middle East and Patagonia (Figure 10). However, the models estimate a large range in the contribution of combustion aerosols to the deposition fluxes of total Fe and LFe. The differences among model results are significantly larger for LFe compared to total Fe and increase with distance from the major dust source regions. This is largely due to the differences in the assumed Fe solubility of dust and combustion aerosols upon emission and the subsequent dissolution schemes leading to Fe solubility enhancement during long-range transport. Therefore, reducing uncertainties in model estimates of LFe deposition fluxes primarily requires parameterization improvements for those factors that control aerosol Fe

dissolution, including atmospheric acidity, organic ligand (for example, oxalate) concentrations, and the relative contribution of combustion aerosols to the labile fraction of aerosol Fe.

Over the Southern Ocean (Figure 11), none of the models was able to reproduce the high Fe solubility ($>10\%$) occasionally reported for aerosols (12/42 samples), because there is no aerosol Fe dissolution mechanism at high pH and low oxalate conditions in three of the models. Thus, the wide range of solubility (from 0.2% to 48%) in this region derived from observations cannot be explained by considering only the chemical aging of Fe-containing aerosols for solutions examined in the laboratory. Moreover, the multi-model mean ($0.06 \pm 0.08 \text{ ng m}^{-3}$) underestimates the observed mean LFe concentration over the Southern Ocean ($0.97 \pm 1.1 \text{ ng m}^{-3}$). Therefore, further studies are required to identify and quantify aerosol sources in the southern hemisphere. Studies of stable Fe isotopes and magnetite may offer additional information on the contribution from anthropogenic sources over the ocean (Conway et al., 2019; Kurisu et al., 2021; Lamb et al., 2021; Moteki et al., 2017).

Uncertainty in modelled aerosol Fe solubility over the Southern Ocean stems from the scarcity of observations. There are fewer field data in the southern hemisphere, and those that exist are sparsely distributed and collected over longer sampling periods during research cruises, partly due to the low concentration of aerosols. Thus, these results should be interpreted with a degree of caution. We suggest that more observations are needed before drawing any firm conclusions on the Fe solubility and the models' performance, particularly in the Pacific (Buck et al., 2013), Indian and Southern Ocean regions. Since Fe plays a key role in marine biogeochemistry within the high-nutrient-low-chlorophyll regions of the Southern Ocean, it is important to gain a deeper understanding of the atmospheric cycle of Fe and resolve these discrepancies between model estimates and field data.

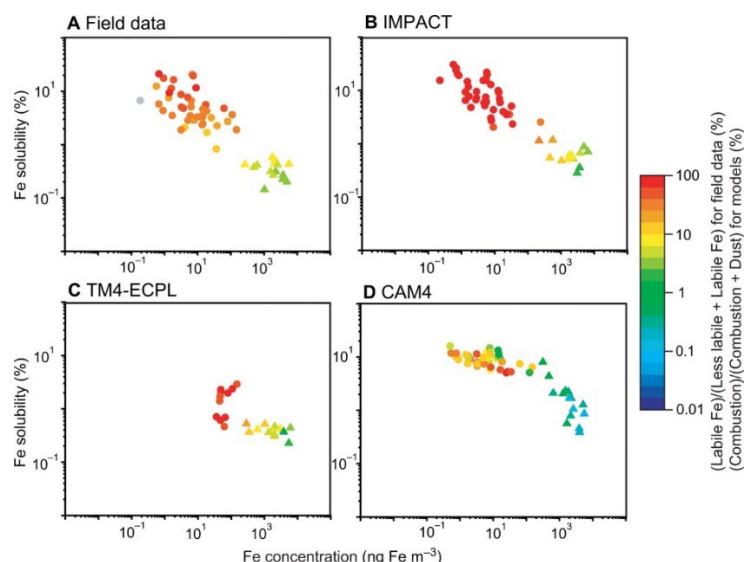


Figure 9. Fe solubility versus Fe concentration (ng Fe m^{-3}) for field data and models over the North Atlantic. The colours represent percentage contributions of LFe to the sum of less labile and labile Fe for field data and the simulated contribution of combustion aerosols to the sum of combustion and dust aerosols to LFe in the models. The field data point in light grey colour represents no data for the 25% acetic acid leach. The aerosol samples are simply classified as sourced by air masses from North Africa (triangles) or other air-mass regimes (circles) including North America, Europe, marine (no interaction with major land masses within five days prior to sample collection) or high latitudes (air masses originating north of 50°N).

Source: Ito et al. (2019).

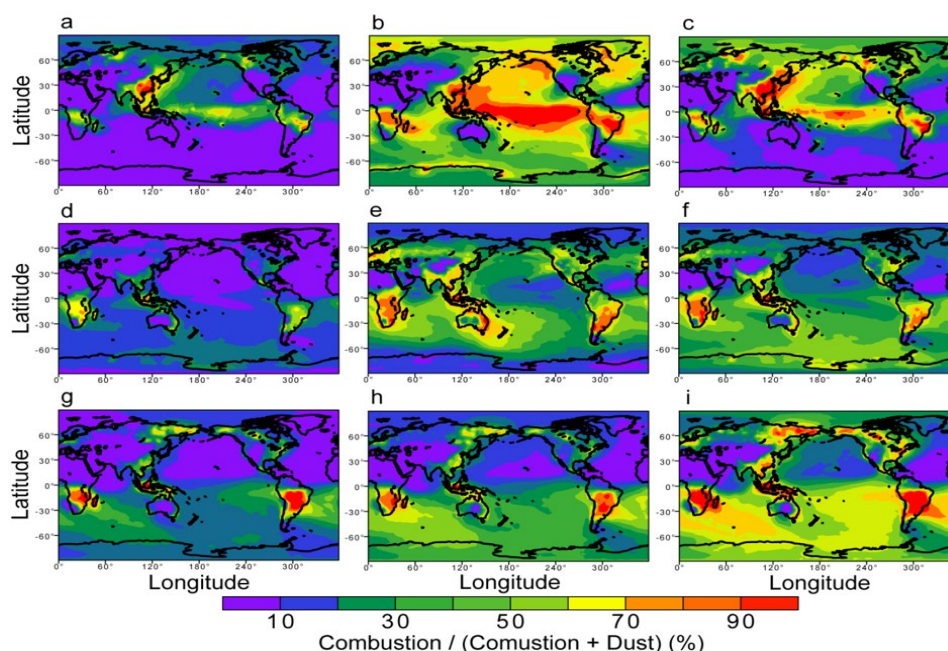


Figure 10. Proportion of (a, d and g) pyrogenic Fe in all aerosol Fe particles, (b, e and h) dissolved pyrogenic Fe, accounting for photochemical reactions in the atmosphere, and (c, f and i) pyrogenic dissolved Fe particles, not accounting for photochemical reactions in the atmosphere. Results are those yielded by the (a, b and c) IMPACT, (d, e and f) TM4-ECPL, and (g, h and i) CAM4 models, with warmer colours indicating higher proportions.

Source: Ito et al. (2019).

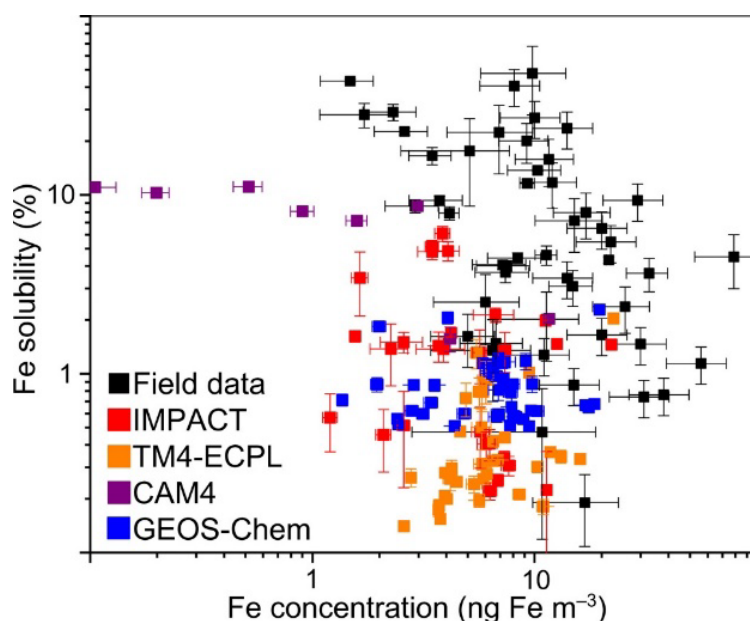


Figure 11. Fe solubility versus Fe concentration (ng m^{-3}) for field data (black squares), IMPACT (red squares), TM4-ECPL (orange squares), CAM4 (purple squares), and GEOS-Chem (blue squares) over the Southern Ocean ($>45^{\circ}\text{S}$). The vertical lines in symbols correspond to ± 1 standard deviation for Fe solubility.

Source: Ito et al. (2019).

