

Evolving research directions in Surface Ocean–Lower Atmosphere (SOLAS) science

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Environmental context. Understanding the exchange of energy, gases and particles at the ocean–atmosphere interface is critical for the development of robust predictions of, and response to, future climate change. The international Surface Ocean–Lower Atmosphere Study (SOLAS) coordinates multi-disciplinary ocean–atmosphere research projects that quantify and characterise this exchange. This article details five new SOLAS research strategies – upwellings and associated oxygen minimum zones, sea ice, marine aerosols, atmospheric nutrient supply and ship emissions – that aim to improve knowledge in these critical areas.

Abstract. This review focuses on critical issues in ocean–atmosphere exchange that will be addressed by new research strategies developed by the international Surface Ocean–Lower Atmosphere Study (SOLAS) research community. Eastern boundary upwelling systems are important sites for CO₂ and trace gas emission to the atmosphere, and the proposed research will examine how heterotrophic processes in the underlying oxygen-deficient waters interact with the climate system. The second regional research focus will examine the role of sea-ice biogeochemistry and its interaction with atmospheric chemistry. Marine aerosols are the focus of a research theme directed at understanding the processes that determine their abundance, chemistry and radiative properties. A further area of aerosol-related research examines atmospheric nutrient deposition in the surface ocean, and how differences in origin, atmospheric processing and composition influence surface ocean biogeochemistry. Ship emissions are an increasing source of aerosols, nutrients and toxins to the atmosphere and ocean surface, and an emerging area of research will examine their effect on ocean biogeochemistry and atmospheric chemistry. The primary role of SOLAS is to coordinate coupled multi-disciplinary research within research strategies that address these issues, to achieve robust representation of critical ocean–atmosphere exchange processes in Earth System models.

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Introduction

The exchange of energy, gases and particles across the air–sea interface is controlled by a variety of biological, chemical and physical processes that operate across a broad range of spatial and temporal scales. These influence the composition and biogeochemical processes of both phases and ultimately interactions and feedbacks with the climate system. The significance of this exchange across the air–sea interface is readily apparent in global budgets; for example, the oceans have taken up ~48 % of the anthropogenic CO₂ released into the atmosphere since the late 18th century,^[1] and 90 % of the total energy increase in the air–sea–land–cryosphere climate system (1961–2003).^[2]

The ocean also accounts for 50 % of global oxygen production,^[3] and annually receives 500 Mt of terrestrially derived dust and aerosols.^[4] The magnitude and variability of air–sea fluxes and associated control processes are the focal point for the Surface Ocean–Lower Atmosphere Study (SOLAS), a multidisciplinary international project involving 1900 scientists from 75 countries. Initiated in 2004, the aim of SOLAS is the ‘quantitative understanding of the key biogeochemical–physical interactions and feedbacks between the ocean and the atmosphere, and of how this coupled system affects and is affected by climate and environmental change’. The SOLAS Science Plan and Implementation Strategy (SP&IS)^[5] promoted



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Gerrit de Leeuw holds a professorship in the field of Satellite Remote Sensing of Aerosol Physical and Optical Properties at the University of Helsinki and at the Finnish Meteorological Institute (FMI), Finland, since 1 January 2007. He has (co-)authored ~135 peer-reviewed articles in the fields of aerosols, remote sensing and ocean–atmosphere interaction and co-edited a book on Aerosol Remote Sensing over Land. He has participated as principal investigator in 22 EU projects (3 as coordinator), 14 ESA projects (2 as coordinator, 1 as science leader) and many other (inter)national research projects.



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Stefan Konradowitz graduated from the University of Kiel in 2009 with a Degree in Physical Geography. After graduating he briefly worked for a space science journal before taking a job as a Research Assistant at GEOMAR Helmholtz Centre for Ocean Research in Kiel where he was introduced to the work of SOLAS. Since early 2011, he has been the Project Officer for the SOLAS International Project Office concentrating on planning and organising the SOLAS Open Science Conferences, SOLAS Summer Schools and Workshops.

coupled studies between ocean and atmosphere in three focus areas: (i) biogeochemical interactions and feedbacks between the ocean and atmosphere; (ii) exchange processes at the air–sea interface and the role of transport and transformation in the atmospheric and oceanic boundary layers and (iii) air–sea flux of CO₂ and other long-lived radiatively active gases (see Fig. 1). The overarching research strategy of the SOLAS SP&IS subsequently stimulated a wide range of experiments and field observations that have increased process-orientated understanding and improved the representation of biogeochemical processes in Earth System models.

There have been major advances in our knowledge of ocean–atmosphere exchange processes in the last decade.^[6] The significance of air–sea exchange to marine nutrient budgets has been established for nitrogen,^[7] iron^[8,9] and phosphorus.^[10] Large databases, such as SOCAT (CO₂), MEMENTO (nitrous oxide (N₂O) and methane),^[11] and GSS (dimethyl sulfide, DMS) have supported the development of global climatologies,^[12] reassessment of regional and global ocean sinks and sources^[13,14] and development of prognostic models.^[15] Studies of physical processes have produced new parameterisations and algorithms^[16–19] and remote sensing approaches^[20] for quantifying air–sea exchange. Observational frameworks and predictive models have increased in coverage, complexity and robustness,^[21–23] which is critical for establishing mitigation and adaptation responses to climate change. SOLAS research

has also become increasingly more relevant to environmental policy in areas such as ocean acidification,^[24] iron fertilisation and geoengineering.^[25–28]

As predicted in the SP&IS new challenges have arisen in this rapidly evolving field of research that now require reassessment of the SOLAS research aims. In 2008 the SOLAS Scientific Steering Committee identified several unresolved issues of significance to the global climate system that would benefit from additional international coordination and networking. These ideas subsequently evolved in a series of white papers that articulated research priorities and identified optimal frameworks and solutions for improved understanding in these novel cross-cutting areas. In the following sections the status of these issues is reviewed with details of the research strategies required to address them, with an appendix of acronym and abbreviation definitions at the end of the article. The five research strategies, two of which are regionally based with the remainder issue based, do not represent an exclusive list of SOLAS research topics but instead focus on areas where international coordination by SOLAS can deliver major advances. Other active areas of SOLAS research, such as ocean carbon and ocean acidification research coordination, are not covered by these strategies, as support mechanisms already exist (e.g. the SOLAS–IMBER carbon working group). The five new research strategies complement the research aims of the SP&IS (see Fig. 1), and maintain the SOLAS focus on multi-disciplinary coupled ocean



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SOLAS SP&IS, 2004	EBUSs and OMZs	Sea ice	Aerosols	Atmospheric nutrients	Ship plumes
Biogeochemical feedbacks and interactions					
1.1 Sea-salt particle formation and transformations		Major	Major	Moderate	Moderate
1.2 Trace gas emissions and photochemical feedbacks	Major	Major	Moderate	Moderate	Major
1.3 Dimethylsulfide and climate	Moderate	Major	Major		Moderate
1.4 Iron and marine productivity	Moderate	Moderate		Major	
1.5 Ocean–atmosphere cycling of nitrogen	Major			Major	Major
Exchange, transport and transformations					
2.1 Exchange across the air–sea interface		Major	Moderate		
2.2 Processes in the oceanic boundary layer	Moderate		Moderate		
2.3 Processes in the atmospheric boundary layer	Moderate	Major	Major	Moderate	
CO₂ and radiative gas fluxes					
3.1 Geographic and sub-decadal variability of air–sea CO ₂ fluxes	Major	Major			
3.2 Surface layer carbon transformations in the surface ocean	Moderate	Moderate			
3.3 Air–sea flux of N ₂ O and CH ₄	Major				



Fig. 1. The new SOLAS research strategies (top row) mapped against the Foci and Activities of the SOLAS Science Plan and Implementation Strategy (SP&IS).^[5]

and atmosphere research. As such they contribute to the goals of the IGBP AIMES project, and represent an important step towards the understanding of climate–ecosystem interactions required for the Future Earth Initiative (<http://www.icsu.org/future-earth>, accessed 26 February 2013).

Air–sea gas fluxes at eastern boundary upwelling systems and oxygen minimum zones

Eastern boundary upwelling systems (EBUSs) are characterised by high biological activity and heterotrophy that, in combination with weak ventilation, leads to the formation of oxygen minimum zones (OMZs) in sub-surface waters. The latter are characterised by intense suboxic waters that extend from shallow depths over several hundred metres of the water column and that support major perturbation of marine biogeochemical cycles (Fig. 2). Surface waters in EBUSs are characterised by high trace gas and CO₂ emissions, elevated nutrients and low pH,^[29] as a result of upwelling of subsurface water that has experienced high levels of heterotrophy, and so influence climate, cloud properties and marine productivity. OMZs contribute to the cycling of climate reactive trace gases,^[30] including methane and hydrogen sulfide,^[31,32] and represent the primary open ocean regions for fixed nitrogen loss, N₂O production^[33] and emission of reactive halogen compounds.^[34,35] However, feedback effects of OMZs are complex and currently largely unquantified. Stramma et al.^[22] have shown that OMZs are

expanding in the equatorial Pacific and eastern tropical Atlantic with decreasing dissolved oxygen concentrations between 300- and 700-m depth over the last 50 years. In contrast to these observations, most models predict an increase in oxygen concentrations in the tropical thermocline with an associated reduction in the extent of suboxic areas in 21st century projections.^[36,37] The tendency towards higher oxygen concentrations in model scenarios of the future tropical thermocline may reflect the mixing intensity employed in the models.^[38] Nevertheless, as ocean warming, acidification and deoxygenation will act synergistically as stressors on marine ecosystems,^[39,40] further insight is required into the functioning of OMZs.

An articulated international project has been developed to address these issues that builds upon collaboration with other IGBP projects (IMBER, IGAC and PAGES), GEOTRACES and CLIVAR. The proposed research will focus primarily on the OMZ in the Eastern Tropical South Pacific, and examine issues relating to reactivity and climate feedbacks. Although EBUSs represent a source of CO₂, N₂O and methane to the atmosphere it is unclear how these emissions are coupled,^[41] and as such what is the magnitude of their net radiative forcing and associated climate effect. EBUSs also influence tropospheric and stratospheric ozone by production of halogen compounds and N₂O, and atmospheric albedo by intensified DMS production or consumption,^[42] with further indirect feedbacks to the climate system. Factors such as the degree of physical mixing and connection with equatorial circulation, and organic matter

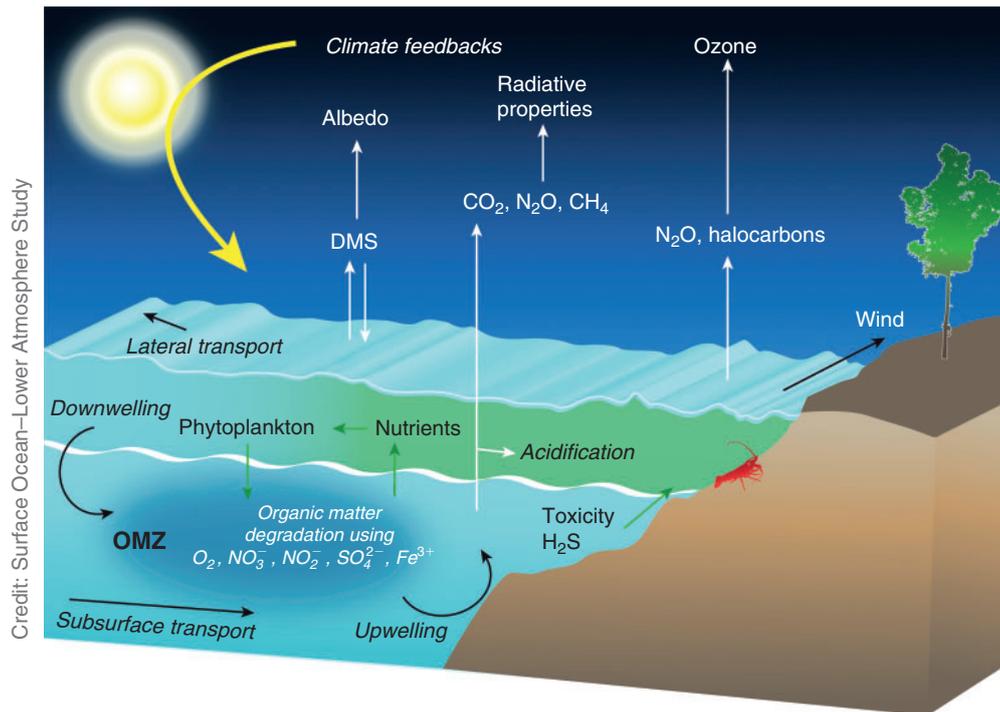


Fig. 2. Conceptual diagram illustrating the main issues, processes and species relating to the SOLAS EBUSs and OMZs research strategy. Processes are indicated in italic.

supply will determine the respiratory status of an OMZ. This will then influence the relative magnitude of heterotrophic processes along a gradient from aerobic remineralisation through denitrification and sulfate reduction to suboxic mechanisms using other electron acceptors (e.g. IO_3^- , MnO_2 and Fe^{3+}) and methanogenesis. The relative spatial extent and temporality of these respiration processes and the factors that determine their distribution and magnitude need to be established, to determine the net effect on CO_2 and trace gas production and emission from EBUSs, and hence the magnitude of feedbacks to climate change.

