

Focus 1: Biogeochemical Interactions and Feedbacks Between Ocean and Atmosphere

The objective of Focus 1 is to quantify feedback mechanisms involving biogeochemical coupling across the air-sea interface, which can only be achieved by studying the ocean and atmosphere in concert. These couplings include emissions of trace gases and particles and their reactions of importance in atmospheric chemistry and climate, and deposition of nutrients that control marine biological activity and ocean carbon uptake.

Climate change can lead to alterations in the exchanges of reactive particles and gases between the ocean and atmosphere. Sea salt particles and sea ice can also release gases and provide surfaces for heterogeneous chemical reactions. Many marine biogenic gases are photochemically active, so that changes in their emissions can lead to alteration in the radiative environment, chemical cycles, acidity and the oxidative capacity of the atmosphere. Significant exchanges of these gases occur between the atmosphere and both open waters and ice surfaces. Changes in the spectral quality and intensity of radiation in the atmosphere and ocean as a result of ozone depletion and climate change can have significant impacts on photochemical processes and cloud cover in the atmosphere. These in turn can lead to alteration of physiology, community structure, and photochemical processes in the marine photic zone.

Climate and environmental change will have significant impacts on and feedbacks to biogeochemical cycling in the ocean, on atmospheric chemistry, and on chemical exchange between the ocean and atmosphere. For example, changes in climate may result in alterations in the distribution patterns of phytoplankton and associated dimethylsulphide (DMS) production and release to the atmosphere. Subsequent oxidation of DMS to sulphate aerosol in the atmosphere may affect cloud albedo and thus climate. Changes in climate can also lead to alteration in the quantity and atmospheric delivery pattern of mineral aerosol from land and its associated nutrient iron to the ocean. In regions where iron limits primary productivity, alteration in food web structure is likely, as are changes in the release of a number of biogenic gases and the biological fixation of carbon and nitrogen in the ocean. Atmospheric inputs of different forms of nitrogen to the ocean as a result of increasing population and industrialisation may lead to increased eutrophication of

coastal regions, as well as productivity increases and food web alterations in oligotrophic ocean areas, each of which would cause changes in carbon storage and biogenic gas emissions. These changes in turn will have a significant impact on the scale and nature of climate and environmental change itself.

These complex and interdependent processes can only be addressed by studying the ocean, the atmosphere, and their interactions in a series of joint and coordinated efforts. Coordination with other SOLAS Foci and with other international projects/programmes is vital. For example, we need improved estimates of atmospheric deposition fluxes, where the direct involvement of scientists working in Focus 2 of SOLAS and the World Climate Research Programme (WCRP) will be beneficial in terms of defining wet and dry deposition fluxes. Similarly, in many cases the study of lower atmospheric chemistry would be done best in conjunction with the International Global Atmospheric Chemistry project (IGAC-II). In turn, information from SOLAS regarding atmospheric nutrient inputs could be helpful to the Global Ecology and Oceanography of Harmful Algal Blooms (GEOHAB) and the Integrated Marine Biogeochemistry and Ecosystem Research (IMBER) projects. Cooperation with these projects should result in the development of more advanced ecosystem models of the marine biosphere that take into account, beyond carbon and nitrogen, the full suite of macro and micronutrients. These models will also have to represent individual species or functional types to adequately describe the effects of competition and adaptation, as well as species-specific biochemistry.

Activity 1.1 - Sea-salt Particle Formation and Transformations

The fluxes of marine particles to the atmosphere will alter as a result of climate change.

Introduction

The ocean emits a large amount of sea-salt aerosols and gases to the atmosphere. These sea-salt aerosols play a significant role in atmospheric chemistry in that they can release gases (e.g. volatile organic compounds (VOCs), sulphur and halogen species), provide surfaces for heterogeneous chemical reactions, and directly or indirectly alter the atmospheric radiation field. In turn, the chemical and physical characteristics of these aerosols reflect their source and subsequent physical and chemical processing (Chameides and Stelson, 1992; O'Dowd et al., 1997). The exchange of sea-salt aerosols between the atmosphere and the ocean is regulated by a variety of physical forcings. Thus, climate-induced changes in the factors controlling particle exchange and transformation would be expected to alter their impact on the state of the atmosphere and in turn feed back to climate. It has recently been argued that sea spray can help cleanse the atmosphere of air pollution with resultant effects on cloud and precipitation formation (Rosenfeld et al., 2002).