Summary and conclusions

Summary of results

- Pyrogenic Fe in aerosols from anthropogenic sources is more labile and is dissolved more quickly in aerosol water than lithogenic Fe from arid and semi-arid soils during atmospheric transport.
- Synthesis of Fe modelling with decades worth of shipborne observations suggests that pyrogenic Fe plays an important role in atmospheric delivery of this micronutrient to marine ecosystems. These new predictions should be considered in future impact assessments for marine environmental conservation policies.

Conclusions

We have compiled model results and observational data from the international community to statistically analyse atmospheric Fe outputs and elucidate the process behind the transformation of Fe from multiple global atmospheric chemical transport models and observational data from various regions of the world ocean. Our analyses show that pyrogenic Fe

undergoes photochemical transformation as it is transported through the atmosphere and deposited to the sea. Subsequently, ocean biogeochemical modelling studies show that pyrogenic Fe plays a crucial role in providing nutrients to marine organisms that live far from arid and semi-arid land, and thus from lithogenic sources of dissolved Fe (Ito et al., 2021). Future research is needed in the characterization and individual contribution of differing aeolian pathways to the ocean to improve understanding on the impact of aerosol deposition (from desert dust, wildfire, volcanic and anthropogenic sources) on marine biogeochemical cycles historically, at present and in the future, and to better comprehend (or anticipate) the fast-evolving human dimension (Hamilton et al., 2021). Future assessments of the impact of nutrient-bearing aerosol deposition on marine phytoplankton (primary productivity) and marine food chains (and therefore ecosystems) are expected to contribute to the creation of more effective environmental conservation plans. This study reveals the considerable potential to incorporate extensive biogeochemical-climatic interactions between the atmosphere and ocean ecosystems in ESMs to aid in marine management and climate policy formation.

2.5 Summary of “The impacts of ocean acidification on marine trace gases and the implications for atmospheric chemistry and climate”

(Frances E. Hopkins, Parvatha Suntharalingam, Marion Gehlen, Oliver Andrews, Stephen D. Archer, Laurent Bopp, Erik Buitenhuis, Isabelle Dadou, Robert A. Duce, Nadine Goris, Tim Jickells, Martin Johnson, Fiona Keng, Cliff S. Law, Kitack Lee, Peter S. Liss, Martine Lizotte, Gillian Malin, J. Colin Murrell, Hema Naik, Andrew P. Rees, Jörg Schwinger and Philip Williamson)

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Introduction

The ocean–atmosphere interface controls the exchange of marine trace gases which influence the chemistry of Earth’s atmosphere and climate, as well as the transfer of elements vital for human health and ecosystem functioning from the ocean to the land. The Earth system is currently facing unprecedented changes to global biogeochemical processes driven by human emissions of greenhouse gases (Ciais et al., 2014), including the rapid uptake of excess CO₂ by the surface ocean, a process known as ocean acidification. To date, most ocean acidification research has focused on potential effects on calcifying organisms (see, for example, Bach et al. (2015), Hoegh-Guldberg et al. (2007), Kroeker et al. (2010) and Riebesell et al. (2000)) and other ecologically- and economically-important species (Lemasson et al., 2017; Munday et al., 2009, 2010; Nagelkerken et al., 2016). The impacts of ocean acidification on marine trace gases and the associated feedbacks on atmospheric chemistry and climate have been less extensively researched, but in recent years a more substantial body of work has emerged, providing insight into how future changes to ocean chemistry may feed back to the Earth’s climate system.

Here, we assess how ocean acidification may affect the production of marine trace gases and result in feedbacks to the

atmosphere. We discuss the role of marine trace gases in the chemistry and climate of the Earth system and provide an overview of the present knowledge on the marine trace gas response to ocean acidification derived from both experimental and modelling studies. We consider regions especially sensitive to ocean acidification, and discuss the effects of other environmental changes, such as rising temperatures and ocean deoxygenation, on the production and emission of marine trace gases.

Carbon dioxide-driven ocean acidification

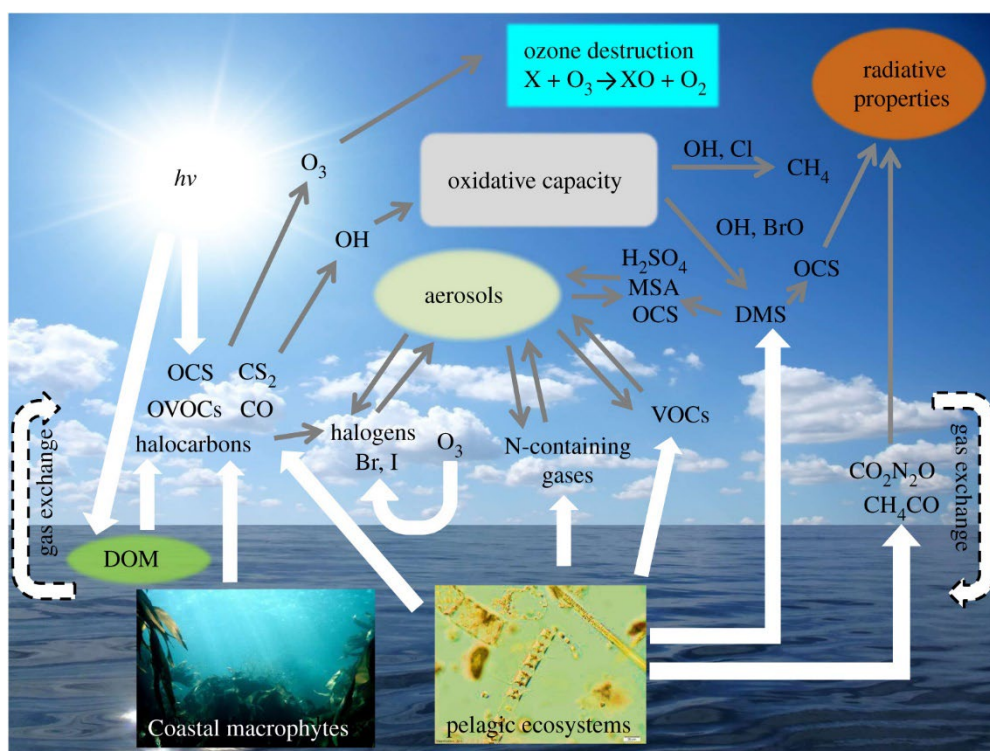
Anthropogenic CO₂ emissions from burning fossil fuels and land-use change are currently the primary driver of global climate change (Bindoff et al., 2013). Atmospheric CO₂ concentrations have risen steadily over the last 150 years and are now higher than at any time during at least the last 800 000 years (Luthi et al., 2008; Willeit et al., 2019). This rise directly results in increased oceanic CO₂ absorption, and ocean acidification (Caldeira and Wickett, 2003), a result of increased hydrogen ion concentration and associated decreasing pH. Globally, a decrease in surface ocean pH of ~0.1 units has already occurred relative to pre-industrial times, with a projected fall of a further ~0.3 units by 2100 under high-emission scenarios (Gattuso et al., 2015). This rate of change to ocean biogeochemistry is rapid on geological timescales, and is probably unprecedented in the last 300 million years of Earth’s history (Hönisch et al., 2012).

Marine trace gases

The surface ocean is a key source of a variety of trace gases, which flow to the atmosphere and play critical roles in the Earth’s biogeochemical cycles, strongly influencing atmospheric chemistry and radiative forcing (Figure 12). These include the greenhouse gases CO₂, N₂O and CH₄, which have well-understood effects on global radiative forcing and atmospheric chemistry (Myhre et al., 2013). The ocean also releases a range of biogenic volatile organic compounds containing carbon, sulfur, nitrogen and halogens (Figure 12). The transfer of these compounds from ocean to land via the atmosphere represents a key step in the global cycling of essential elements that provide benefits

to ecosystem function and human health (Fuge and Johnson, 2015). Furthermore, the atmospheric oxidation products of some trace gases, such as DMS, methylamines and a variety of biogenic volatile organic compounds, can have an impact on marine aerosols, thereby influencing cloud-related processes and global radiative forcing (Andreae and Crutzen, 1997; Charlson et al., 1987; Korhonen et al., 2008; Leaitch et al., 2013). Other marine trace gases, including halocarbons and oxygenated volatile organic compounds, produce highly reactive atmospheric radicals that readily destroy protective stratospheric O₃ and drive the rapid cycling of tropospheric photo-oxidants and O₃, with implications for coastal air quality (Carpenter, 2003; Carpenter et al., 2013; Hossaini et al., 2015; Read et al., 2008). Biogenic marine trace gases are directly produced by micro- and macro-algae and by prokaryotic microbes (Keng et al., 2013; Leedham et al., 2013; Nightingale et al., 1995). Given

the known and predicted effects of ocean acidification on biological processes (Riebesell and Gattuso, 2015), it is likely that the net production of many biogenic trace gases (including both production and loss processes) is influenced by ocean acidification. Trace gases are also released from sediments (Shaw et al., 2010), seafloor seeps (Naqvi et al., 2010; Shakhova and Semiletov, 2007), as a result of bacterial degradation of precursor compounds (Hughes and Sun, 2016; Laturnus, 1996; Stefels et al., 2007), and via reactions between organic matter, sunlight and O₃ (Martino et al., 2009) (Figure 12). Whereas the sources and sinks of CO₂, N₂O and DMS are reasonably well established, others remain poorly understood. Marine trace gases play a critical role in atmospheric chemistry and climate-related processes, so it is important to consider the influence of global environmental change on their oceanic flux, and associated feedbacks to climate.