Initial research missions will focus on acquiring short- and long-term data from a variety of platforms (research cruises, laboratory experiments, moorings and glider networks, ARGO floats, ASIP and aircraft) to contribute to historical and new databases (SOCAT, MEMENTO and potentially a H_2S database), remote sensing and analysis. In parallel there will be development of parameterisations, coupled biogeochemical–physical–atmospheric models, new numerical tools and large-scale validations. This will also involve regional comparisons between the Atlantic and Pacific EBUSs, which exhibit some differences. For example, Mauritanian EBUSs tend to have weaker N_2O emissions, lower denitrification and negligible hydrogen sulfide emissions.^[43] There are also other critical regional differences including aeolian dust deposition, which is high off North-west Africa but low in the Tropical East Pacific, and the additional influence of benthic–pelagic coupling in the Mauritanian EBUS as a result of the overlap of the OMZ with the continental shelf. Field activities have already been initiated, with science flights (TORERO) coupled with research cruises (EqPOS, SFB754, AMOP), and synoptic remotely sensed data collection (ESA OceanFlux). Complementary autonomous platforms, including fixed position moorings for time-series datasets, gliders and AUVs for submesoscale

coverage, and Lagrangian profiler floats, will provide localised data collection. Regional high resolution coupled biogeochemical–physical and ocean–atmosphere models will achieve coupling between differing spatial scales and complement data collection and interpretation.

Sea-ice biogeochemistry and interactions with the atmosphere

Sea ice plays an important role in the cycling and exchange of climate relevant gases, and consequently the observed and predicted decline in sea-ice cover has implications for regional biogeochemistry and climate change (Fig. 3). Climate related feedbacks may occur in response to changes in the surface area of both ice sheets and open water. However our understanding of these processes is still in its infancy and so associated models currently contain a high degree of uncertainty. Due to inherently different properties of the polar regions, climate change affects the Arctic and Southern Ocean in different ways. In the Arctic, both sea-ice extent and thickness are reducing rapidly, with a new record low summer ice extent in 2012 (http://nsidc.org/news/press/20121002_MinimumPR.html, accessed 26 February 2013) and dramatic shifts from multi-year ice to first-year ice. Conversely a modest increase of total sea-ice extent has been observed in the Antarctic but with significant regional variability, with major reductions in sea-ice extent along the west coast of the Antarctic Peninsula^[44] associated with dramatic shifts in plankton biomass and diversity.^[45] With the ongoing rapid changes, it is important to realise that although sea ice may not completely disappear, it will undergo a profound change in seasonality with feedbacks to regional biogeochemical and physical properties.

Current global models include the seasonal wax and wane of sea ice but representation of associated properties is limited to a

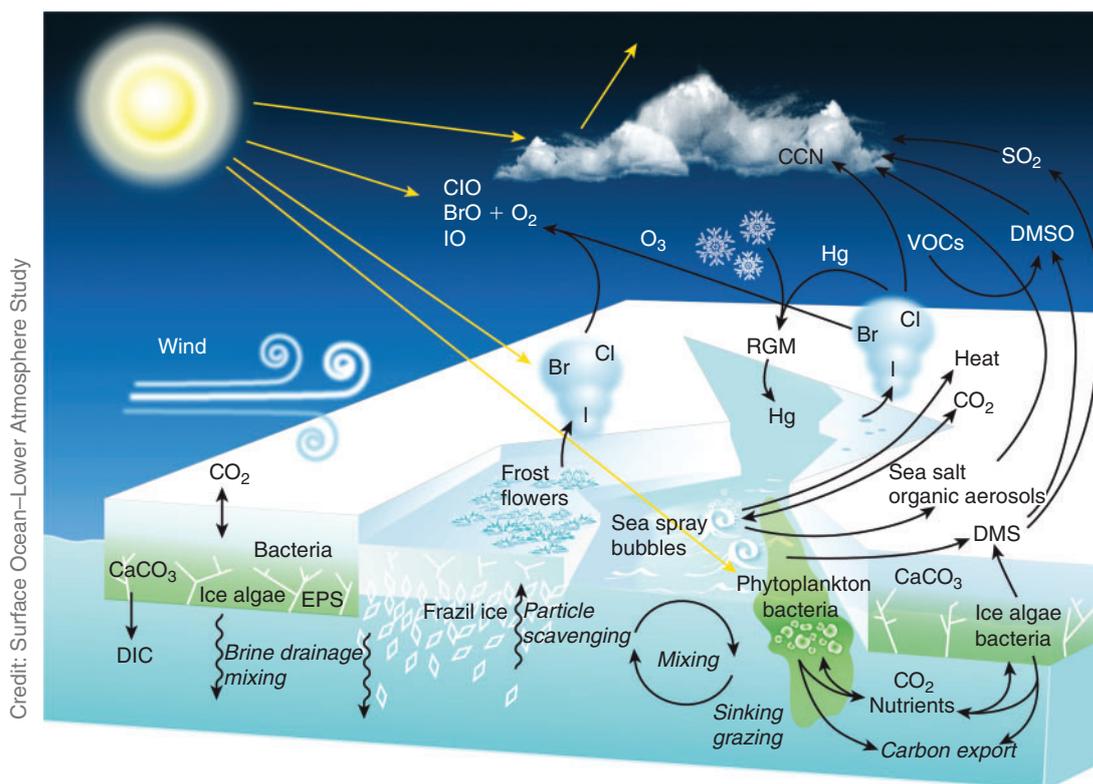


Fig. 3. Conceptual diagram illustrating the main issues, processes and species relating to the SOLAS Sea Ice strategy (after Shepson et al.^[54]). Processes are indicated in *italic*. (DIC, dissolved inorganic carbon; EPS, extracellular polymeric substances; CCN, cloud condensation nuclei; RGM, reactive gaseous mercury; VOCs, volatile organic compounds; DMS, dimethyl sulfide; DMSO, dimethyl sulfoxide.)

few physical features, and biogeochemical effects are poorly represented. In such models, the major climatic effects of sea ice are associated with albedo, deep water formation and air–sea heat exchange, with sea ice generally represented as a ‘lid’ that suppresses gas exchange across the ocean surface.^[46] Although simulations have been developed that resolve biogeochemical cycles within sea ice,^[47] many of these models are one-dimensional and trace gases are yet to be included. In many respects, Earth System models contain significant uncertainties in polar regions. For example, observed reductions in Arctic sea ice appear to be accelerated with respect to current model forecasts.^[48] In addition, simulations of primary production are systematically less realistic in polar regions compared with the rest of the ocean,^[49,50] with disagreement in the sign of the change predicted for primary production in end-of-century scenarios for the Arctic Ocean.^[50] Although sea ice reduces the surface area available for air–sea fluxes, processes such as turbulent ice–ocean and ice–air interfacial stresses, buoyant convection and wind waves potentially increase gas transfer in leads and cracks above that expected over a continuous, quiescent ice cover.^[51] The effect on the air–sea exchange of CO₂ of a reduction in ice cover is therefore uncertain, as illustrated by contrasting estimates of an increase^[52] and decrease,^[53] in associated ocean CO₂ uptake. Clearly these model studies are limited by insufficient representation of gas fluxes in ice-covered regions.

The IPY initiated several large-scale projects that focussed on the interaction of biotic and abiotic processes at the sea–ice and air–ice interfaces. One of the primary findings of the initial

research was that physical, chemical and biological processes interact in distinct and complex ways, and cannot be studied independently.^[54] For instance, the sea-ice microbial community alters the microstructure and albedo of sea ice, produces organic aerosols that function as cloud condensation nuclei (CCN)^[55] (see next section) and climatically active trace gases, such as DMS and halocarbons, that alter the oxidising capacity of the atmosphere and remove ozone in the lower troposphere in spring.^[56–58] In addition, physical forcing and changes in UV light influence the chemical and biological processes involved in the production of DMS and CO₂.^[59,60]

As Arctic sea ice retreat continues, anthropogenic pressure on polar systems will increase. An increase in ship traffic (see *Ship plumes* section below) and resource development will elevate pollutant loading from sulfur, nitrogen oxides and black carbon emissions, influencing atmospheric and sea-ice albedo, and tropospheric chemistry. A robust scientific understanding of feedback processes between anthropogenic activities and the polar environment from local to global scales is necessary to assist policymakers in the development of effective management strategies for polar environments. The rate at which the Arctic is currently changing requires both rapid advances in understanding and the development of robust models by international collaboration. A SCOR working group, BEPSII, has been recently initiated in which SOLAS and a second phase of the OASIS project will collaborate to address these issues. The aim of BEPSII is to promote collaboration between experimentalists and modellers from biological, chemical and physical disciplines, with emphasis

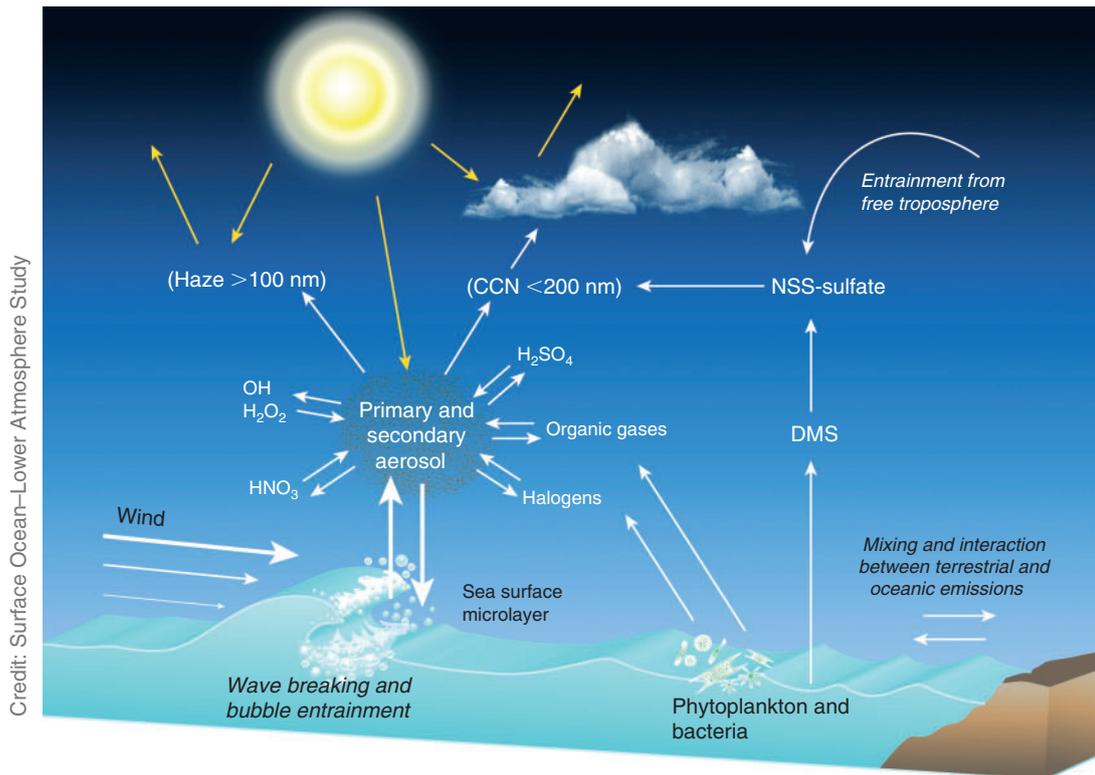


Fig. 4. Conceptual diagram illustrating the main issues, processes and species relating to the SOLAS Marine Aerosols strategy. Processes are indicated in *italic*. (CCN, cloud condensation nuclei; DMS, dimethyl sulfide; NSS sulfate, non-sea-salt sulfate.)

on those working at the ice–ocean–atmosphere interfaces. Two important goals are the standardisation of sea-ice measurement methodologies to improve future data intercomparisons and summaries of existing knowledge for prioritising processes and model parameterisations. A major issue is the lack of databases on relevant time and space scales, and standardisation of databases of priority parameters is urgently needed. In this respect, a first inventory of sea-ice chlorophyll-*a* has been produced by ASPECT, which may serve as a template for other databases. The ultimate goal of BEPSII is to upscale priority processes from one-dimensional to Earth System models to enable analysis of the role of sea-ice biogeochemistry in climate simulations.