State of Present Understanding

Sea-salt aerosols are a major reactive medium in the marine atmospheric boundary layer (MABL), as well as a significant source of atmospheric alkalinity and organic material. They are also precursors for volatile reactive halogens. The production of several classes of compounds (particularly the reactive halogen gases discussed in Activity 1.2), in addition to the chemical processing and deposition of important sulphur and nitrogen species, are directly tied to sea-salt reactions. Sea salt is also an important source of cloud condensation nuclei and thus can change cloud properties, including the radiative effects of clouds (Andreae and Crutzen, 1997; Keene et al., 1998; Murphy et al., 1998). As a consequence, sea salt can directly or indirectly lead to effective scattering of incident radiation in the MABL. Since the flux of sea-salt particles from the ocean is thought to vary as the cube of the wind speed (Monahan and O'Muircheartaigh, 1986), climatically driven changes in global wind fields will significantly alter concentrations and lifetimes of atmospheric sea-salt aerosols, their asso-

ciated reactant and product species, and their effects on radiative transfer. However, quantification of this sea-salt flux is difficult, and published estimates vary by an order of magnitude (Focus 2).

Another important class of particles is formed by gas-to-particle conversion. These particles usually have diameters smaller than 1 μm . For example, dimethylsulphide (DMS, $(\text{CH}_3)_2\text{S}$) and carbonylsulphide (COS) are emitted from the ocean, after which they are oxidised and can produce new particles in the atmosphere, as well as leading to growth of existing particles. The chemistry of DMS is described in detail under Activity 1.3 but it should be noted that condensation of the products of DMS oxidation on sea salt represents an important sink. COS, which is produced by photochemical reactions in the surface ocean (discussed in Activities 1.2 and 1.3), has a much longer atmospheric residence time than DMS, so the primary impact of its oxidation is to form sulphate aerosols in the stratosphere. Photochemical particle bursts, which may be initiated by trace gas emissions, are discussed in Activity 1.2.

Condensed organic material is one of the least understood components of marine aerosols, even though it may have a dramatic effect on hygroscopic growth and cloud-nucleating properties (Jacobson et al., 2000). While continental emissions of VOCs are important in some marine areas, a significant amount of the organic material processed through the MABL is emitted from the ocean in association with sea-salt aerosols. This occurs by concentration from bulk seawater onto the walls of bubbles and subsequent ejection into the atmosphere during bubble bursting. Organics associated with sea salt react in atmospheric aqueous phases to produce both volatile and particulate products (Kawamura et al., 1996). Other sources of condensed organic material include primary processes that release biological aerosols (such as bacteria and cell fragments) to the atmosphere.

Major Issues that Require Resolution

- ▶ **What are the details of the physical and chemical processing of sea-salt aerosols?** Sea-salt aerosols are increasingly recognised as aqueous reactors for gases such as sulphur dioxide. In many regions non-sea-salt aerosols control particle number and cloud properties, yet their atmospheric cycling is poorly understood. For example, are algae and bacteria and other biota involved? Hence we need to consider, in addition to sea salt, alternative particle sources. What are the heterogeneous reactions leading to autocatalytic release of reactive halogen species in polar and other regions?
- ▶ **What are the source strengths, distributions, and removal rates of sea-salt aerosols?** The current large uncertainties in aerosol production and removal rates for both sea-salt and non-sea-salt aerosols (which are discussed in Activities 1.2, 1.3, and 1.4) lead to large ranges in estimates of their atmospheric lifetimes. Better precipitation scavenging data and improved techniques for measuring aerosol dry deposition are needed (Focus 2). Source terms are also poorly constrained, with current uncertainties in the sea-spray source function in the open sea of one order of magnitude. An important source of sea spray is production in the surf zone, with local concentrations observed sometimes to be two orders of magnitude larger than advected from the open sea. This source is particularly difficult to quantify.
- ▶ **What are the chemical constituents of the sea surface organic microlayer, how can it be accurately sampled, and what are its impacts on organic aerosols?** Among other things, the surface microlayer (up to a few hundred microns) influences the composition of sea-salt particles. A large number of compounds and ill-defined complex organic substances are involved. These compounds need to be characterised and their effect on aerosol properties elucidated.

Specific Goals

- I. Constrain the source of sea-salt aerosols (as a function of controlling factors such as local wind speed) to within a factor of two.
- II. Quantify the wet and dry removal of sea-salt aerosols under various conditions to within a factor of two.

- III. Integrate this understanding into models that can use remotely sensed parameters to predict the regional distribution of sea-salt aerosols for use in climate models.
- IV. Identify the heterogeneous reaction mechanisms leading to the release of halogen gases from sea-salt aerosols.
- V. Develop sampling methods for the sea surface microlayer that can support studies of its chemical and physical properties.
- VI. Develop analytical methods with the aim of identifying the key components of the chemical constituents of the sea surface microlayer.

Promising Approaches and Implementation Strategy

The first step towards understanding the atmospheric behaviour of sea-salt aerosols and mixed particles is to characterise their size-dependent chemical composition, morphology, and spatial and temporal distribution. Process understanding may require more extensive observations than have been made to date, some with multiple platforms in large experiments. Higher time and space resolution may be needed to resolve some processes. Testing our integrated understanding, however, may require decade-long time series measurements of some species or remote sensing from space to probe global patterns and variability of measurable parameters.