Key: MSA – methanesulfonic acid, OCS – carbonyl sulfide, OVOCs – oxygenated volatile organic compounds.

Figure 12. Overview of the production of marine trace gases and their role in atmospheric and climate processes

Source: Hopkins et al. (2020b).

Results

Experimental evidence: exploring effects of ocean acidification on marine trace gases

Our knowledge of the effects of ocean acidification on marine trace gas production stems from the results of a suite of experimental approaches. These include the following:

- Incubations with single species algal cultures (<1 L, 2–3 replicates, 7–40 d), which serve as a means to establish baseline concepts and identify the most sensitive or relevant physiological processes and mechanisms for trace gas production.
- In situ mesocosm experiments, which allow field-based, community-level assessments of the effects of ocean acidification on natural surface ocean plankton communities (2 400–75 000 L, 1–3 replicates, 25–35 d).
- Shipboard microcosm experiments (5–10 L, 3–12 replicates, 4–10 d), which are multiple short-term experiments carried out over extensive spatial scales enabling the physiological effects of ocean acidification to be assessed as well as the spatial variability in responses of surface ocean communities to future ocean acidification scenarios.

Dimethyl sulfide

DMS is produced in the surface ocean via enzymatic breakdown of the algal and bacterial secondary metabolite dimethylsulfoniopropionate (DMSP) (Curson et al., 2018; Stefels et al., 2007), and is the largest natural source of sulfur to the atmosphere (ocean–atmosphere flux of 15–40 Tg S y⁻¹ (Lana et al., 2011; Wang et al., 2020). Upon entering the atmosphere, DMS is rapidly oxidized to species which contribute to aerosol formation and growth, atmospheric acidity (Charlson et al., 1987; Enami et al., 2016) and the formation and growth of cloud condensation nuclei (Sanchez et al., 2018). Annually averaged DMS-derived aerosol radiative forcing at the top of the atmosphere has been estimated to have a climate cooling effect of between –1.69 W m⁻² (Fiddes et al., 2018) and –1.79 W m⁻² (Mahajan et al.,

2015), compared to the warming effect of +1.83 W m⁻² for CO₂ (Etminan et al., 2016).

Key findings from ocean acidification experiments:

- Single species cultures of algae (7–25 d) (2 seaweed species: *Ulva lactuca* and *U. clathrate*, 3 strains of the well-studied DMSP-producer *Emiliania huxleyi*, 2 species of diatom) exposed to short-term ocean acidification conditions show a variety of physiological responses and both increases and decreases in production of DMSP/DMS (Arnold et al., 2013; Avgoustidi et al., 2012; Kerrison et al., 2012; Spielmeyer and Pohnert, 2012; Webb et al., 2015).
- Shipboard microcosm experiments with natural communities (5–10 L, 7–10 d) (Hopkins and Archer, 2014; Hopkins et al., 2020a; Hussherr et al., 2017) exposed to a range of high CO₂ treatments reported large increases in DMS in experiments in temperate waters, and little or no DMS response in polar experiments (Hopkins et al., 2020), which may imply that polar communities are adapted to, and able to tolerate, large variations in carbonate chemistry, as reflected in the low sensitivity of DMS production to ocean acidification.
- In situ mesocosm experiments (24 000–55 000 L, 25–40 d) were carried out with complex natural planktonic communities, ranging from arctic to sub-tropical latitudes and covering early summer to winter seasons. Experimental-time integrated DMS concentrations (see Figure 13) showed differences between pCO₂ treatments (~350 versus ~750 µatm) of +26% to –42%, with seven of nine experiments showing decreased DMS concentrations with increased acidity.
- Discrepancies in DMS response between different experimental techniques can make interpretation of the overall response challenging, but an understanding of the strengths and weaknesses of each technique, and the specific hypotheses each technique is designed to address, can mitigate this limitation. Short-term microcosm

experiments consider the physiological plasticity of the community (that is, how well its members are adapted to rapidly changing carbonate chemistry) and may aid in the identification of regions sensitive to ocean acidification in terms of DMS production. Longer-term mesocosm experiments allow multigenerational ocean acidification-

induced changes in taxonomy and community structure to affect DMS concentrations, thus revealing how community composition shifts in response to ocean acidification may affect the processes controlling the DMSP/DMS cycling and net production.

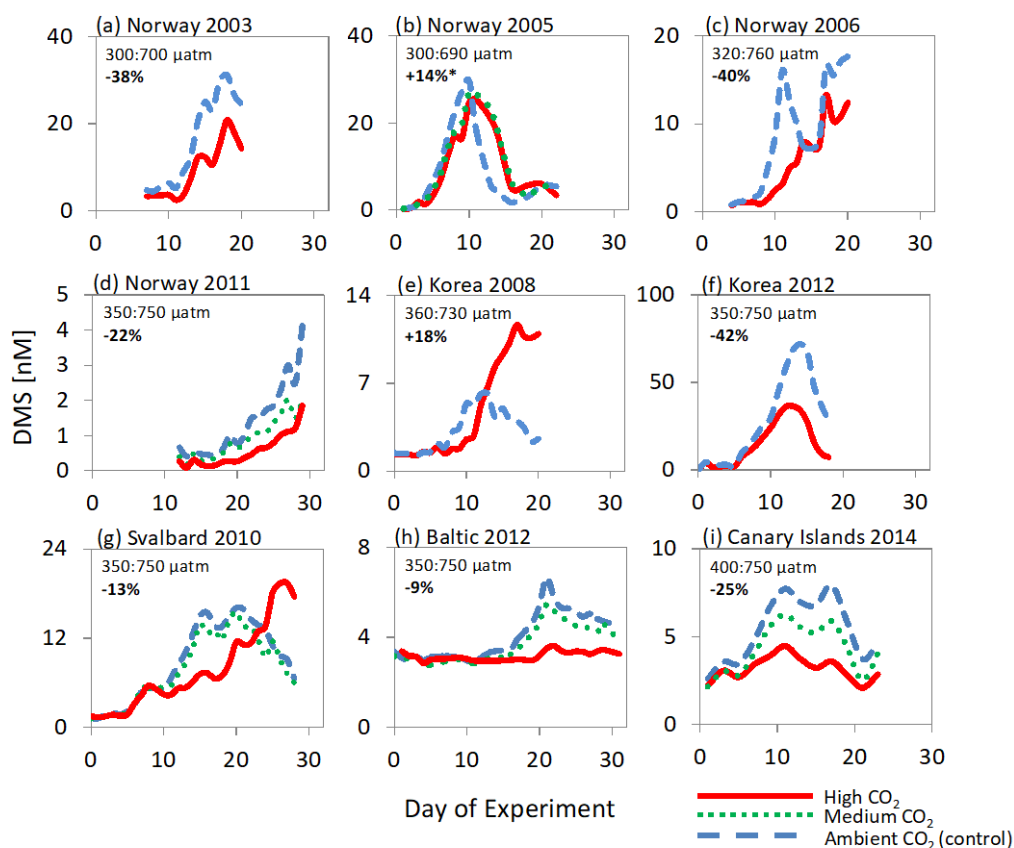


Figure 13. Overview of the DMS response from all published ocean acidification mesocosm experiments carried out under natural environmental conditions, to date.

Four experiments took place in early summer in Raunefjord, Norway (60.3°N, 5.2°E): (a) Avgoustidi et al. (2012), (b) Vogt et al. (2008), (c) Hopkins et al. 2010, (d) Webb et al. (2015). Two took place in the coastal waters of Jangmok, Korea (34.6°N, 128.5°E), one in winter: (e) Kim et al. (2010), and the other in early summer: (f) Park et al. (2014). Single experiments were carried out in (g) summer in the Svalbard Archipelago (78.9°N, 11.9°E): Archer et al. (2013), (h) summer in the Baltic Sea off Finland (59.8°N, 23.2°E): Webb et al. (2016), and (i) late summer in the subtropical North Atlantic (27.9°N, 15.4°W): Archer et al. (2018). To compare results between experiments, the percentage changes in DMS concentrations between the pCO₂ treatments (~350 versus ~750 μatm, shown as a percentage change on each panel) were calculated using time-integrated DMS concentrations over the duration of each experiment. See electronic supplementary material, table S2, in Hopkins et al. (2020a). For experiments (a), (b), (c) and (d), the % response in DMS was calculated from two pCO₂ treatments (duplicate mesocosm for (a) and triplicate for (b–d)); for the remaining experiments, the % response was obtained from the linear fit between pCO₂ and DMS concentration (n = 8 pCO₂ treatments for (e), (f) and (h); n = 6 for (g)).

Notes:

* value not significant at 95% confidence interval.