Ocean-derived aerosols: production, evolution and impacts

Ocean-derived aerosols play an important role in controlling aerosol optical depth, cloud formation and properties, radiation balance and chemistry of the marine atmosphere^[61,62] (Fig. 4). Wind-driven breaking waves and bubble-bursting at the sea surface inject inorganic ions (Na^+ , Mg^{2+} , Cl^- and SO_4^{2-}) associated with seawater into the overlying atmosphere.^[62–64] In addition, ocean-derived aerosols also contain inorganic and organic species produced through secondary (gas to particle conversion) processes.^[65,66] Numerous studies in coastal and productive waters^[67] and oligotrophic seawater^[68] have identified that marine aerosol is highly enriched in organic matter (OM) relative to bulk seawater, with OM accounting for >50% of non-water mass of particles of $\leq 500\text{-nm}$ radius.^[66,68,69]

However, production mechanisms, composition, chemical properties including solubility and hygroscopicity, and the contribution of ocean-derived OM to aerosol mass and number concentration are not well understood.^[64]

Primary production of sea spray aerosol is the main source of aerosol mass to the atmosphere.^[70] The mass concentration of ocean-derived aerosols is dominated by particles of radius $>1\ \mu\text{m}$ (super-micrometre), composed primarily of sea salt, with lifetimes of hours to several days, whereas the ocean-derived aerosol number production flux is dominated by particles smaller than 200-nm radius (r_{80} , i.e. at relative humidity of 80%),^[63] with lifetimes ranging from hours to weeks.^[71] Ocean-derived aerosols influence the Earth's radiation balance by scattering and absorption of solar radiation (direct effects), and also by cloud formation and microphysical, macrophysical and optical properties (indirect effects). However observations and model estimates of the contribution of sea salt aerosol to the total (natural and anthropogenic) global short-wave direct radiative effect and the global aerosol optical depth have large uncertainties, with values ranging from 18 to 50%.^[72] Furthermore sea salt source functions used in different global models and model estimations of sea salt dry mass vary by a factor of five.^[62,63,73,74]

Recent advances in understanding and quantification of emission and production mechanisms include the extension of the sea spray source function to particles with r_{80} of $\sim 10\ \text{nm}$, which is important for the assessment of aerosol effects on clouds. Large-number production fluxes of particles with r_{80} of $\sim 100\ \text{nm}$, and decreasing fluxes below 100 nm, have also been identified.^[63] Nevertheless, large uncertainties in the number

production flux remain,^[63] although recent results converge within a factor of 2–3.^[75] Advances have also been made in our understanding of the effect of ocean-derived aerosols on climate, particularly with respect to the effects of OM on CCN production,^[76–78] and on boundary layer chemistry.^[79–81] There has also been recent recognition that particles of $<1\ \mu\text{m}$ may be a significant source of CCN in marine regions,^[70] that is potentially more important than the contribution from the oxidation of DMS.^[61,82,83] Emissions and chemical processing of primary ocean-derived particulate OM are now being integrated into ocean-derived aerosol source functions,^[84,85] and the effects of sea surface temperature^[86] and wind-speed dependent size-resolved OM production^[87,88] incorporated into global models.^[88,89]

However, several fundamental questions remain. Characterisation of the magnitude of size-resolved aerosol fluxes is required, particularly in terms of temporal and spatial variation such as between coastal and open ocean regions. Both physical and biological controls on aerosol production require resolution, particularly in relation to aerosols derived from the large pool of OM in surface seawater. Satellite derived chlorophyll-*a* and particulate organic carbon offer some potential as proxies for parameterising ocean OM emissions,^[84,85] but investigation of alternatives is warranted given the uncertainties associated with the present proxies. Measurements in different ocean regimes are required to formulate an accurate parameterisation for the incorporation of OM into ocean-derived aerosols. The relationship between ocean-derived aerosols and CCN also requires attention to establish how the chemical composition of aerosols influences both cloud-drop activation and size-resolved fluxes of ocean-derived CCN on global and regional scales. Furthermore, there is uncertainty in the relative influence of ocean and continental-derived CCN in coastal regions. To fully understand the effect of ocean-derived aerosol on climate and tropospheric chemistry, it will be important to determine how ocean-derived aerosols evolve physically and chemically, especially with respect to OM, once injected into the troposphere.

To address these questions, multi-disciplinary field campaigns are proposed in diverse oceanic (productive *v.* oligotrophic) regions to develop parameterisations for the production, composition and evolution of primary ocean-derived aerosols. Characterisation of surface ocean and aerosol OM will determine sources and processes of incorporation of OM into ocean-derived aerosols. Ideally these campaigns will be coordinated with satellite observations of whitecap coverage, sea surface temperature, salinity, ocean colour, waves and aerosol properties to extend local field observations to global scales. Particular focus areas include: parameterisation of sea-spray aerosol production as a function of wave breaking, seawater temperature, salinity and surfactant concentration; inter-comparison of aerosols generated *in situ* and *in vitro* in laboratory experiments to evaluate ocean-derived aerosol source function parameterisations; and characterisation of OM composition in newly formed sea-spray aerosol particles and ambient aerosols. Coupling of satellite observations with integrated multi-disciplinary field studies will further constrain the size-resolved sea-spray source functions, both with respect to physics and chemical composition. These new parameterisations will improve the accuracy in estimates of the direct and indirect effects of ocean-derived aerosols on climate, and so optimise regional and global climate models. The ultimate aim of the proposed research is to establish both direct and indirect

effects of ocean-derived aerosols on the Earth's radiation balance and tropospheric chemistry, particularly in the marine boundary layer.

Atmospheric nutrient supply to the surface ocean

Material transported in the atmosphere originates from a variety of natural and anthropogenic sources and contains both macro- and micronutrients (N, P, C, Si and trace metals including Fe and Cu), and potentially toxic elements (e.g. Cu and Pb).^[90–92] Consequently deposition represents an important source of new nutrients and particles for large regions of the open ocean.^[90,91] This deposition is being perturbed directly and indirectly by anthropogenic activities; for example, atmospheric pollution has greatly increased the deposition of nitrogen,^[7] and the magnitude of dust deposition to the oceans has been shown to be climate dependent.^[93] There is variability in the relative ratios of the major nutrients and their speciation when delivered by atmospheric deposition at both temporal and spatial scales. Furthermore, as deposited nutrients differ in both concentration and stoichiometry to that delivered by vertical supply from subsurface waters,^[94] this may modify nutrient inventories and plankton nutrient stoichiometry and biodiversity with resulting feedbacks to atmospheric CO₂ (Fig. 5). Yet, despite significant experimental, field and modelling studies over the past decade,^[72] the links between atmospheric deposition of nutrients, ocean productivity and feedbacks to climate are still poorly understood. Consequently, the role of atmospheric inputs remains under-represented in budgets and marine biogeochemical models (C. Guieu, O. Aumont, L. Bopp, C. Law, N. Mahowald, E. P. Achterberg, et al., unpubl. data).

New observational, experimental and modelling approaches are required to characterise interactions between natural and anthropogenic atmospheric deposition, and surface ocean ecosystem community structure and biogeochemical cycling. Critical uncertainties include how the nutrient and trace metal content of natural and anthropogenic aerosols vary from initial uplift to oceanic deposition, and how processing in the atmosphere, including mixing with anthropogenic species, influences subsequent nutrient supply and availability. Emission sources, such as volcanoes, biomass burning and anthropogenic sources including ship plumes (see section below), differ in composition and spatial and temporal distribution, and so establishing how each affects ocean biogeochemistry will be key to determining variability in regional response. The effect of atmospheric deposition in the surface ocean may vary with the biogeochemical state of the receiving waters,^[95] and result in fundamental differences in the response of the microbial community structure (e.g. stimulation of heterotrophy *v.* autotrophy^[96]), and so vertical carbon export and nutrient cycling. Particle deposition to the ocean can also provide ballast for sinking particles,^[97] which may augment the export flux resulting from increased nutrient supply by atmospheric deposition.^[98] In addition it is currently unclear how future ocean conditions (e.g. ocean acidification, temperature and stratification) will influence the availability and reactivity of deposited material. For example, the interaction of climate forcing with changes in nutrient deposition may result in changes in both biodiversity and microorganism adaptive strategies for competing for nutrients.

Systematic measurements are required of atmospheric deposition and nutrients in the surface mixed layer in regions where atmospheric supply plays an important role,^[99] as in LNLC (low-nutrient low-chlorophyll) regions (C. Guieu et al., unpubl.

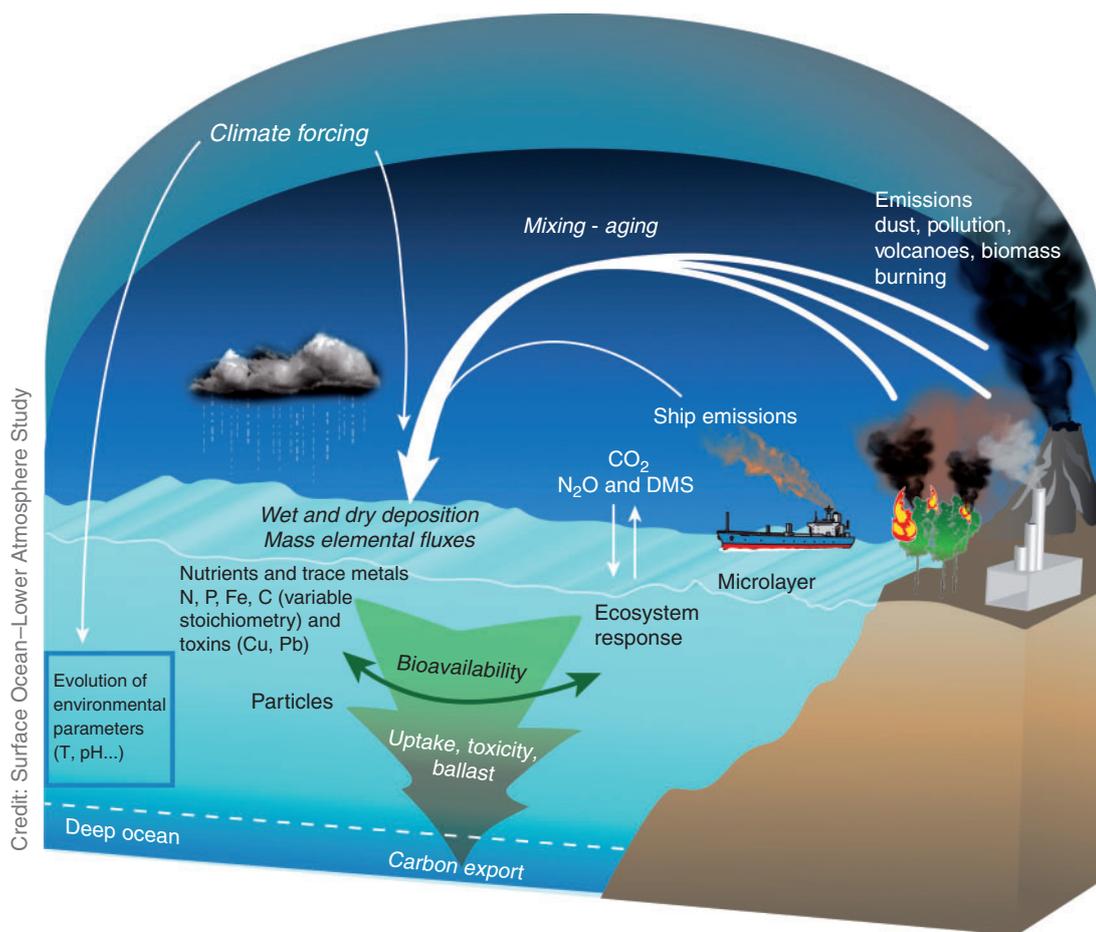


Fig. 5. Conceptual diagram illustrating the main issues, processes and species relating to the SOLAS Atmospheric nutrients strategy. Processes are indicated in italic. (DMS, dimethyl sulfide.)