The sources and removal rates of sea-salt aerosols are difficult to characterise, in part because production and loss occur simultaneously. The largest sea-salt particles dry deposit rapidly, while smaller aerosols are primarily removed by wet deposition on a longer time scale. Detailed observations of particle size distributions under various source and loss scenarios can be coupled with aerosol process models to constrain these terms (Vignati et al., 2001). Particular attention is needed for submicron particles, which are no longer thought to be solely sulphates. Murphy (1998) showed that in remote marine air about half the mass near 100 nm was sea salt. Nilsson et al. (2001) measured sea-spray particles as small as 20 nm over the open ocean, the formation of which from bubbles was confirmed through laboratory experiments by Mårtensson et al. (2003). However, since these laboratory experiments used artificial seawater, the resulting aerosol may have differed considerably from that produced naturally. Sea spray plays other roles that are described in Activity 2.3. Elemental and organic

carbon and perhaps even halogen nuclei may also play important roles in the accumulation mode.

One reason why some of the issues above are poorly understood is that tropospheric trace gas and aerosol composition and their temporal and spatial distributions have not been adequately characterised. In many cases this is because measurement techniques are biased (e.g. aerosol inlet losses), instruments are not widely available due to the cost and technical sophistication required for operation (e.g. Differential Optical Absorption Spectrometer (DOAS), Light Detection and Ranging (LIDAR), low-level NO_x), or suitable techniques do not exist (e.g. aerosol organic speciation, direct measurement of halogen atoms, HOBr , etc.). In other cases, relatively simple and inexpensive measurement methods are available, but they need to be deployed much more widely to generate representative distributions. For organic compounds, new approaches are needed. Instruments such as single particle mass spectrometers might be modified to ablate only the outer layers of marine aerosols, thus helping to understand the layering of inorganic and organic species. Single particle laboratory experiments with organic vapours may also help in identification of organic material.

Among the major unknowns are the amount, nature and functionality of organic fractions of the aerosol, in part because existing analytical methods are incapable of identifying even the major compounds. Development work is needed on methods to characterise organic compounds (at least in terms of their functional groups), including the water-soluble portions, to support studies of growth with humidity and cloud droplet nucleation. Since the microlayer-derived materials that accompany large sea-salt aerosols are very different from the secondary organic compounds that condense onto the accumulation mode, it is important that these studies at least distinguish between modes above and below $1 \mu\text{m}$, if measuring a more detailed size distribution is impractical. Knowledge of the concentrations of precursor organic vapours is clearly essential for establishing the source of accumulation mode organic aerosols (Activity 1.2).

Some marine regions are strongly impacted by mineral dust, which tends to be in supermicron aerosol particles. The carbonates often found in dust can impact the pH of marine aerosols, so it is important to study dust mineralogy (Activity 1.4). Changing emission patterns of SO_2 , NO_x and NH_3 can also alter aerosol pH. Since pH is a major controller of chemical processes in

aerosol solutions, reliable characterisation of the acidity/alkalinity of aerosols will provide important constraints on the nature of the associated transformations.

Halogen compounds in aerosols also need to be specified by size. Simultaneous measurements of associated vapour-phase compounds will be critical for quantifying the impact of inorganic halogens on oxidation of other compounds. Single-particle studies (microscopic and mass spectrometric) will be needed to determine the presence of unicellular algae, for example, or other unique nuclei. The time and place of these measurements should be tailored to the specific question to be addressed: before and after polar sunrise, in and out of continental plumes, and rapidly enough to see diurnal cycles, for instance. Time series studies on scales from hours to years provide unique and valuable constraints on models; stable funding mechanisms must be developed to ensure the continuity of these important records so that we can test diagnostic model forecasts in the presence of perturbations such as ENSO (El Niño-Southern Oscillation) and decadal oscillations.

The distribution of marine aerosols in time and space needs to be established. Satellite observations using retrieval algorithms that can discriminate between marine and other aerosol types (Kusmierczyk-Michulec et al., 2002; Robles-Gonzalez, 2003) provide information on the spatial distribution which can then be assimilated in diagnostic chemical transport models to cover periods when no satellite data are available. The data assimilation constrains the models, but the results must be tested against observations on various time scales in all the major air mass types, accompanied by profile measurements using lidar or airborne platforms. On longer time scales, ice core records can provide further constraints on the sea-salt source variability. There is no substitute for *in situ* observations, which need to be made over time (ships and coastal sites) and at multiple altitudes (aircraft), to complement satellite and LIDAR data for the development and testing of 4D data assimilation models, along with developing ocean observing systems based on buoys. A scheme to provide the most likely aerosol type for each region can be based on climatologies, but a major improvement is expected by using a chemical transport model employing emissions of primary aerosols and aerosol precursor gases to provide the initial aerosol composition for use in the retrieval, as proposed by Verver et al. (2002). Remote sensing by LIDAR and satellites should be used to study production and loss, including rainfall. A high priority should be given to the development of new

methods for measuring the source of sea-salt particles, and aerosol dry deposition to the ocean surface, for example, direct flux measurement by eddy correlation (Nilsson et al., 2001; 2003) (see also Activity 2.3). Lagrangian observations should be considered for testing models of deposition.