Source: Hopkins, Suntharalingam et al. (2020).

Nitrogen species: ammonia, methylated amines, alkyl nitrates

Oceanic emissions of the soluble trace gas NH_3 play a role in marine aerosol formation, and the related NH_4^+ provides an inorganic nutrient fundamental to phytoplankton productivity in the surface ocean (Johnson and Bell, 2008; Paulot et al., 2015). Ocean acidification-induced change to oceanic NH_3 production could have a major impact on marine aerosol chemistry over the open ocean, with feedback on atmospheric acidity, Fe solubilization and particle formation (Baker et al., 2021).

Key findings from ocean acidification studies:

- There was decreased availability of gas phase NH_3 for air–sea transfer due to direct effects of ocean acidification on NH_3 and its organic analogues (methylated amines). Decreased seawater pH will result in a shift in $\text{NH}_3:\text{NH}_4^+$ equilibrium towards NH_4^+ , reducing NH_3 concentrations by 50% by the year 2100 assuming a decline in ocean pH from 8.1 to 7.8 (Wyatt et al., 2010).
- Ocean acidification has driven inhibition (by 29%) of marine nitrification of NH_4^+ to NH_3 (Beman et al., 2011, Wannicke et al., 2018) due to an equilibrium shift towards NH_4^+ .
- Nitrogen fixation was enhanced (by 29%) (Das and Mangwani, 2015, Wannicke et al., 2018).
- Uptake of NH_4^+ by diatoms was suppressed (Gu et al., 2017).

Nitrous oxide

Approximately one-third of natural global emissions of the trace gas N_2O originate from the ocean (Menon et al., 2007; Nevison et al., 1995). Nitrous oxide has the third largest global radiative forcing of the anthropogenic greenhouse gases (~ 300 times that of CO_2 on a molecule per molecule basis) (Myhre et al., 2013), and is also a dominant stratospheric ozone-depleting substance (Ravishankara et al., 2009). It is produced primarily via nitrification in the open ocean, as a by-product of the oxidation of NH_4^+ to NO_2^- or as a by-product of the reductive

denitrification pathway in hypoxic and suboxic environments such as oxygen minimum zones and sediments, where O_2 concentrations are sufficient to inhibit N_2O consumption by nitrous oxide reductase enzymes (Babbin et al., 2015; Naqvi et al., 2010).

Key findings from ocean acidification studies:

- Nitrification was inhibited by ocean acidification at Pacific and Atlantic sites over the pH range 8.09–7.42 (Beman et al., 2011).
- In oxic temperate waters, there was no observed relationship between ocean acidification and N_2O concentrations or nitrification rates (Clark et al., 2014).
- In cold temperate and polar waters, there was a decrease in N_2O production rate of 2.4%–44%, corresponding to a pH decrease of 0.06–0.4, directly related to a calculated decrease of 28%–67% in NH_3 substrate for nitrification due to a pH-driven equilibrium shift.
- Ocean acidification-driven changes to marine microbial community composition result in changes to nitrification rates in response to competition for $\text{NH}_4^+/\text{NH}_3$ (Fulweiler et al., 2011) or changes to NH_4^+ oxidation/ N_2O production (Löscher et al., 2012; Santoro et al., 2011).
- Nitrification was reduced by 29%, equating to a global decrease in N_2O production for the next 2–3 decades of 0.06–0.83 Tg N y^{-1} (Wannicke et al., 2018).
- Ocean acidification may have a small negative feedback on climate change via a reduction in radiative forcing attributed to marine N_2O emissions.

Halocarbons

The surface ocean is a key source of short-lived brominated and iodinated organic compounds (halocarbons) to the atmosphere. Marine emissions of halocarbons, dominated by bromoform (CHBr_3), dibromomethane (CH_2Br_2) and methyl iodide (CH_3I) originate from a range

of biological and photochemical processes. These include direct biosynthesis by bacteria (Amachi et al., 2001), phytoplankton (Tokarczyk and Moore, 1994) and macroalgae (Nightingale et al., 1995), and indirect production via reactions between dissolved organic matter and light (Happell and Wallace, 1996; Moore and Zafiriou, 1994) and/or ozone (Martino et al., 2009). Upon entering the atmosphere, halocarbons are rapidly oxidized to release highly reactive halogen radicals (e.g., I, IO, Br, BrO), which exert an important control on tropospheric ozone (Davis et al., 1996; Glasow and Sander, 2002; Read et al., 2008; Solomon et al., 1994) and contribute to the production of new particles and cloud condensation nuclei with the potential to influence climate (Makela et al., 2002).

Key findings from ocean acidification studies:

- According to mesocosm studies, there was no obvious effect of ocean acidification on the production of CHBr_3 or CH_2Br_2 (for example, in temperate waters, the Arctic at Spitsbergen (Hopkins et al., 2010) and brackish waters in the Baltic Sea (Webb et al., 2016)).
- The same studies showed that concentrations of CH_3I were significantly reduced (by up to 67%) under high $p\text{CO}_2$ conditions (Hopkins et al., 2010) in some areas, while in the Baltic Sea, no response was observed (Webb et al., 2016).
- The response of halocarbon production by five tropical seaweed species (important localized sources of halocarbons (Keng et al., 2013; Nightingale et al., 1995)) to four ocean acidification treatments (pH 7.8, 7.6, 7.4, 7.2; ambient pH is ~ 8.0) showed higher halocarbon emission rates under lower pH (Mithoo-Singh et al., 2017).

Ocean acidification sensitive regions

Polar ocean regions

Although ocean acidification is a global phenomenon, it is progressing with greatest speed in regions of the ocean that have naturally high DIC levels and low alkalinity, such as the high-latitude waters of the

Southern Ocean and Arctic (Orr et al., 2005). The polar regions are also important for the production of trace gases, such as DMS, that influence cloud condensation nuclei production and radiative forcing (Jarníková and Tortell, 2016; Leaitch et al., 2013). Thus, any climate change-induced modification to DMS emissions from polar regions could influence radiative forcing at both regional and global scales.

Key findings from ocean acidification studies:

- A mesocosm experiment in Svalbard (78°N) found a 35% decrease in DMS at 750 μatm (Archer et al., 2013), attributed to decreased bacterial DMSP-to-DMS yields.
- Microcosm experiments in Baffin Bay (71°N) found a 25% decrease in DMS at 1500 μatm , attributed to an ocean acidification-related increase in sulfur demand by the bacterial assemblage (Hussherr et al., 2017).
- Little biological effect and minimal DMS response to ocean acidification were found in a series of shipboard microcosm experiments in Arctic and Southern Ocean surface waters (Hopkins et al., 2010), suggesting a high level of resilience to changes in the carbonate chemistry environment within the sampled communities.

Eastern boundary upwelling systems

Eastern boundary upwelling systems (EBUSs) (for example, the California and Peru/Humboldt EBUS in the Pacific, and the Canary and Benguela EBUS in the Atlantic) are considered particularly susceptible to ocean acidification, given the combined effects of their naturally high DIC concentrations and enhanced uptake of anthropogenic CO_2 (Feely et al., 2008). EBUSs are also considered to be 'hot spots' for emissions of marine trace gases (Löscher et al., 2016; Naqvi et al., 2010; Nevison et al., 2004; Ohde and Dadou, 2018; Weeks et al., 2002;). However, little experimental work has been conducted on ocean acidification in EBUSs (see, for example, Frame et al. (2017)), and the impact on trace gas production in these regions is still highly uncertain.

Multi-stressor effects

Ocean acidification is not occurring in isolation to other global environmental changes. In addition to having taken up ~28% of the excess anthropogenic CO₂ since 1750, the ocean has also absorbed ~93% of the excess heat over the past 45 years (Gattuso et al., 2015). Warming enhances metabolic rates (López-Urrutia et al., 2006; O'Connor et al., 2009) and decreases the solubility of gases, resulting in decreasing global ocean oxygen inventories (Bopp et al., 2013). Warming and freshening enhances surface ocean stratification (Capotondi et al., 2012), which in turn decreases mixed layer depth and reduces the entrainment of nutrients into the euphotic layer, while resulting in higher levels of irradiance experienced by organisms (Bopp et al., 2013). Numerous modelling studies have addressed future changes in marine ecosystems and biogeochemistry in response to these drivers, either in isolation or combined (Barton et al., 2016; Bopp et al., 2013; Dutkiewicz et al., 2015). Below, we describe the few that have focused on trace gas emissions and ocean acidification-related feedbacks to the Earth system (Gehlen et al., 2011; Schwinger et al., 2017; Six et al., 2013).

Earth system feedbacks

Changing dimethyl sulfide emissions

Although experimental data provide useful information on the potential future DMS response to ocean acidification, these data become most powerful when included in an ESM to facilitate upscaling and estimation of feedbacks of projected changes in DMS emissions on future climate. Two studies have used ESMs to provide evidence for a potential positive climate feedback arising from pH sensitivity in DMS production (Schwinger et al., 2017; Six et al., 2013):

- A baseline high emission scenario (RCP 8.5) led to average surface pH reductions of 0.44 units in the year 2100 and 0.73 units in the year 2200. The corresponding reduction of DMS fluxes is 4 Tg S y⁻¹ (17%) in 2100 and 7.3 Tg S y⁻¹ (31%) in 2200.
- By 2100, major pH-induced reductions are predicted in DMS production for areas of high biological production,

such as the upwelling equatorial Pacific and other EBUS, the eddy-driven upwelling in the Southern Ocean around 40°S and the subpolar biome in the North Atlantic.