data) such as the South-west and North-east Pacific and Mediterranean Sea. Anthropogenic nitrogen forcing is primarily a northern hemisphere phenomenon but, as climate and ocean acidification are global drivers, there is a requirement for time-series sampling sites in both hemispheres. Although reliable measurement of dry deposition still represents a technical challenge, it will be beneficial to extend wet and dry deposition measurements and particle characterisation to repeat sampling lines across regional deposition gradients and surface water biogeochemical gradients, using research vessels and voluntary observing ships. These transects should ideally accommodate rate measurements and nutrient manipulation experiments to gain insight into the proximal controls of plankton community composition and process rates. Existing time series stations that monitor both the atmosphere and ocean (e.g. HOT, BATS, CVOO and DYFAMED) could become focal points for more detailed experiments and process studies, possibly employing Lagrangian studies using tracers or drifting buoys. Trace-element clean mesocosms and tracer-labelled in situ manipulations could also be used to address whole-ecosystem effects of atmospheric nutrient input, including particulate organic carbon export (C. Guieu et al., unpubl. data). The challenge is to assimilate this information into more realistic models of deposition and associated mechanisms, taking into account the variable stoichiometry of atmospheric nutrients and surface ocean biota, with better representation of competitive interactions between plankton groups (C. Guieu et al., unpubl. data).

Transport, deposition and biogeochemical models require thorough testing and validation against in-situ time series datasets and remote-sensing observations. In addition, methodological intercalibration, sample sharing, common reference materials and standardisation of techniques are required to ensure global coherence and quality control. Linking time-series studies of aerosol composition with oceanic time-series data^[99] is valuable for constraining the response of the marine ecosystem to deposition events. In addressing these goals, there is considerable mutual interest and benefit of collaborative research with the ocean-derived aerosol strategy (see section above), GESAMP^[90] and the GEOTRACES project.^[100]

Ship plumes: impacts on atmospheric chemistry, climate and nutrient supply to the oceans

Emissions of trace gases, primarily NO_x and SO₂, and particles from ocean-going ships have major effects on photochemistry in the marine boundary layer, cloud properties and aerosol direct and indirect radiative effects, and are also potentially important for the deposition of nutrients to the ocean (Fig. 6). Ship traffic has increased significantly in recent years and is projected to continue increasing.^[101] In addition, new shipping routes are becoming available in the Arctic Ocean due to decreasing sea-ice cover in summer.^[102] Yet, regulation of ship emissions is only just being initiated and shipping currently often relies on the use of 'dirty' fuels that are not used for land-based transport.

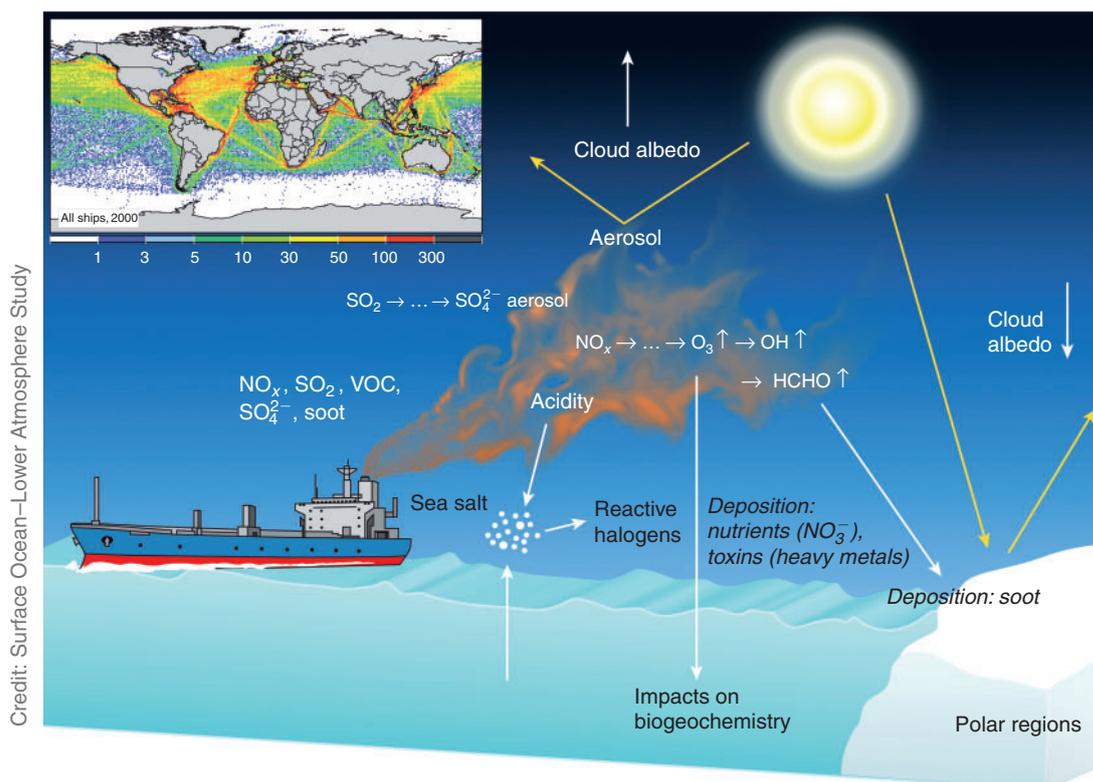


Fig. 6. Conceptual diagram illustrating the main issues, processes and species relating to the SOLAS strategy on Ship plumes. The insert figure shows total global vessel traffic in 2000, with the colour bar indicating the number of vessels per box, which is reproduced from Eyring et al.^[123] (with permission of Wiley). Processes are indicated in *italic*. (VOCs, volatile organic compounds.)

The primary aim of this research strategy is to determine the regional and global effects of ship emissions on photochemistry, climate forcing and ocean biogeochemical cycling and productivity, and establish whether sub-grid scale ship plumes can be parameterised in numerical models. Ship plumes have been successfully mapped and investigated using satellite data and detailed characterisation of chemical signatures^[103,104] in field campaigns such as MAST^[105] and CalNEX 2010. Investigation of individual plumes and characterisation of individual ship turbines have led to important advances,^[106,107] and a number of modelling studies of the effects of ship plumes on climate and atmospheric chemistry have been carried out or are ongoing.^[101,108–110] These have been complemented by emissions inventories^[101,111,112] and large scale assessments on climate,^[113,114] health and mortality.^[115] However, as yet no assessment has been carried out on the effects of deposition from ship plumes on ocean biogeochemistry.

For most numerical models, ship plumes are sub-grid scale (i.e. smaller than the size of grid boxes). However as many related processes, such as photochemistry, are non-linear it cannot be assumed that emissions are homogeneously distributed within a grid box as this leads to overestimation of the effects on photochemistry.^[109] Alternative attempts to address this have included a box model approach,^[110] a large eddy model approach^[116] and a ship plume parameterisation in a regional model.^[117] A promising approach is the ‘plume-in-grid’ formulation by Vinken et al.,^[118] which, when incorporated in a global model, showed that ignoring these effects leads to overestimation of NO_x and O_3 concentrations in the North Atlantic by 50

and 10–25% respectively. Further work is clearly required to determine how grid-scale ship plumes can be parameterised in numerical models.

Some progress has been made on quantifying regional and global effects of ship emissions on atmospheric photochemistry over the last decade. The most critical effects include ozone production in ship-plume affected regions that were formally ozone sinks,^[108–110] and increases in OH concentrations leading to increased oxidation capacity and a corresponding reduction in the atmospheric lifetime of methane. Furthermore, ship emissions may induce release of reactive chlorine from sea salt,^[80] which has a lifetime of several days due to multi-phase cycling.^[119] As the increase in chlorine atoms is maintained for a longer period than the lifetime of the ship plume this will further reduce the atmospheric lifetime of methane. Elevated levels of formaldehyde (HCHO) in ship plumes detected by satellite^[104] are probably attributable to enhanced oxidation of methane caused by elevated OH concentrations.^[120] A robust assessment of these effects requires global models that include multispecies chemistry with realistic reaction rates.

Non-linearities in ship plumes are less critical for the assessment of the climate impact of ship emissions, but robust emission inventories are crucial to producing reliable studies of the climate effect of ship plumes in conjunction with state-of-the-art aerosol models. Overall, direct and indirect aerosol effects of ship emissions lead to a net negative radiative forcing (cooling), partly due to the reduced atmospheric lifetime of methane.^[113,114] Current attempts to reduce the sulfur content in fuels and NO_x emissions from ships may reduce pollution

effects, but may also cause a shift from net cooling to net warming due to the continued release of CO₂ which remains unaffected by these measures.^[113] Black carbon has a positive radiative effect, which is thought to be minor,^[114] although deposition of black carbon on snow could influence snow albedo and increase snow melt during the Arctic summer.

A further aspect of ship emissions is their elevated nutrient and heavy metal content, which may affect ocean biogeochemistry. Duce et al.^[7] estimated that anthropogenic emissions are responsible for approximately a third of nitrogen input to the open ocean, although this estimate did not include deposition from ship emissions and so may be an underestimate. Dalsøren et al.^[112] used a global transport model to calculate the contribution of ship emissions to global wet deposition and identified a respective contribution of 11 and 4.5% to depositions of NO₃⁻ and SO₄²⁻, which increased to 25–50 and 15–25% in coastal regions. Nitrate is an important nutrient for phytoplankton growth, but the deposition of NO₃⁻ and SO₄²⁻ also increases acidification of surface waters,^[121] although it has been argued that the effects of this are minor.^[122] Conversely, ship fuels contain high levels of heavy metals, many of which are toxic, which may influence biodiversity and productivity of marine ecosystems.^[92] A full assessment of the effect of ship emissions on ocean biogeochemistry, including the effect of nutrient v. toxin input, has yet to be undertaken but coordination with the Atmospheric Nutrient and Ocean-derived Aerosols research strategies (see previous two sections) will assist in the development of this emerging SOLAS research theme.

Summary

1. EBUSs and their associated OMZs are critical sites for greenhouse and trace gas, aerosol and nutrient cycling. These regions influence climate, cloud properties and marine productivity, yet feedbacks are complex and poorly quantified. The proposed research will determine the net radiative forcing and overall climate effect of these regions, by considering CO₂ and trace gas production and emission, with a primary focus in the East Tropical South Pacific, using multiple sampling platforms to develop new databases, remote sensing, parameterisations, models, numerical tools and validation for OMZs.
2. Sea ice plays an important role in the cycling and air–sea exchange of climate relevant gases, and so the observed and predicted decline in sea-ice cover has implications for regional biogeochemistry and climate change. The goals of future research will be to examine the biological, chemical and physical controls of greenhouse and reactive trace gas cycling at the sea-ice interfaces, by coordination of international studies, to improve the representation of sea-ice biogeochemistry in models. An important aspect will be the evaluation and standardisation of currently used sea-ice methodology to improve future data intercomparison.
3. Marine aerosol particles influence atmospheric chemistry, aerosol optical depth, cloud properties and radiation balance. The aim of this strategy is to further constrain sources, particle composition and the spatio-temporal variability of ocean-derived aerosols, their effect on processes in both open ocean and coastal regions, and their contribution to aerosol radiative effects (both direct and indirect, by their effects on cloud properties). This will be achieved by campaigns and experiments in contrasting oceanic regions

that will examine physical and biological influences on sea spray aerosol properties, characterise their cloud-nucleating properties and develop aerosol production parameterisations.