- Significant radiative forcing and surface warming are predicted in response to the decreased DMS flux to the atmosphere and subsequent changes in aerosol and cloud properties (transient surface temperature change of -0.041 °C Tg S⁻¹ y⁻¹).

Marine nitrogen cycle feedbacks

Current model projections suggest a future decline in global marine N₂O emissions (of 4%–24%) and a small negative feedback to climate change (Landolfi et al., 2017; Martinez-Rey et al., 2015). However, these analyses do not account for the influences of ocean acidification due to limited evidence for direct effects, and they have limited capability to assess key influences on the marine nitrogen cycle such as deoxygenation. Elucidating these influences will require a combination of improved process knowledge and incorporation of this knowledge into more representative biogeochemical process models.

Conclusions and recommendations for future research

Marine trace gas emissions strongly influence atmospheric chemistry and climate. The changes in net production of some trace gases, such as DMS and N₂O, indicated in ocean acidification studies and models, point to potentially large and globally significant modifications to air–sea fluxes. This could lead to either warming (for example, via lower DMS emissions) or cooling (for example, via lower N₂O emissions) effects on climate. Where data for other trace gases are scant, we cannot yet be confident in the direction of change, but we can have greater certainty that there is the potential for impacts on net production, and therefore on chemistry and climate, with global-scale effects.

We outline several recommendations for future research to improve understanding of the effects of ocean acidification on marine trace gases, and improve upon the current use of empirical relationships in predictive models:

- Longer-term experimental studies encompassing multiple generations to detect adaptation of planktonic communities to ocean acidification and other climate change stressors. These studies would include parallel measurements of process rates and standing stocks of trace gases to provide greater insight into the role of ocean acidification in influencing trace gas production.
- Further ecological-level experiments (for example, mesocosms) which provide important information on the role of species interactions and succession on trace gas production.
- The integration of multiple stressors into all future experimental designs to close some of the gaps in our understanding of the trace gas response to climate change.
- Future surface ocean measurements of trace gases accompanied by quantification of at least two components of the carbonate system. This would make it possible to use global databases to relate spatial variability in trace gas concentrations to variations in surface ocean pH and increase our understanding of the influence of the carbonate system on trace gas concentrations in the surface ocean.

2.6 **Summary of “Changing atmospheric acidity as a modulator of nutrient deposition and ocean biogeochemistry”**

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Introduction

Atmospheric deposition supplies nutrients such as N, P and Fe to the ocean. The quantities of nutrients supplied in this way are sufficient to affect ocean productivity. Anthropogenic emissions of NO_x and NH₃, generated from combustion (NO_x) and agricultural activities (NO_x and NH₃), dominate the atmospheric N cycle. Wind-blown mineral dust, predominantly generated by processes associated with desert regions, is a major source of bioactive trace elements (e.g., P, Fe, Cu, Co, Ni, Cd, Zn) to the atmosphere. There are also significant anthropogenic emissions of some of these elements (Fe, Cu, Zn, Cd, Ni).

Airborne nutrients are removed from the atmosphere by processes of dry and wet deposition. The deposition rate of the nutrient is determined by whether it is in the gas phase (primarily N) or contained in aerosol particles (N, P, Fe, etc.), together with the solubility of nutrient-bearing particles in water (which affects their incorporation into precipitation). This determines atmospheric lifetime and thus the geographic distribution of deposition.

The atmospheric flux of N to the ocean has at least doubled since the Industrial Revolution. Anthropogenic emissions of NO_x and SO₂ have also substantially increased the acidity of the atmosphere over this period. Most of the deposited N is readily available to the phytoplankton communities of the ocean, while much of the P, Fe and other trace elements contained in dust have limited solubility and thus are less accessible to phytoplankton. Laboratory experiments, ambient observations and modelling all suggest that the soluble fraction of this latter group of nutrients increases as dust is transported as a result of a solubility-enhancing reaction with acidic constituents in the atmosphere.

Anthropogenic emissions therefore directly (in the case of N) and indirectly (through acidification and other effects discussed below) impact the atmospheric supply of nutrients to the ocean. This supply has changed in magnitude and distribution as a consequence of global industrialization and will continue to evolve over time with economic development and changes in regulatory emissions frameworks. This study examines the impact of changing

atmospheric acidity on the delivery of available nutrients to the ocean and the expected effects of these changes on the biogeochemistry of the ocean.

What controls acidity in the atmosphere?

Acidity for any atmospheric particle is directly related to the concentration of hydronium ion (H_3O^+ , or H_{aq}^+ for simplicity) in the aqueous phase of aerosol particles or cloud droplets):

$$\text{pH} = -\log_{10} \gamma_{\text{H}^+} H_{aq}^+ = -\log_{10} \frac{1000 \gamma_{\text{H}^+} H_{air}^+}{W} \quad (2)$$

where γ_{H^+} is the hydronium ion activity coefficient, H_{aq}^+ (mol L^{-1}) is its concentration in aerosol or cloud water, H_{air}^+ ($\mu\text{g m}^{-3}$) is its concentration per volume of air and W ($\mu\text{g m}^{-3}$) is the particle water content.

The two main drivers of pH are W and H_{aq}^+ . W in clouds is driven by the meteorology (large-scale cooling rate). For aerosol, W is governed by the amount of soluble species with which water is associated (given that it is in chemical equilibrium with water vapour) and the relative humidity. H_{aq}^+ is controlled by the relative amounts and nature of dissolved ions present in the solution.

Sulfuric acid (formed through oxidation of SO_2) is the primary strong acid in the atmosphere. Because of its extremely low volatility, it resides almost exclusively in aerosol and cloud particles. It is partially neutralized by the uptake of NH_3 from the gas phase to form NH_4^+ ions and by non-volatile cations (e.g., K^+ , Na^+ , Ca^{2+} , Mg^{2+}) found in sea salt and mineral dust. The latter cations can also react with acidic gases, including HCl and HNO_3 , and affect the acidity of aerosol and droplets.

Aerosol particles and cloud and rain droplets have very different acidities and responses to changes in acidity, largely because of their very different liquid water contents (W). Cloud and rain waters are relatively dilute solutions, with substantially lower acidity (as much as 4 pH units) than aerosols. Acidity also varies strongly depending on aerosol particle size, with smaller particles generally being more acidic. This causes acid processing that increases trace element solubility to be

most efficient in the 1 μm to 2.5 μm particle diameter range.

In some regions, emissions controls have led to a reduction in the acidity of rain and cloud water. However, fine aerosols remain acidic due to the buffering effect of NH_3 – when aerosol sulfate decreases, the $\text{NH}_3/\text{NH}_4^+$ gas-to-particle partitioning shifts in favour of gas phase NH_3 and regulates aerosol pH.

How does acidity affect nutrients in the atmosphere?

Figure 14 summarizes how natural and anthropogenic inputs to the atmosphere affect atmospheric acidity and nutrient levels, and how their interactions impact the supply of bioavailable (labile) nutrients to the ocean. Emissions of NH_3 , NO_x , SO_2 and dust influence atmospheric acidity, while dust, anthropogenic trace element emissions (abbreviated as Fe in the figure), and anthropogenic and biological sources of P, NH_3 and NO_x contribute to the atmospheric nutrient/trace element burden. Most sources are terrestrial, although ship-based emissions of Fe and NO_x are important, and marine emissions of DMS are a significant source of SO_2 , particularly in the southern hemisphere. Acidity-driven atmospheric processing alters the labile nutrient flux to the ocean, either by affecting gas–aerosol partitioning or by altering the labile fractions of Fe (L-Fe), P (L-P) and trace metals (L-TM). Organic N compounds (OrgN) are also generated during atmospheric processing, but they are not discussed here.

Acidity controls the distribution of N-containing species between the gas and aerosol phases. Uptake of NH_3 into the aerosol phase is driven in many locations by the amount of aerosol sulfate, with an increase in atmospheric sulfate leading to a decrease in the proportion of total NH_x ($\text{NH}_3 + \text{NH}_4^+$) present as gaseous NH_3 . However, if the acidity is sufficiently low and liquid water content sufficiently high, the partitioning of HNO_3 to aerosol phase NO_3^- is promoted, during which nitrate then becomes a controlling factor for NH_x partitioning as well. The atmospheric lifetimes of NH_3 and NH_4^+ (and NO_3^- and HNO_3) are significantly different; hence aerosol acidity and liquid water changes affect the long-range transport of NH_x and total NO_3 ($\text{NO}_3^- + \text{HNO}_3$).

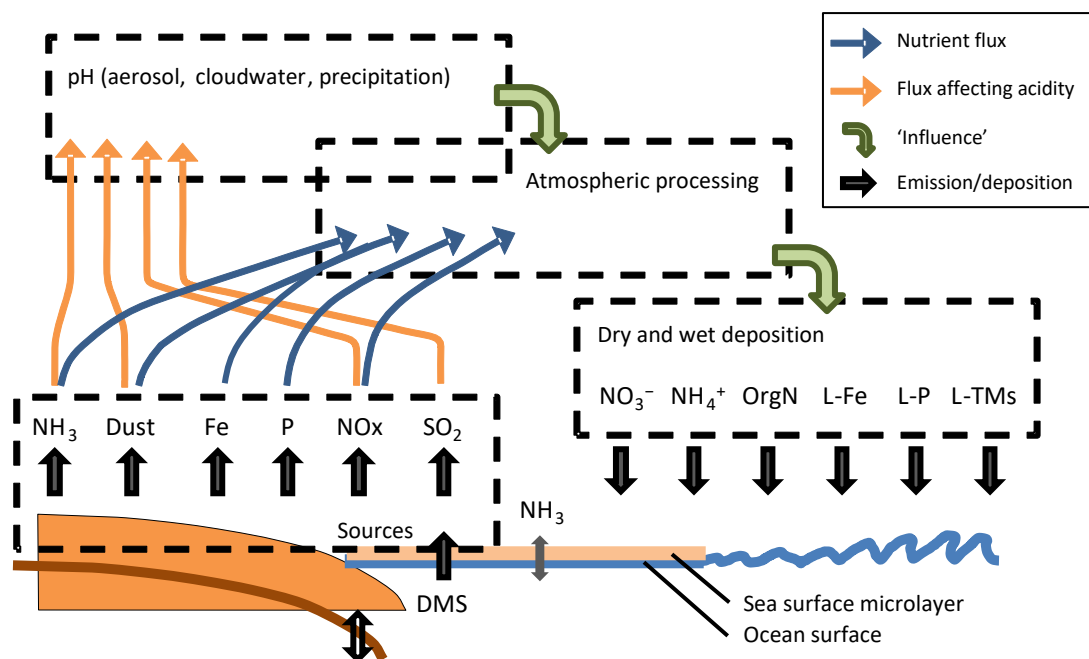


Figure 14. Overview of the atmospheric acidity, nutrient and trace element cycles

Source: Baker et al. (2021).

The soluble fraction of many trace elements in mineral dust is low when they first enter the atmosphere but increases during transport as dust is exposed to atmospheric processing. Acids and organic complexing agents can help to sustain high Fe solubility in solution, although organic complexation of Fe becomes less important as acidity increases. Combustion sources appear to have a disproportionate impact on soluble trace elements in the atmosphere because they emit both highly soluble trace elements (such as Fe) associated with fine aerosol particles and acids that may further enhance solubility.

How does acidity change affect nutrient deposition to the ocean?

A global model of atmospheric chemistry was used to examine the effects of changing acidity on nutrient deposition to the ocean for the years 1850, 2010 and 2100. The model (TM4-ECPL) has been extensively evaluated against observations for acidity and deposition of N, P and Fe.

Since the Industrial Revolution, aerosol acidity has increased substantially over

broad regions of the mid-latitude northern hemisphere ocean, especially over the margins of the North Atlantic and North Pacific (Figures 15(a) and (b)). This increase in acidity has increased the proportion of NH_x as aerosol NH_4^+ and decreased the proportion of total NO_3 as aerosol NO_3^- . These shifts in partitioning increased the atmospheric lifetime of NH_x and decreased the lifetime of total NO_3 , with significant changes for total NO_3 over the mid-latitude northern hemisphere ocean regions. Thus, increased acidity causes NH_x to be deposited farther away from its sources, while causing total NO_3 to be transported over shorter distances. Changes in partitioning also affect the deposition mode for N, as illustrated by the changes in the ratio of wet to total deposition flux for NH_x and total NO_3 (Figures 15(c) and (d)). Therefore, atmospheric acidity controls both the spatial distribution of N deposition and its deposition mode, while the total magnitude of N deposition varies in response to emissions changes.

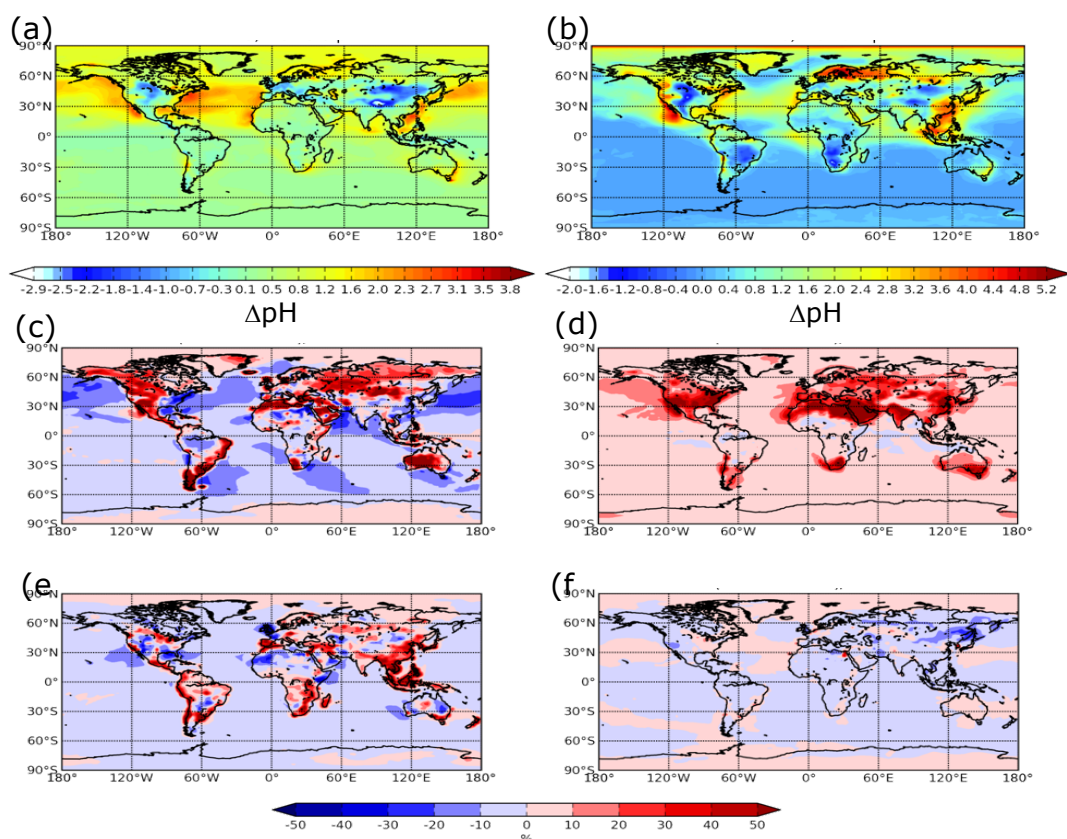


Figure 15. Impact of anthropogenic and biomass burning emissions changes (1850 to 2010) on aerosol pH and nutrient wet deposition fractions. Change in the annual mean near-surface (a) fine aerosol pH and (b) coarse aerosol pH, and change in the fractions of (c) wet NH_4^+ to total NH_x , (d) wet NO_3^- to total NO_3 , (e) wet LFe to total LFe and (f) wet L-P to total L-P between 1850 and 2010. Panels (c)–(f) show the difference between 1850 and 2010, expressed as a percentage of the 2010 condition. Negative values denote higher values in 2010 than in 1850.

Source: Baker et al. (2021).

According to the model simulations, the fraction of total NO_3 global deposition that is deposited to the ocean (total NO_3 deposited to the ocean/global total NO_3 deposition) has been reduced by about 10% since 1850 and will increase by about 5% by 2100. The equivalent fraction of total NH_x deposition entering the ocean decreased by 32% from 1850 to the present and is projected to decrease by a further 9% by 2100, but these changes are predominantly due to changes in NH_x emissions rather than changes in acidity.

The model results also indicate that the proportion of total LFe deposition that is mainly due to solubilization by acids in the atmosphere increased from 30% to 35% between 1850 and 2010 and is projected to decrease to 20% by 2100 (under RCP 6.0). Corresponding values for P deposition are 28% (1850), 32% (2010) and 26% (2100).

The total labile fluxes of Fe and P were projected to have increased by 34% (Fe) and 27% (P) since 1850 and are projected to decrease by 14% (Fe) and 13% (P) by 2100. Acid processing also affects the hygroscopicity of aerosol particles, which leads to changes in the proportions of LFe and P in wet deposition (Figures 15(e) and (f)).

The specific impact of these changes in labile nutrient deposition fluxes and distribution varies between N, P and Fe; therefore, acidity change alters the N:P and N:Fe ratios of atmospheric deposition (in addition to changes in these ratios induced by emissions changes over time).

What are the implications of these changes in nutrient deposition to the ocean?