4. The role of atmospheric input is poorly represented in marine biogeochemical models and there is a need to determine the linkages between atmospheric deposition, nutrient availability, the response of the biota, carbon cycling and feedbacks to climate. The proposed research strategy will develop coordinated approaches to assessing the sensitivity of ocean biota to atmospheric deposition in different regions, by simultaneous observation of aerosol, flux and sea-water composition.
5. Ship emissions are a poorly characterised source of NO_x, sulfate aerosols and nitrogen and influence photochemistry, reactive gas chemistry and aerosol production in the marine boundary layer, and nutrient and toxin supply to surface waters. The aims of this emerging research theme are to determine the regional and global effects of ship emissions on atmospheric chemistry, climate forcing and ocean biogeochemical cycling and productivity, and establish whether sub-grid scale ship plumes can be parameterised in numerical models.

Acronyms and abbreviations

All websites in this list were accessible as of 14 February 2013.

- AIMES – Analysis, Integration and Modelling of the Earth System; IGBP project; <http://www.imes.ucar.edu/>
- AMOP – *Activités de recherche dédiées au Minimum d'Oxygène dans le Pacifique est*; French research project on development of instrumentation and sensors for understanding Oxygen Minimum Zones and deoxygenation
- ARGO – International integrated observation program utilising free-floating profilers, <http://www.argo.ucsd.edu/>
- ASPeCT (Antarctic Sea Ice Processes and Climate) – SCAR Physical Sciences program expert group on multi-disciplinary Antarctic sea ice zone research, <http://aspect.antarctica.gov.au/>
- ASIP – air–sea interaction profiler
- AUV – autonomous underwater vehicle
- BATS – Bermuda Atlantic Time-Series Study, <http://bats.bios.edu/>
- BEPSII – Biogeochemical Exchange Processes at the Sea–Ice Interfaces, SCOR Working Group, http://www.scor-int.org/Working_Groups/wg140.htm
- CalNEX 2010 – California Nexus US multi-agency study of Air Quality and Climate Change, <http://www.esrl.noaa.gov/csd/calnex/>
- CLIVAR – Climate Variability and Predictability, WCRP project, <http://www.clivar.org/>
- CCN – cloud condensation nuclei
- CVOO – Cape Verde Ocean Observatory
- DMS – dimethyl sulfide
- DYFAMED – Dynamics of Atmospheric Fluxes in the Mediterranean Sea Time Series Station, <http://www.eurosites.info/dyfamed.php>
- ESA OceanFlux – European Space Agency Greenhouse gas project, <http://www.oceanflux-ghg.org/>
- GEOTRACES – International Study of Marine Biogeochemical Cycles and their Isotopes, a SCOR project, <http://www.geotraces.org/>

- GESAMP – United Nations Working Joint Group of Experts on the Scientific Aspects of Marine Environmental Protection, <http://www.gesamp.org/>
- GSS – Global Surface Seawater DMS database, <http://saga.pmel.noaa.gov/dms/>
- HOT – Hawaii Ocean Time-series, <http://hahana.soest.hawaii.edu/hot/>
- iCACGP – international Commission on Atmospheric Chemistry and Global Pollution
- IGAC – International Global Atmospheric Chemistry, IGBP project, <http://www.igacproject.org/>
- IGBP – International Geosphere–Biosphere Programme, <http://www.igbp.net/>
- IMBER – Integrated Marine Biogeochemistry and Ecosystem Research, a SCOR & IGBP project, <http://www.imber.info/>
- IPY – International Polar Year, <http://www.ipy.org/>
- EqPOS – Equatorial Pacific Ocean and Stratospheric–Tropospheric Atmospheric Study, Japanese SOLAS project
- MAST – Monterey Area Ship Track (MAST) Experiment^[105]
- MEMENTO – marine nitrous oxide and methane database^[11]
- OASIS – Ocean–Atmosphere–Sea–Ice–Snowpack, <http://www.acd.ucar.edu/oasis/>
- OM – organic matter
- PAGES – Past Global Changes, IGBP project, <http://www.pages-igbp.org/>
- SP&IS – SOLAS Science Plan & Implementation Strategy (2004)^[5]
- SCOR – Scientific Committee on Oceanic Research, <http://www.scor-int.org/>
- SOCAT – Surface Ocean CO₂ Atlas, <http://www.socat.info/>
- SOLAS – Surface Ocean–Lower Atmosphere Study, <http://solas-int.org/>; Mid-Term Strategy White Papers, <http://solas-int.org/about/mid-term-strategy.html>
- SFB754 – German Research project on climate–biogeochemical interactions in the tropical oceans, <http://oceanrep.geomar.de>
- TORERO – Tropical Ocean Troposphere Exchange of Reactive halogen species and Oxygenated VOC project, <http://www.eol.ucar.edu/deployment/field-deployments/field-projects/torero>
- WCRP – World Climate Research Programme, <http://www.wcrp-climate.org/>

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References

- [1] C. L. Sabine, R. A. Feely, N. Gruber, R. M. Key, K. Lee, J. L. Bullister, R. Wanninkhof, C. S. Wong, D. W. R. Wallace, B. Tilbrook, T.-H. Peng, A. Kozyr, A. F. Rios, The oceanic sink for anthropogenic CO₂. *Science* **2004**, *305*, 367. doi:10.1126/SCIENCE.1097403

- [2] N. L. Bindof, J. Willebrand, V. Artale, A. Cazenave, J. Gregory, S. Gulev, K. Hanawa, C. LeQuéré, S. Levitus, Y. Nojiri, C. Shum, L. Talley, A. Unnikrishnan, Observations: Oceanic Climate Change and Sea Level, in *Climate Change 2007: the Physical Science Basis. Contribution of Working Group I to the Fourth Assessment Report of the Intergovernmental Panel on Climate Change 2007* (Cambridge, United Kingdom, New York, USA).
- [3] C. B. Field, M. J. Behrenfeld, J. T. Randerson, P. Falkowski, Primary production of the biosphere: integrating terrestrial and oceanic components. *Science* **1998**, *281*, 237. doi:10.1126/SCIENCE.281.5374.237
- [4] Y. Shao, K.-H. Wyrwoll, A. Chappell, J. Huang, Z. Lin, G. H. McTainsh, M. Mikami, T. Y. Tanaka, X. Wang, S. Yoon, Dust cycle: an emerging core theme in Earth system science. *Aeolian Research* **2011**, *2*, 181.
- [5] *Science Plan and Implementation Strategy, IGBP Report Number 50 2004* (SOLAS: Stockholm).
- [6] P. S. Liss, M. T. Johnson (Eds), *Ocean–Atmosphere Interactions of Gases and Particles*, in press (Springer: Heidelberg).
- [7] R. A. Duce, J. LaRoche, K. Altieri, K. R. Arrigo, A. R. Baker, D. G. Capone, S. Cornell, F. Dentener, J. Galloway, R. S. Ganeshram, R. J. Geider, T. Jickells, M. M. Kuypers, R. Langlois, P. S. Liss, S. M. Liu, J. J. Middelburg, C. M. Moore, S. Nickovic, A. Oschlies, T. Pedersen, J. Prospero, R. Schlitzer, S. Seitzinger, L. L. Sorensen, M. Uematsu, O. Ulloa, M. Voss, B. Ward, L. Zamora, Impacts of atmospheric anthropogenic nitrogen on the open ocean. *Science* **2008**, *320*, 893. doi:10.1126/SCIENCE.1150369
- [8] N. M. Mahowald, A. R. Baker, G. Bergametti, N. Brooks, T. D. Jickells, R. A. Duce, T. D. Jickells, N. Kubilay, J. M. Prospero, I. Tegen, The atmospheric global dust cycle and iron inputs to the ocean. *Global Biogeochem. Cycles* **2005**, *19*, GB4025. doi:10.1029/2004GB002402
- [9] T. D. Jickells, Z. S. An, K. K. Andersen, A. R. Baker, G. Bergametti, N. Brooks, J. J. Cao, P. W. Boyd, R. A. Duce, K. A. Hunter, H. Kawahata, N. Kubilay, J. LaRoche, P. S. Liss, N. Mahowald, J. M. Prospero, A. J. Ridgwell, I. Tegen, R. Torres, Global iron connections between dust, ocean biogeochemistry and climate. *Science* **2005**, *308*, 67. doi:10.1126/SCIENCE.1105959
- [10] N. M. Mahowald, T. D. Jickells, A. R. Baker, P. Artaxo, C. R. Benitez-Nelson, G. Bergametti, T. C. Bond, Y. Chen, D. D. Cohen, B. Herut, N. Kubilay, R. Losno, C. Luo, W. Maenhaut, K. A. McGee, G. S. Okin, R. L. Siefert, S. Tsukuda, Global distribution of atmospheric phosphorous sources, concentrations and deposition rates, and anthropogenic impacts. *Global Biogeochem. Cycles* **2008**, *22*, GB4026. doi:10.1029/2008GB003240
- [11] H. W. Bange, T. G. Bell, M. Cornejo, A. Freing, G. Uher, R. C. Upstill-Goddard, G. Zhang, MEMENTO: a proposal to develop a database of marine nitrous oxide and methane measurements. *Environ. Chem.* **2009**, *6*, 195. doi:10.1071/EN09033
- [12] A. Lana, T. G. Bell, R. Simó, S. M. Vallina, J. Ballabrera-Poy, A. J. Kettle, J. Dachs, L. Bopp, E. S. Saltzman, J. Stefels, J. E. Johnson, P. S. Liss, An updated climatology of surface dimethylsulfide concentrations and emission fluxes in the global ocean. *Global Biogeochem. Cycles* **2011**, *25*, GB1004. doi:10.1029/2010GB003850
- [13] A. J. Watson, U. Schuster, D. C. E. Bakker, N. Bates, A. Corbiere, M. Gonzalez-Davila, Tracking the variable North Atlantic sink for atmospheric CO₂. *Science* **2009**, *326*, 1391. doi:10.1126/SCIENCE.1177394
- [14] T. Takahashi, S. C. Sutherland, R. Wanninkhof, C. Sweeney, R. A. Feely, D. W. Chipman, B. Hales, G. Friederich, F. Chavez, C. Sabine, A. Watson, D. C. E. Bakker, U. Schuster, N. Metzl, H. Yoshikawa-Inoue, M. Ishii, T. Midorikawa, Y. Nojiri, A. Körtzinger, T. Steinhoff, M. Hoppema, J. Olafsson, T. S. Arnarson, B. Tilbrook, T. Johannessen, A. Olsen, R. Bellerby, C. S. Wong, B. Delille, N. R. Bates, H. J. W. de Baar, Climatological mean and decadal changes in surface ocean pCO₂, and net sea–air CO₂ flux over the global oceans. *Deep Sea Res. Part II Top. Stud. Oceanogr.* **2009**, *56*, 554. doi:10.1016/J.DSR2.2008.12.009