Atmospheric deposition must pass through the sea-surface microlayer (SML) before reaching bulk seawater. The SML transition zone exhibits large gradients in pH and inorganic and organic complexing agents and contains a microbial community that is very different from that of bulk seawater. Inputs of N are readily soluble in seawater, but this is not the case for Fe, P and other trace metals. Organic complexation is known to stabilize dissolved Fe (and other metals) in seawater, so the organic complexing agents in atmospheric deposition may be important in maintaining Fe in soluble form once deposited. Not enough is known about the properties of the SML to predict the influence of decreasing atmospheric acidity (which will occur concurrently with ocean acidification) on the SML's impact on atmospheric nutrient deposition. Rainfall can disrupt the SML, so acidity-induced changes in deposition mode can also affect the atmosphere-to-bulk seawater nutrient transfer process.

Changes in nutrient supply ratios (N:P, N:Fe, P:Fe) from atmospheric deposition over the timescale considered here may alter phytoplankton communities (affecting taxonomy and nutritional quality) and lead to wider ecological changes in the ocean. For instance, coupling the global N, Fe and P deposition fluxes presented here to an ocean biogeochemistry model has indicated a shift from diatom to nanophytoplankton production in the north-eastern Pacific and an increase in primary production of 2.6% in the global ocean and up to 20% in the northern hemisphere subtropical gyres since 1850.

Conclusions and recommendations for future work

Changing emissions from industry, agriculture and biomass burning have had substantial impacts on the acidity of the atmosphere, and these emissions will continue to change for decades to come. Acidity, in turn, affects the magnitude, distribution and mode of deposition of nutrients deposited into the ocean, and the relative proportions in which nutrients are received by the ocean. Changes in deposition mode will alter the way in which

atmospheric deposition interacts with the SML. Overall, these changes in nutrient supply will affect the microbial ecology and productivity of the ocean and should be considered as one of a number of stressors on the ocean, together with ocean warming, ocean deoxygenation and ocean acidification.

Recommendations for future work in this area include:

- High-frequency long-term monitoring of atmospheric composition over representative regions of the remote ocean (essential for understanding the impacts of long-term changes).
- Systematic observations of wet deposition. This is the dominant input across large areas of the global ocean, but its amounts and composition are very poorly sampled.
- Direct observations of aerosol pH.
- Improved understanding of trace element solubility in aerosols.
- Better understanding of the role of the SML in the air-to-sea transfer of nutrients and trace elements, and the inclusion of these processes in biogeochemical models.
- Improvements in knowledge of the complex interactions that lead to nutrient co-limitation in marine microbial communities.

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ANNEX 1. AGENDAS

Agendas for the two workshops on the changes in the acid/base balance of the atmosphere and ocean and their subsequent impacts on air-sea chemical exchange

Agenda (Plenary session for both workshops)

Monday, 27 February 2017
Environmental Sciences Seminar Room
University of East Anglia, Norwich, United Kingdom

9 a.m.– 9.30 a.m.	Introduction and local logistics	Tim Jickells, Co-Chair, WG 38
9.30 a.m.– 10 a.m.	What is GESAMP?	Peter Kershaw, Chair, GESAMP
10 a.m.– 10.30 a.m.	Working Group 38 and its activities	Robert Duce, Co-Chair, WG 38
10.30 a.m.	Coffee and move to the Blackdale Bldg	

Agenda of Workshop 1. Changing Atmospheric Acidity and the Oceanic Solubility of Nutrients
Co-Chairs: Alex Baker and Manmohan Sarin

Terms of reference:

- Review and synthesize the current scientific information on the solubility of aerosol associated key biogeochemical elements, the biogeochemical controls on aerosol solubility and the pH sensitivity of those controls.
- Consider the likely changes in solubility of key species in the future and the potential biogeochemical consequences of such changes.
- Identify the key future research needs to reduce uncertainties in predictive capability in this area.
- Publish the results of this activity in the open peer-reviewed scientific literature.
- Interact with and provide information to leading relevant international groups including the Future Earth core

projects SOLAS (Surface Ocean–Lower Atmosphere Study), IGAC (International Global Atmospheric Chemistry) and IMBER (Integrated Marine Biosphere Research); SCOR, particularly its GEOTRACES programme; and WMO programmes such as GAW.

Monday, 27 February 2017
Blackdale Building
University of East Anglia, Norwich, United Kingdom

11 a.m.– 12.30 p.m.	Introduction	Alex Baker and Manmohan Sarin, WG 38
12.30 p.m.– 13.15 p.m.	Lunch	
13.15 p.m.– 17.30 p.m.	Initial discussion presentations	Robert Duce, Co-Chair, WG 38

Underlying chemical controls on nutrient/trace element solubility
(David Turner)

Potential changes in relevant emissions and their likely impact on atmospheric acidity
(Maria Kanakidou)

Model schemes for simulating the influence of acidity of nutrient/trace element solubility
(Thanos Nenes and Akinori Ito)

Modelled nutrient/trace element deposition fields
(Natalie Mahowald and Stelios Myriokefalitakis)

Ocean regions likely to be impacted by atmospheric nutrient/trace element supply
(Peter Croot and Cecile Guieu)

Tuesday, 28 February 2017
Blackdale Building
University of East Anglia, Norwich, United Kingdom

9 a.m.– 10.30 a.m.	Conclude discussion presentations (if necessary) and begin open discussion. Where do we go from here?
10.30 a.m.– 10.45 a.m.	Coffee break
10.45 a.m.– 12.30 p.m.	Continuing evaluation of workshop science questions and how to focus publications
12.30 p.m.– 13.15 p.m.	Lunch

13.15 p.m.– 15.30 p.m.	We will continue with a flexible schedule, if appropriate splitting into smaller topic groups. The aim will be to go with the science flow, but with an ultimate goal of developing one or more topical review papers.
15.30 p.m.– 15.45 p.m.	Tea break
15.45 p.m.– 17.30 p.m.	Continuing discussions and end-of-day stock-take

Wednesday, 1 March 2017

*Blackdale Building
University of East Anglia, Norwich, United Kingdom*

9 a.m.– 10.30 a.m.	Continuing discussions
10.30 a.m.– 10.45 a.m.	Coffee break
11 a.m.– 12.30 p.m.	Continuing discussions
12.30 p.m.– 13.15 p.m.	Lunch
13.15 p.m.– 15.30 p.m.	Continuing discussions/planning
15.30 p.m.– 15.45 p.m.	Tea break
15.45 p.m.– 17.30 p.m.	Continuing discussions/planning/writing and end-of-day stock-take

Thursday, 2 March 2017

*Blackdale Building
University of East Anglia, Norwich, United Kingdom*

9 a.m.– 12.30 p.m.	Discussion, assignment of writing tasks and plenary session
12.30 p.m.– 13.15 p.m.	Lunch and close of workshop

Agenda of Workshop 2. Impact of Ocean Acidification on Fluxes of non-CO₂ Climate-active Species

Tri-Chairs: Parv Suntharalingam, Marion Gehlen and Frances Hopkins

Terms of reference

- Review and synthesize the current science on the direct impacts of ocean acidification on marine production and emissions to the atmosphere of key species important for climate and atmospheric chemistry.
- Identify the primary needs for new research to improve process understanding and to quantify the impact of ocean acidification on these marine fluxes (that is, provide

recommendations on the specific laboratory process studies, field measurements and model analyses needed to support targeted research activities and improved understanding on this topic).

- Publish the results of this activity in the open peer-reviewed scientific literature.
- Provide input to and interact with national and international research programmes on ocean acidification (for example, the UK Ocean Acidification (UKOA) research programme, the US National Oceanic and Atmospheric Administration Ocean Acidification Program (NOAA-OAP)) and with relevant WMO programmes (for example, Global Atmosphere Watch (GAW)) to build on their recent relevant activity in achieving the above-mentioned objectives.