- [15] Y. Le Clainche, A. Vezina, M. Levasseur, R. A. Cropp, J. R. Gunson, S. M. Vallina, M. Vogt, C. Lancelot, J. I. Allen, S. D. Archer, L. Bopp, C. Deal, S. Elliott, M. Jin, G. Malin, V. Schoemann, R. Simó, K. D. Six, J. Stefels, A first appraisal of prognostic ocean DMS models and prospects for their use in climate models. *Global Biogeochem. Cycles* **2010**, *24*, GB3021. doi:10.1029/2009GB003721
- [16] B. J. Huebert, B. W. Blomquist, M. X. Yang, S. D. Arche, P. D. Nightingale, M. J. Yelland, J. Stephens, R. W. Pascal, B. I. Moat, Linearity of DMS transfer coefficient with both friction velocity and wind speed in the moderate wind speed range. *Geophys. Res. Lett.* **2010**, *37*, L01605. doi:10.1029/2009GL041203
- [17] D. T. Ho, C. S. Law, M. J. Smith, P. Schlosser, M. Harvey, P. Hill, Measurements of air–sea gas exchange at high wind speeds in the Southern Ocean: implications for global parameterizations. *Geophys. Res. Lett.* **2006**, *33*, L16611. doi:10.1029/2006GL026817
- [18] R. Wanninkhof, W. E. Asher, D. T. Ho, C. Sweeney, W. R. McGillis, Advances in quantifying air–sea gas exchange and environmental forcing. *Annu. Rev. Mar. Sci.* **2009**, *1*, 213. doi:10.1146/ANNUREV.MARINE.010908.163742
- [19] C. W. Fairall, M. Yang, L. Bariteau, J. B. Edson, D. Helmig, W. McGillis, S. Pezoa, J. E. Hare, B. Huebert, B. Blomquist, Implementation of the COARE flux algorithm with CO₂, DMS, and O₃. *J. Geophys. Res.* **2011**, *116*, C00F09. doi:10.1029/2010JC006884
- [20] N. M. Frew, D. M. Glover, E. J. Bock, S. J. McCue, A new approach to estimation of global air–sea gas transfer velocity fields using dual-frequency altimeter backscatter. *J. Geophys. Res. – Oceans* **2007**, *112*, C11003. doi:10.1029/2006JC003819
- [21] M. Steinacher, F. Joos, T. L. Frölicher, G.-K. Plattner, S. C. Doney, Imminent ocean acidification projected with the NCAR global coupled carbon cycle climate model. *Biogeosciences* **2009**, *6*, 515. doi:10.5194/BG-6-515-2009
- [22] L. Stramma, G. C. Johnson, J. Sprintall, V. Mohrholz, Expanding oxygen-minimum zones in the tropical oceans. *Science* **2008**, *320*, 655. doi:10.1126/SCIENCE.1153847
- [23] W. D. Collins, C. M. Bitz, M. L. Blackmon, G. B. Bonan, C. S. Bretherton, J. A. Carton, P. Chang, S. C. Doney, J. J. Hack, T. B. Henderson, J. T. Kiehl, W. G. Large, D. S. McKenna, B. D. Santer, R. D. Smith, The Community Climate System Model Version 3 (CCSM3). *J. Clim.* **2006**, *19*, 2122. doi:10.1175/JCLI3761.1
- [24] M. Hood, W. Broadgate, E. Urban, O. Gaffney, (Eds) *Ocean Acidification: a Summary for Policymakers from the Second Symposium on the Ocean in a High-CO₂ World* **2011**. Available at <http://www.us-ocb.org/publications/SPM-lorenzv2.pdf> [Verified 14 February 2013].
- [25] P. W. Boyd, T. Jickells, C. S. Law, S. Blain, E. A. Boyle, K. O. Buesseler, K. H. Coale, J. J. Cullen, H. J. W. de Baar, M. Follows, M. Harvey, C. Lancelot, M. Levasseur, N. P. J. Owens, R. Pollard, R. B. Rivkin, J. Sarmiento, V. Schoemann, V. Smetacek, S. Takeda, A. Tsuda, S. Turner, A. J. Watson, Mesoscale iron-enrichment experiments 1993–2005: synthesis and future directions. *Science* **2007**, *315*, 612. doi:10.1126/SCIENCE.1131669
- [26] H. Browman, P. W. Boyd, Implications of large-scale iron fertilization of the oceans. *Mar. Ecol. Prog. Ser.* **2008**, *364*, 213. doi:10.3354/MEPS07541
- [27] D. W. R. Wallace, C. S. Law, P. W. Boyd, Y. Collos, P. Croot, K. Denman, P. J. Lam, U. Riebesell, S. Takeda, P. Williamson, *Ocean Fertilization. A Scientific Summary for Policy Makers, IOC/BRO/2010/2* **2010** (IOC–UNESCO: Paris). Available at <http://unesdoc.unesco.org/images/0019/001906/190674e.pdf> [Verified 14 February 2013].
- [28] A.-I. Partanen, H. Kokkola, S. Romakkaniemi, V.-M. Kerminen, K. E. J. Lehtinen, T. Bergman, A. Arola, H. Korhonen, Direct and indirect effects of sea spray geoengineering and the role of injected particle size. *J. Geophys. Res.* **2012**, *117*, D02203. doi:10.1029/2011JD016428
- [29] A. Paulmier, D. Ruiz-Pino, V. Garçon, CO₂ maximum in the oxygen minimum zone (OMZ). *Biogeosciences* **2011**, *8*, 239. doi:10.5194/BG-8-239-2011
- [30] A. Paulmier, D. Ruiz-Pino, Oxygen minimum zones (OMZs) in the modern ocean. *Prog. Oceanogr.* **2009**, *80*, 113. doi:10.1016/J.POCEAN.2008.08.001
- [31] R. Dugdale, J. Goering, R. Barber, R. Smith, T. Packard, Denitrification and hydrogen sulfide in Peru upwelling region during 1976. *Deep-Sea Res.* **1977**, *24*, 601. doi:10.1016/0146-6291(77)90530-6
- [32] R. J. Cicerone, R. S. Oremland, Biochemical aspects of atmospheric methane. *Global Biogeochem. Cycles* **1988**, *2*, 299. doi:10.1029/GB0021004P00299
- [33] L. A. Codispoti, J. A. Brandes, J. P. Christensen, A. H. Devol, S. W. A. Naqvi, H. W. Paerl, T. Yoshinari, The oceanic fixed nitrogen and nitrous oxide budgets: moving targets as we enter the Anthropocene? *Sci. Mar.* **2001**, *65*, 85.
- [34] A. Saiz-Lopez, A. S. Mahajan, R. A. Salmon, S. J.-B. Bauguitte, A. E. Jones, H. K. Roscoe, J. M. C. Plane, Boundary layer halogens in coastal. *Antarct. Sci.* **2007**, *317*, 348.
- [35] A. S. Mahajan, J. C. Gómez Martín, T. D. Hay, S.-J. Royer, S. Yvon-Lewis, Y. Liu, L. Hu, C. Prados-Roman, C. Ordóñez, J. M. C. Plane, A. Saiz-Lopez, Latitudinal distribution of reactive iodine in the Eastern Pacific and its link to open ocean sources. *Atmos. Chem. Phys. Discuss.* **2012**, *12*, 15541. doi:10.5194/ACPD-12-15541-2012
- [36] L. Bopp, C. Le Quere, M. Heimann, A. C. Manning, P. Monfray, Climate induced oceanic fluxes: implications for the contemporary carbon budget. *Global Biogeochem. Cycles* **2002**, *16*, 1022. doi:10.1029/2001GB001445
- [37] R. J. Matear, A. C. Hirst, Long-term changes in dissolved oxygen concentrations in the ocean caused by protracted global warming. *Global Biogeochem. Cycles* **2003**, *17*, 1125. doi:10.1029/2002GB001997
- [38] O. Duteil, A. Oschlies, Sensitivity of simulated extent and future evolution of marine suboxia to mixing intensity. *Geophys. Res. Lett.* **2011**, *38*, L06607. doi:10.1029/2011GL046877
- [39] R. F. Keeling, A. Körtzinger, N. Gruber, Ocean deoxygenation in a warming world. *Annu. Rev. Mar. Sci.* **2010**, *2*, 199. doi:10.1146/ANNUREV.MARINE.010908.163855
- [40] N. Gruber, Warming up, turning sour, losing breath: ocean biogeochemistry under global change. *Philos. Trans. R. Soc. Lond. A* **2011**, *369*, 1980. doi:10.1098/RSTA.2011.0003
- [41] A. Paulmier, D. Ruiz-Pino, V. Garçon, The oxygen minimum zone (OMZ) off Chile as intense sources of CO₂ and N₂O. *Cont. Shelf Res.* **2008**, *28*, 2746. doi:10.1016/J.CSR.2008.09.012
- [42] R. P. Kiene, T. S. Bates, Biological removal of dimethylsulphide from seawater. *Nature* **1990**, *345*, 702. doi:10.1038/345702A0
- [43] E. Ryabenko, A. Kock, H. W. Bange, M. A. Altabet, D. W. R. Wallace, Contrasting biogeochemistry of nitrogen in the Atlantic and Pacific oxygen minimum zones. *Biogeosciences* **2012**, *9*, 203. doi:10.5194/BG-9-203-2012
- [44] D.J. Cavalieri, C. L. Parkinson, Antarctic sea ice variability and trends, 1979–2006. *J. Geophys. Res. – Oceans* **2008**, *113*, C07004. doi:10.1029/2007JC004564
- [45] M. Montes-Hugo, S. C. Doney, H. W. Ducklow, W. Fraser, D. Martinson, S. E. Stammerjohn, O. Schofield, Recent changes in phytoplankton communities associated with rapid regional climate change along the Western Antarctic Peninsula. *Science* **2009**, *323*, 1470. doi:10.1126/SCIENCE.1164533
- [46] B. B. Stephens, R. F. Keeling, The influence of Antarctic sea ice on glacial–interglacial CO₂ variations. *Nature* **2000**, *404*, 171. doi:10.1038/35004556
- [47] B. Loose, L. A. Miller, S. Elliot, T. Papakyriakou, Sea ice biogeochemistry and material transport across the frozen interface. *Oceanography* **2011**, *24*, 202. doi:10.5670/OCEANOGRAPHY.2011.72
- [48] D. K. Perovich, J. A. Richter-Menge, Loss of sea ice in the arctic. *Annu. Rev. Mar. Sci.* **2009**, *1*, 417. doi:10.1146/ANNUREV.MARINE.010908.163805
- [49] M.-E. Carr, M. A. M. Friedrichs, M. Schmeltz, M. Noguchi Aita, D. Antoine, K. R. Arrigo, I. Asanuma, O. Aumont, R. Barber, M. Behrenfeld, R. Bidigare, E. T. Buitenhuis, J. Campbell, A. Ciotti, H. Dierssen, M. Dowell, J. Dunne, W. Esaias, B. Gentili, W. Gregg,