Monday, 27 February 2017

*Blackdale Building
University of East Anglia, Norwich, United Kingdom*

12.30 p.m.– 13.15 p.m.	Lunch
13.15 p.m.– 17.30 p.m.	Initial discussion presentations

*Introduction to Ocean-Acidification and non-CO₂ Trace-Gas Session
(Chair: Parv Suntharalingam)*

Introduction and workshop aims (Parv Suntharalingam)

*Overview of recent progress in ocean acidification research
(talks of ~30 minutes, including 5 minutes for discussion)*

*Lessons learned from the UK Ocean Acidification research programme
(Phil Williamson)*

Challenges and tools for ocean acidification research (Cliff Law)

Trace gases (non-CO₂) and ocean acidification: overview of experimental methodologies (Frances Hopkins)

1530–1600	Tea break
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Ocean Acidification Impacts on Ocean Biogeochemistry and Ecosystems
(talks of ~30 minutes, including 5 minutes for discussion)

Ocean acidification: biogeochemical impacts and feedbacks to the Earth system
(Marion Gehlen)

Re-evaluation of enhanced export production by carbon overconsumption under high CO₂
(Kitack Lee)

Indirect impact of ocean acidification on trace gases through pteropod mortality/aragonite dissolution (Erik Buitenhuis)

Tuesday, 28 February 2017

Blackdale Building
University of East Anglia, Norwich, United Kingdom

9.00 a.m.– 12.30 p.m.	Initial discussion presentations (continued)
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Ocean Acidification Influences on Trace Gases: Chair: Frances Hopkins
(talks of 20–30 minutes, including 5 minutes for discussion)

Metabolism of trace gases: the importance of metals
(Colin Murrell)

Reactive trace gases: DMS and halocarbons

Effects of ocean acidification on marine DMS emissions: results from experimental studies (Steve Archer)

Ocean acidification and DMS: what can we learn from cultures?
(Gill Malin)

Influence of ocean acidification on biogenic short-lived halocarbons by marine algae
(Fiona Keng)

10.30 a.m.– 11.00 a.m.	Coffee break
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Methane, N₂O and the Nitrogen Cycle

Impact of ocean acidification on N₂O and CH₄
(Andy Rees)

Ocean acidification impacts on the nitrogen cycle
(Cliff Law)

Modelling impacts of ocean acidification on organic matter stoichiometry: implications for marine nitrous oxide production
(Oliver Andrews)

Ammonia, pH and interactions with the sulphur cycle
(Martin Johnson)

Impact of deoxygenation and ocean acidification on N₂O and CH₄
(Hema Naik)

12.30 p.m.– 13.30 p.m.	Lunch
13.30 p.m.– 17.30 p.m.	Continue session after lunch if needed

Trace-gas Synthesis for Workshop Paper: Break-out groups to work on individual trace-gas sections of summary paper. Suggested breakout groups:
(a) Short-lived species (DMS, halocarbons); and (b) CH₄, N₂O.

Aims: Produce summary from observational perspective for the different species, drawing on available observations, lab and in-situ studies. Identify information on process controls. Identify data gaps.

Wednesday, 1 March 2017

Blackdale Building
University of East Anglia, Norwich, United Kingdom

9.00 a.m.– 10.30 a.m.	Discussion, presentations (continued)
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Trace Gases and Multiple Stressors: Chair: Marion Gehlen (talks of 20–30 minutes, including 5 minutes for discussion)

Expected response of greenhouse gases to multiple stressors: thoughts on an experimental approach
(Andy Rees)

Expected response of trace gas emissions to multiple stressors: insights from ocean biogeochemical models
(Laurent Bopp)

Amplification of global warming through pH-dependence of DMS-production
(Nadine Goris)

10.30 a.m.– 11.00 a.m.	Coffee
11.00 a.m.– 12.30 p.m.	---

Regions Vulnerable to the Impacts of Ocean Acidification: High Latitudes, Coastal and Upwelling Zones: Chair: Frances Hopkins (talks of 20–30 minutes, including 5 minutes for discussion)

Ocean acidification in the Arctic Ocean and its impacts on DMS cycling
(Martine Lizotte)

DMS concentrations in the polar oceans are resilient to short-term ocean acidification
(Frances Hopkins)

Nitrogen cycle dynamics in upwelling zones
(Isabelle Dadou)

12.30 p.m.– 13.15 p.m.	Lunch
13.15 p.m.– 17.30 p.m.	---

Knowledge Gaps and Uncertainties, and Future Research Needs

- Reports from rapporteurs: synthesis of key points from previous sessions
- Break-out sessions to work on the following for summary paper:
 - Main knowledge gaps, uncertainties and challenges
 - Future research needs: observational programmes, experimental methods and requirements for improved model predictions

Contributors: All participants

Thursday, 2 March 2017

Blackdale Building

University of East Anglia, Norwich, United Kingdom

9.00 a.m.– 12.30 p.m.	Workshop paper synthesis activities Report back to Bob/Tim and WG 38
12.30 p.m.– 13.15 p.m.	Lunch – Close of workshop

ANNEX 2. PARTICIPANTS AT THE TWO GESAMP 38 WORKSHOPS

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ANNEX 3. GESAMP REORTS AND STUDIES

The following reports and studies have been published to date by GESAMP They are available from the GESAMP website: <http://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
2. Review of harmful substances. (1976). Rep. Stud. GESAMP (2): 80 p.
3. Scientific criteria for the selection of sites for dumping of wastes into the sea. (1975). Rep. Stud. GESAMP (3): 21 p. Available also in French, Spanish and Russian
4. Report of the eighth session, Rome, 21-27 April 1976. (1976). Rep. Stud. GESAMP (4): pag.var. Available also in French and Russian
5. Principles for developing coastal water quality criteria. (1976). Rep. Stud. GESAMP (5): 23 p.
6. Impact of oil on the marine environment. (1977). Rep. Stud. GESAMP (6): 250 p.
7. Scientific aspects of pollution arising from the exploration and exploitation of the seabed. (1977). Rep. Stud. GESAMP (7): 37 p.
8. Report of the ninth session, New York, 7-11 March 1977. (1977). Rep. Stud. GESAMP (8): 33 p. Available also in French and Russian
9. Report of the tenth session, Paris, 29 May - 2 June 1978. (1978). Rep. Stud. GESAMP (9): pag.var. Available also in French, Spanish and Russian
10. Report of the eleventh session, Dubrovnik, 25-29 February 1980. (1980). Rep. Stud. GESAMP, (10):pag.var. Available also in French and Spanish
11. Marine Pollution implications of coastal area development. (1980). Rep. Stud. GESAMP (11): 114 p.
12. Monitoring biological variables related to marine pollution. (1980). Rep. Stud. GESAMP (12): 22 p. Available also in Russian
13. Interchange of pollutants between the atmosphere and the oceans. (1980). Rep. Stud. GESAMP (13): 55 p.
14. Report of the twelfth session, Geneva, 22-29 October 1981. (1981). Rep. Stud. GESAMP (14): pag.var. Available also in French, Spanish and Russian
15. The review of the health of the oceans.(1982). Rep. Stud. GESAMP (15): 108 p.
16. Scientific criteria for the selection of waste disposal sites at sea. (1982). Rep. Stud. GESAMP (16): 60 p.
17. The evaluation of the hazards of harmful substances carried by ships. (1982). Rep. Stud. GESAMP (17): pag.var.
18. Report of the thirteenth session, Geneva, 28 February - 4 March 1983. (1983). Rep. Stud. GESAMP (18): 50 p. Available also in French, Spanish and Russian
19. An oceanographic model for the dispersion of wastes disposed of in the deep sea. (1983). Rep. Stud. GESAMP (19): 182 p.

20. Marine pollution implications of ocean energy development. (1984). Rep. Stud. GESAMP (20): 44 p.
21. Report of the fourteenth session, Vienna, 26-30 March 1984. (1984). Rep. Stud. GESAMP (21): 42 p. Available also in French, Spanish and Russian
22. Review of potentially harmful substances. Cadmium, lead and tin. (1985). Rep. Stud. GESAMP (22): 114 p.
23. Interchange of pollutants between the atmosphere and the oceans (part II). (1985). Rep. Stud. GESAMP (23): 55 p.
24. Thermal discharges in the marine Environment. (1984). Rep. Stud. GESAMP (24): 44 p.
25. Report of the fifteenth session, New York, 25-29 March 1985. (1985). Rep. Stud. GESAMP (25): 49 p. Available also in French, Spanish and Russian
26. Atmospheric transport of contaminants into the Mediterranean region. (1985). Rep. Stud. GESAMP (26): 53 p.
27. Report of the sixteenth session, London, 17-21 March 1986. (1986). Rep. Stud. GESAMP (27): 74 p. Available also in French, Spanish and Russian
28. Review of potentially harmful substances. Arsenic, mercury and selenium. (1986). Rep. Stud. GESAMP (28): 172 p.
29. Review of potentially harmful substances. Organosilicon compounds (silanes and siloxanes). (1986). Published as UNEP Reg. Seas Rep. Stud. (78): 24 p.
30. Environmental capacity. An approach to marine pollution prevention. (1986). Rep. Stud. GESAMP (30): 49 p.
31. Report of the seventeenth session, Rome, 30 March - 3 April 1987. (1987). Rep. Stud. GESAMP (31): 36 p. Available also in French, Spanish and Russian
32. Land-sea boundary flux of contaminants: contributions from rivers. (1987). Rep. Stud. GESAMP (32): 172 p.
33. Report on the eighteenth session, Paris, 11-15 April 1988. (1988). Rep. Stud. GESAMP (33): 56 p. Available also in French, Spanish and Russian
34. Review of potentially harmful substances. Nutrients. (1990). Rep. Stud. GESAMP (34): 40 p.
35. The evaluation of the hazards of harmful substances carried by ships: Revision of GESAMP Reports and Studies No. 17. (1989). Rep. Stud. GESAMP (35): pag.var.
36. Pollutant modification of atmospheric and oceanic processes and climate: some aspects of the problem. (1989). Rep. Stud. GESAMP (36): 35 p.
37. Report of the nineteenth session, Athens, 8-12 May 1989. (1989). Rep. Stud. GESAMP (37): 47 p. Available also in French, Spanish and Russian
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