- S. Lohrenz, N. Hoepffner, J. Ishizaka, T. Kameda, C. Le Quéré, S. Lohrenz, J. Marra, F. Mélin, K. Moore, A. Morel, T. E. Reddy, J. Ryan, M. Scardi, T. Smyth, K. Turpie, G. Tilstone, K. Waters, Y. Yamanaka, A comparison of global estimates of marine production from ocean color. *Deep Sea Res. Part II Top. Stud. Oceanogr.* **2006**, *53*, 741. doi:10.1016/J.DSR2.2006.01.028
- [50] M. Steinacher, F. Joos, T. L. Fröhlicher, L. Bopp, P. Cadule, V. Cocco, S. C. Doney, M. Gehlen, K. Lindsay, J. K. Moore, B. Schneider, J. Segsneider, Projected 21st century decrease in marine productivity: a multi-model analysis. *Biogeosciences* **2010**, *7*, 979. doi:10.5194/BG-7-979-2010
- [51] B. G. T. Else, T. N. Papakyriakou, R. J. Galley, W. M. Drennan, L. A. Miller, H. Thomas, Eddy covariance measurements of wintertime CO₂ fluxes in an arctic polynia: evidence for enhanced gas transfer during ice formation. *J. Geophys. Res.* **2011**, *116*, C00G03. doi:10.1029/2010JC006760
- [52] N. R. Bates, S. B. Moran, D. A. Hansel, J. T. Mathis, An increasing CO₂ sink in the Arctic Ocean due to sea-ice loss. *Geophys. Res. Lett.* **2006**, *33*, L23609. doi:10.1029/2006GL027028
- [53] W.-J. Cai, L. Chen, B. Chen, Z. Gao, S. H. Lee, J. Chen, D. Pierrot, K. Sullivan, Y. Wang, X. Hu, W.-J. Huang, Y. Zhang, S. Xu, A. Murata, J. M. Grebmeier, E. P. Jones, H. Zhang, Decrease in the CO₂ uptake capacity in an ice-free Arctic Ocean Basin. *Science* **2010**, *329*, 556. doi:10.1126/SCIENCE.1189338
- [54] P. B. Shepson, P. A. Ariya, C. J. Deal, D. J. Donaldson, T. A. Douglas, B. Loose, T. Maksym, P. A. Matrai, L. M. Russell, B. Saenz, J. Stefels, N. Steiner, Changing polar environments: interdisciplinary challenges. *Eos Trans. AGU* **2012**, *11*, 112.
- [55] M. V. Orellana, P. A. Matrai, C. Leck, C. D. Rauschenberg, A. M. Lee, C. Esther, Marine microgels as a source of cloud condensation nuclei in the high Arctic. *Proc. Natl. Acad. Sci. USA* **2011**, *108*, 13612. doi:10.1073/PNAS.1102457108
- [56] T. J. Breider, M. P. Chipperfeld, N. A. D. Richards, K. S. Carslaw, G. W. Mann, D. V. Spracklen, Impact of BrO on dimethylsulfide in the remote marine boundary layer. *Geophys. Res. Lett.* **2010**, *37*, L02807. doi:10.1029/2009GL040868
- [57] W. R. Simpson, R. von Glasow, K. Riedel, P. Anderson, P. Ariya, J. Bottenheim, J. Burrows, L. J. Carpenter, U. Frieß, M. E. Goodsite, D. Heard, M. Hutterli, H.-W. Jacobi, L. Kaleschke, B. Neff, J. Plane, U. Platt, A. Richter, H. Roscoe, R. Sander, P. Shepson, J. Sodeau, A. Steffen, T. Wagner, E. Wolff, Halogens and their role in polar boundary-layer ozone depletion. *Atmos. Chem. Phys.* **2007**, *7*, 4375. doi:10.5194/ACP-7-4375-2007
- [58] A. Saiz-Lopez, R. von Glasow, Reactive halogen chemistry in the troposphere. *Chem. Soc. Rev.* **2012**, *41*, 6448. doi:10.1039/C2CS35208G
- [59] J.-L. Tison, F. Brabant, I. Dumont, J. Stefels, High-resolution dimethyl sulfide and dimethylsulfoniopropionate time series profiles in decaying summer first-year sea ice at Ice Station Polarstern, western Weddell Sea, Antarctica. *J. Geophys. Res. – Biogeosciences* **2010**, *115*, 2156.
- [60] G. S. Dieckmann, G. Nehrke, S. Papadimitriou, J. Göttlicher, R. Steininger, H. Kennedy, D. Wolf-Gladrow, D. N. Thomas, Calcium carbonate as ikaite crystals in Antarctic sea ice. *Geophys. Res. Lett.* **2008**, *35*, L08501. doi:10.1029/2008GL033540
- [61] P. K. Quinn, T. S. Bates, The case against climate regulation via oceanic phytoplankton sulfur emissions. *Nature* **2011**, *480*, 51. doi:10.1038/NATURE10580
- [62] E. R. Lewis, S. E. Schwartz, Sea salt aerosol production: mechanisms, methods, measurements and models – a critical review. *Geophys. Monogr.* **2004**, *152*, GM152. doi:10.1029/GM152
- [63] G. de Leeuw, E. L. Andreas, M. D. Anguelova, C. W. Fairall, E. R. Lewis, C. O'Dowd, M. Schulz, S. E. Schwartz, Production flux of sea spray aerosol. *Rev. Geophys.* **2011**, *49*, RG2001. doi:10.1029/2010RG000349
- [64] B. Gantt, N. Meskhidze, The physical and chemical characteristics of marine organic aerosols: a review. *Atmos. Chem. Phys. Discuss.* **2012**, *12*, 21779. doi:10.5194/ACPD-12-21779-2012
- [65] C. D. O'Dowd, G. de Leeuw, Marine aerosol production: a review of the current knowledge. *Phil. Trans. R. Soc. A* **2007**, *365*, 1753. doi:10.1098/RSTA.2007.2043
- [66] M. C. Facchini, M. Rinaldi, S. Decesari, C. Carbone, E. Finessi, M. Mircea, S. Fuzzi, D. Ceburnis, R. Flanagan, E. D. Nilsson, G. de Leeuw, M. Martino, J. Woeltjen, C. D. O'Dowd, Primary submicron marine aerosol dominated by insoluble organic colloids and aggregates. *Geophys. Res. Lett.* **2008**, *35*, L17814. doi:10.1029/2008GL034210
- [67] C. D. O'Dowd, M. C. Facchini, F. Cavalli, D. Ceburnis, M. Mircea, S. Decesari, S. Fuzzi, Y. J. Yoon, J.-P. Putaud, Biogenically driven organic contribution to marine aerosol. *Nature* **2004**, *431*, 676. doi:10.1038/NATURE02959
- [68] W. C. Keene, H. Maring, D. J. Kieber, J. R. Maben, A. A. P. Pszenny, E. E. Dahl, M. A. Izaguirre, A. J. Davis, M. S. Long, X. Zhou, L. Smoydzin, R. Sander, Chemical and physical characteristics of nascent aerosols produced by bursting bubbles at a model air–sea interface. *J. Geophys. Res.* **2007**, *112*, D21202. doi:10.1029/2007JD008464
- [69] E. J. Hoffman, R. A. Duce, Organic carbon in marine atmospheric particulate matter: concentration and particle size distribution. *Geophys. Res. Lett.* **1977**, *4*, 449. doi:10.1029/GL004I010P00449
- [70] M. O. Andreae, D. Rosenfeld, Aerosol–cloud–precipitation interactions. Part 1. The nature and sources of cloud-active aerosols. *Earth Sci. Rev.* **2008**, *89*, 13. doi:10.1016/J.EARSCIREV.2008.03.001
- [71] W. A. Hoppel, G. M. Frick, J. W. Fitzgerald, Surface source function for sea-salt aerosol and aerosol dry deposition to the ocean surface. *J. Geophys. Res.* **2002**, *107*, 4382. doi:10.1029/2001JD002014
- [72] G. de Leeuw, C. Guieu, A. Arneth, N. Bellouin, L. Bopp, P. W. Boyd, H. A. C. Denier van der Gon, K. V. Desboeufs, F. Dulac, M. C. Facchini, B. Gantt, B. Langmann, N. M. Mahowald, E. Marañón, C. O'Dowd, N. Olgun, E. Pulido-Villena, M. Rinaldi, E. G. Stephanou, T. Wagener, Ocean–atmosphere interactions of particles, in *Ocean–Atmosphere Interactions of Gases and Particles* (Eds P. S. Liss, M. T. Johnson), in press (Springer: Heidelberg).
- [73] C. Textor, M. Schulz, S. Guibert, S. Kinne, Y. Balkanski, S. Bauer, T. Bernsten, T. Berglen, O. Boucher, M. Chin, F. Dentener, T. Diehl, R. Easter, H. Feichter, D. Fillmore, S. Ghan, P. Ginoux, S. Gong, A. Grini, J. Hendricks, L. Horowitz, P. Huang, I. Isaksen, I. Iversen, S. Kloster, D. Koch, A. Kirkevåg, J. E. Kristjansson, M. Krol, A. Lauer, J. F. Lamarque, X. Liu, V. Montanaro, G. Myhre, J. Penner, G. Pitari, S. Reddy, Ø. Seland, P. Stier, T. Takemura, X. Tie, Analysis and quantification of the diversities of aerosol life cycles within AeroCom. *Atmos. Chem. Phys.* **2006**, *6*, 1777. doi:10.5194/ACP-6-1777-2006
- [74] S. Kinne, M. Schulz, C. Textor, S. Guibert, Y. Balkanski, S. E. Bauer, T. Bernsten, T. F. Berglen, O. Boucher, M. Chin, W. Collins, F. Dentener, T. Diehl, R. Easter, J. Feichter, D. Fillmore, S. Ghan, P. Ginoux, S. Gong, A. Grini, J. Hendricks, M. Herzog, L. Horowitz, I. Isaksen, T. Iversen, A. Kirkevåg, S. Kloster, D. Koch, J. E. Kristjansson, M. Krol, A. Lauer, J. F. Lamarque, G. Lesins, X. Liu, U. Lohmann, V. Montanaro, G. Myhre, J. Penner, G. Pitari, S. Reddy, O. Seland, P. Stier, T. Takemura, X. Tie, An AeroCom initial assessment – optical properties in aerosol component modules of global models. *Atmos. Chem. Phys.* **2006**, *6*, 1815. doi:10.5194/ACP-6-1815-2006
- [75] A. D. Clarke, S. R. Owens, J. Zhou, An ultrafine sea salt flux from breaking waves: implications for cloud condensation nuclei in the remote marine atmosphere. *J. Geophys. Res.* **2006**, *111*, D06202. doi:10.1029/2005JD006565
- [76] E. Fuentes, H. Coe, D. Green, G. de Leeuw, G. McFiggans, On the impacts of phytoplankton-derived organic matter on the properties of primary marine aerosol – Part 1: source fluxes. *Atmos. Chem. Phys.* **2010**, *10*, 9295. doi:10.5194/ACP-10-9295-2010
- [77] J. Ovadnevaite, D. Ceburnis, J. Bialek, C. Monahan, G. Martucci, M. Rinaldi, M. C. Facchini, H. Berresheim, D. R. Worsnop, C. O'Dowd, Primary marine organic aerosol: a dichotomy of low hygroscopicity and high CCN activity. *Geophys. Res. Lett.* **2011**, *38*, L21806. doi:10.1029/2011GL048869
- [78] S. M. King, A. C. Butcher, T. Rosenoern, E. Coz, K. I. Lieke, G. de Leeuw, E. D. Nilsson, M. Bilde, Investigating primary marine aerosol properties: CCN activity of sea salt and mixed inorganic-organic particles. *Environ. Sci. Technol.* **2012**, *46*, 10405. doi:10.1021/ES300574U

- [79] W. C. Keene, J. Stutz, A. A. P. Pszenny, J. R. Maben, E. V. Fischer, A. M. Smith, R. von Glasow, S. Pechtl, B. C. Sive, R. K. Varner, Inorganic chlorine and bromine in coastal New England air during summer. *J. Geophys. Res.* **2007**, *112*, D10S12. doi:10.1029/2006JD007689
- [80] H. D. Osthoff, J. M. Roberts, A. R. Ravishankara, E. J. Williams, B. M. Lerner, R. Sommariva, T. S. Bates, D. Coffman, P. K. Quinn, J. E. Dibb, H. Stark, J. B. Burkholder, R. K. Talukdar, J. Meagher, F. C. Fehsenfeld, S. S. Brown, High levels of nitryl chloride in the polluted subtropical marine boundary layer. *Nat. Geosci.* **2008**, *1*, 324. doi:10.1038/NGEO177
- [81] X. Zhou, A. J. Davis, D. J. Kieber, W. C. Keene, J. R. Maben, H. Maring, E. E. Dahl, M. A. Izaguirre, R. Sander, L. Smoydzy, Photochemical production of hydroxyl radical and hydroperoxides in water extracts of nascent marine aerosols produced by bursting bubbles from Sargasso seawater. *Geophys. Res. Lett.* **2008**, *35*, L20803. doi:10.1029/2008GL035418
- [82] R. J. Charlson, J. E. Lovelock, M. O. Andreae, S. G. Warren, Oceanic phytoplankton, atmospheric sulphur, cloud albedo and climate. *Nature* **1987**, *326*, 655. doi:10.1038/326655A0
- [83] M. H. Smith, Sea-salt particles and the CLAW hypothesis. *Environ. Chem.* **2007**, *4*, 391. doi:10.1071/EN07071
- [84] C. D. O'Dowd, B. Langmann, S. Varghese, C. Scannell, D. Ceburnis, M. C. Facchini, A combined organic-inorganic sea-spray source function. *Geophys. Res. Lett.* **2008**, *35*, L01801. doi:10.1029/2007GL030331
- [85] M. S. Long, W. C. Keene, D. J. Kieber, D. J. Erickson, H. Maring, A sea-state based source function for size- and composition-resolved marine aerosol production. *Atmos. Chem. Phys.* **2011**, *10*, 22279.
- [86] L. Jaeglé, P. K. Quinn, T. S. Bates, B. Alexander, J.-T. Lin, Global distribution of sea salt aerosols: new constraints from in situ and remote sensing observations. *Atmos. Chem. Phys.* **2011**, *11*, 3137. doi:10.5194/ACP-11-3137-2011
- [87] N. Meskhidze, J. Xu, B. Gantt, Y. Zhang, A. Nenes, S. J. Ghan, X. Liu, R. Easter, R. Zaveri, Global distribution and climate forcing of marine organic aerosol. 1. Model improvements and evaluation. *Atmos. Chem. Phys.* **2011**, *11*, 11689. doi:10.5194/ACP-11-11689-2011
- [88] B. Gantt, M. S. Johnson, N. Meskhidze, J. Sciare, J. Ovadnevaite, D. Ceburnis, C. D. O'Dowd, Model evaluation of marine primary organic aerosol emission schemes. *Atmos. Chem. Phys. Discuss.* **2012**, *12*, 12853. doi:10.5194/ACPD-12-12853-2012
- [89] D. M. Westervelt, R. H. Moore, A. Nenes, P. J. Adams, Effect of primary organic sea spray emissions on cloud condensation nuclei concentrations. *Atmos. Chem. Phys.* **2012**, *12*, 89. doi:10.5194/ACP-12-89-2012
- [90] *The atmospheric input of trace species to the world ocean. GESAMP Reports and Studies 38* **1989** (World Meteorological Organization). Available at <http://www.gesamp.org/publications/publicationdisplaypages/rs38> [Verified 14 February 2013].
- [91] R. A. Duce, P. S. Liss, J. T. Merrill, E. L. Atlas, P. Buat-Menard, B. B. Hicks, J. M. Miller, J. M. Prospero, R. Arimoto, T. M. Church, W. Ellis, J. N. Galloway, L. Hansen, T. D. Jickells, A. H. Knap, K. H. Reinhardt, B. Schneider, A. Soudine, J. J. Tokos, S. Tsunogai, R. Wollast, M. Zhou, The atmospheric input of trace species to the world ocean. *Global Biogeochem. Cycles* **1991**, *5*, 193. doi:10.1029/91GB01778
- [92] A. Paytan, K. R. M. Mackey, Y. Chen, I. D. Lima, S. C. Doney, N. Mahowald, R. Labiosa, A. F. Post, Toxicity of atmospheric aerosols on marine phytoplankton. *Proc. Natl. Acad. Sci. USA* **2009**, *106*, 4601. doi:10.1073/PNAS.0811486106
- [93] N. M. Mahowald, S. Kloster, S. Engelstaedter, J. K. Moore, S. Mukhopadhyay, J. R. McConnell, S. Albani, S. C. Doney, A. Bhattacharya, M. A. J. Curran, M. G. Flanner, F. M. Hoffman, D. M. Lawrence, K. Lindsay, P. A. Mayewski, J. Neff, D. Rothenberg, E. Thomas, P. E. Thornton, C. S. Zender, Observed 20th century desert dust variability: impact on climate and biogeochemistry. *Atmos. Chem. Phys.* **2010**, *10*, 10875. doi:10.5194/ACP-10-10875-2010
- [94] P. W. Boyd, D. S. Mackie, K. A. Hunter, Aerosol iron deposition to the surface ocean – modes of iron supply and biological responses. *Mar. Chem.* **2010**, *120*, 128. doi:10.1016/J.MARCHEM.2009.01.008
- [95] T. Wagener, E. Pulido-Villena, C. Guieu, Dust iron dissolution in seawater: results from a one-year time-series in the Mediterranean Sea. *Geophys. Res. Lett.* **2008**, *35*, L16601. doi:10.1029/2008GL034581
- [96] E. Maraño, A. Fernández, B. Mouriño-Carballido, S. Martínez-García, E. Teira, P. Cermeño, P. Chouciño, M. Huete-Ortega, E. Fernández, A. Calvo-Díaz, X. A. G. Morán, A. Bode, E. Moreno-Ostos, M. M. Varela, M. D. Patey, E. P. Achterberg, Degree of oligotrophy controls the response of microbial plankton to Saharan dust. *Limnol. Oceanogr.* **2010**, *55*, 2339. doi:10.4319/LO.2010.55.6.2339
- [97] R. A. Armstrong, C. Lee, J. I. Hedges, S. Honjo, S. G. Wakeham, A new, mechanistic model for organic carbon fluxes in the ocean based on the quantitative association of POC with ballast minerals. *Deep Sea Res. Part II Top. Stud. Oceanogr.* **2001**, *49*, 219. doi:10.1016/S0967-0645(01)00101-1
- [98] M. Bressac, C. Guieu, D. Doxaran, F. Bourrin, G. Obolensky, J. M. Grisoni, A mesocosm experiment coupled with optical measurements to assess the fate and sinking of atmospheric particles in clear oligotrophic waters. *Geo-Mar. Lett.* **2012**, *32*, 153. doi:10.1007/S00367-011-0269-4
- [99] M. Schulz, J. M. Prospero, A. R. Baker, F. Dentener, L. Ickes, P. S. Liss, N. M. Mahowald, S. Nickovic, C. Pérez García-Pando, S. Rodriguez, M. Sarin, I. Tegen, R. A. Duce, Atmospheric transport and deposition of mineral dust to the ocean: implications for research needs. *Environ. Sci. Technol.* **2012**, *46*, 10390. doi:10.1021/ES300073U
- [100] SCOR-Working-Group, GEOTRACES – an international study of the global marine biogeochemical cycles of trace elements and their isotopes. *Chem. Erde* **2007**, *67*, 85. doi:10.1016/J.CHEMER.2007.02.001
- [101] V. Eyring, D. S. Stevenson, A. Lauer, F. J. Dentener, T. Butler, W. J. Collins, K. Ellingsen, M. Gauss, D. A. Hauglustaine, I. S. A. Isaksen, M. G. Lawrence, A. Richter, J. M. Rodriguez, M. Sanderson, S. E. Strahan, K. Sudo, S. Szopa, T. P. C. van Noije, O. Wild, Multi-model simulations of the impact of international shipping on atmospheric chemistry and climate in 2000 and 2030. *Atmos. Chem. Phys.* **2007**, *7*, 757. doi:10.5194/ACP-7-757-2007
- [102] J. J. Corbett, D. A. Lack, J. J. Winebrake, S. Harder, J. A. Silberman, M. Gold, Arctic shipping emissions inventories and future scenarios. *Atmos. Chem. Phys.* **2010**, *10*, 9689. doi:10.5194/ACP-10-9689-2010
- [103] S. Beirle, U. Platt, R. von Glasow, M. Wenig, T. Wagner, Estimate of nitrogen oxide emissions from shipping by satellite remote sensing. *Geophys. Res. Lett.* **2004**, *31*, L18102. doi:10.1029/2004GL020312
- [104] T. Marbach, S. Beirle, U. Platt, P. Hoor, F. Wittrock, A. Richter, M. Vrekoussis, M. Grzegorski, J. P. Burrows, T. Wagner, Satellite measurements of formaldehyde linked to shipping emissions. *Atmos. Chem. Phys.* **2009**, *9*, 8223. doi:10.5194/ACP-9-8223-2009
- [105] P. A. Durkee, K. J. Noone, R. T. Bluth, The Monterey area ship track experiment. *J. Atmos. Sci.* **2000**, *57*, 2523. doi:10.1175/1520-0469(2000)057<2523:TMASTE>2.0.CO;2
- [106] G. Chen, L. G. Huey, M. Trainer, D. Nicks, J. Corbett, T. Ryerson, D. Parrish, J. A. Neuman, J. Nowak, D. Tanner, J. Holloway, C. Brock, J. Crawford, J. R. Olson, A. Sullivan, R. Weber, S. Schauffler, S. Donnelly, E. Atlas, J. Roberts, F. Flocke, G. Hübler, F. Fehsenfeld, An investigation of the chemistry of ship emission plumes during ITCT 2002. *J. Geophys. Res.* **2005**, *110*, D10S90. doi:10.1029/2004JD005236
- [107] A. Petzold, J. Hasselbach, P. Lauer, R. Baumann, K. Franke, C. Gurk, H. Schlager, E. Weingartner, Experimental studies on particle emissions from cruising ship, their characteristic properties, transformation and atmospheric lifetime in the marine boundary layer. *Atmos. Chem. Phys.* **2008**, *8*, 2387. doi:10.5194/ACP-8-2387-2008

- [108] M. G. Lawrence, P. J. Crutzen, Influence of NO_x emissions from ships on tropospheric photochemistry and climate. *Nature* **1999**, *402*, 167. doi:10.1038/46013
- [109] P. Kasibhatla, H. Levy, W. J. Moxim, S. N. Pandis, J. J. Corbett, M. C. Peterson, R. E. Honrath, G. J. Frost, K. Knapp, D. D. Parrish, T. B. Ryerson, Do emissions from ships have a significant impact on concentrations of nitrogen oxides in the marine boundary layer? *Geophys. Res. Lett.* **2000**, *27*, 2229. doi:10.1029/2000GL011387
- [110] R. von Glasow, M. G. Lawrence, R. Sander, P. J. Crutzen, Modeling the chemical effects of ship exhaust in the cloud-free marine boundary layer. *Atmos. Chem. Phys.* **2003**, *3*, 233. doi:10.5194/ACP-3-233-2003
- [111] J. J. Corbett, P. S. Fischbeck, S. N. Pandis, Global nitrogen and sulfur inventories for ocean-going ships. *J. Geophys. Res.* **1999**, *104*, 3457. doi:10.1029/1998JD100040
- [112] S. B. Dalsøren, M. S. Eide, Ø. Endresen, A. Mjelde, G. Gravir, I. S. A. Isaksen, Update on emissions and environmental impacts from the international fleet of ships: the contribution from major ship types and ports. *Atmos. Chem. Phys.* **2009**, *9*, 2171. doi:10.5194/ACP-9-2171-2009
- [113] J. Fuglestedt, T. Berntsen, V. Eyring, I. Isaksen, D. S. Lee, R. Sausen, Shipping emissions: from cooling to warming of climates and reducing impacts on health. *Environ. Sci. Technol.* **2009**, *43*, 9057. doi:10.1021/ES901944R
- [114] V. Eyring, I. S. A. Isaksen, T. Berntsen, W. J. Collins, J. J. Corbett, O. Endresen, R. G. Grainger, J. Moldanova, H. Schlager, D. S. Stevenson, Transport impacts on atmosphere and climate: shipping. *Atmos. Environ.* **2010**, *44*, 4735. doi:10.1016/J.ATMOSENV.2009.04.059
- [115] J. J. Corbett, J. J. Winebrake, E. H. Green, P. Kasibhatla, V. Eyring, A. Lauer, Mortality from ship emissions: a global assessment. *Environ. Sci. Technol.* **2007**, *41*, 8512. doi:10.1021/ES071686Z
- [116] C. L. Charlton-Perez, M. J. Evans, J. H. Marsham, J. G. Esler, The impact of resolution on ship plume simulations with NO_x chemistry. *Atmos. Chem. Phys.* **2009**, *9*, 7505. doi:10.5194/ACP-9-7505-2009
- [117] P. Huszar, D. Cariolle, R. Paoli, T. Halenka, M. Belda, H. Schlager, J. Miksovsky, P. Pisoft, Modeling the regional impact of ship emissions on NO_x and ozone levels over the Eastern Atlantic and Western Europe using ship plume parameterization. *Atmos. Chem. Phys.* **2010**, *10*, 6645. doi:10.5194/ACP-10-6645-2010
- [118] G. C. M. Vinken, K. F. Boersma, D. J. Jacon, E. W. Meijer, Accounting for non-linear chemistry of ship plumes in the GEOS-Chem global chemistry transport model. *Atmos. Chem. Phys.* **2011**, *11*, 11707. doi:10.5194/ACP-11-11707-2011
- [119] S. Pechtl, R. von Glasow, Reactive chlorine in the marine boundary layer in the outflow of polluted continental air: a model study. *Geophys. Res. Lett.* **2007**, *34*, L11813. doi:10.1029/2007GL029761
- [120] C. H. Song, H. S. Kim, R. von Glasow, P. Brimblecombe, J. Kim, R. J. Park, J. H. Woo, Y. H. Kim, Source identification and budget analysis on elevated levels of formaldehyde within the ship plumes: a ship-plume photochemical/dynamic model analysis. *Atmos. Chem. Phys.* **2010**, *10*, 11969. doi:10.5194/ACP-10-11969-2010
- [121] S. C. Doney, N. Mahowald, I. Lima, R. A. Feely, F. T. Mackenzie, J.-F. Lamarque, P. J. Rasch, Impact of anthropogenic atmospheric nitrogen and sulfur deposition on ocean acidification and the inorganic carbon system. *Proc. Natl. Acad. Sci. USA* **2007**, *104*, 14580. doi:10.1073/PNAS.0702218104
- [122] K. A. Hunter, P. S. Liss, V. Surapipith, F. Dentener, R. Duce, M. Kanakidou, N. Kubilay, N. Mahowald, G. Okin, M. Sarin, M. Uematsu, T. Zhu, Impacts of anthropogenic SO_x, NO_x and NH₃ on acidification of coastal waters and shipping lanes. *Geophys. Res. Lett.* **2011**, *38*, L13602. doi:10.1029/2011GL047720
- [123] V. Eyring, H. W. Köhler, A. Lauer, B. Lemper, Emissions from international shipping: 2. Impact of future technologies on scenarios until 2050. *J. Geophys. Res.* **2005**, *110*, D17306. doi:10.1029/2004JD005620