In addition to establishing the time-varying nature of sea-salt aerosols for areas of interest, laboratory measurements of thermodynamic properties and reaction rates under conditions similar to ambient are needed to support chemical modelling of processes on sea-salt aerosol, such as halogen release and SO₂ oxidation. These reaction mechanisms depend on many factors, such as solubility and reaction rate constants, that are poorly known. There is a need for the laboratory determination of reliable thermodynamic and kinetic data, especially in condensed phases and gas/aerosol mixtures. The models based on these data should then be used to simulate observable quantities that can be compared to laboratory or field data. Size-dependence of halogen loss, product concentrations over time, and diurnal cycles of various compounds are examples of characteristics that might provide good process model tests. This effort would benefit greatly from close collaboration with IGAC-II.

If our wet and dry removal models are correct, most submicron marine particles (including sea-salt particles) are removed by wet deposition. It is therefore important to make accurate measurements of aerosol loss in rainfall (Focus 2). Of course, it is impossible to sample marine rain in enough places to provide a truly representative picture, so time series observations at a modest number of sites should be used to improve precipitation chemistry process models.

The sea-surface microlayer presents special challenges due to its small vertical dimension and the inability to reproduce its chemistry and dynamics adequately in the laboratory. New sampling methods are needed, as is development work on spectroscopic methods that can be deployed from ships, aircraft and satellites to probe near the surface of the ocean.

The ultimate test of our understanding of marine aerosol processes is Lagrangian observations, of the type used in ASTEX/MAGE, ACE-1 and ACE-2. Such studies can address key questions such as, how do the sea salt and accumulation mode concentrations recover after a rain event? During dry periods, does the submicron mass

grow at the rate predicted by models of sulphur chemistry? Observing a tagged air mass for a day or more allows tests of many process model predictions, including source, transformation, and loss terms. In some remote areas the environment is sufficiently homogeneous that Eulerian observations may be used for some purposes as if they were Lagrangian. In either case, vertical profiles of the atmospheric marine boundary layer are critical for interpreting Lagrangian budget studies.

Activity 1.2 - Trace Gas Emissions and Photochemical Feedbacks

Changes in factors that affect and are affected by radiation will alter trace gas fluxes between the ocean and atmosphere.

Introduction

Radiation-driven processes have been identified as a critical link in the understanding of trace gas exchange between the ocean and atmosphere in future climate scenarios (e.g. Zepp et al., 1998). This evaluation follows from recent findings that many photochemical and photobiological reactions are important in the natural cycling of climate-relevant trace gases (e.g. sulphur gases, organo-halogens, CO and hydrocarbons). Because many of the trace gases emitted from the ocean are photochemically and/or infrared (IR) active (i.e. they influence the climate), these gas emissions can lead to considerable changes in the radiative environment. They also influence chemical cycles, acidity, and the oxidation capacity of the atmosphere. For example, the oceanic emission of reactive halogen compounds (Cl, Br, and I) is known to influence the ozone budget and the oxidation capacity of the MABL in some, and perhaps most, marine regions. Factors that control these emissions (either via organic precursors or due to sea-salt aerosol, as discussed under Activity 1.1) include wind speed, temperature, aqueous photochemistry and biological activity, which in turn depend on radiative, chemical and physical phenomena. In this way, changes in any of these factors would be expected to change organo-halogen emissions and their feedback on the chemical condition of the atmosphere, with possible consequences for other important trace gases.

Despite new recognition of the climatic importance of radiation-driven biogeochemical processes, most known photo-processes in the surface ocean are still not yet fully understood or treated in a quantitative manner in atmospheric models. In addition, it is likely that other important photochemical and/or photobiological reactions have not yet even been identified. Consequently, regardless of changes in radiation arising from future climate change, the impact of radiation on important trace gas cycles needs to be better understood and quantitatively integrated into process models.

As discussed under Activity 1.1, in many cases adequate measurement instrumentation is not widely available

due to the cost and technical sophistication required for operation (e.g. miniaturised systems for buoy deployment for autonomous long term sampling), or suitable techniques are non-existent (e.g. aerosol organic speciation, direct measurement of halogen atoms, HOBr, etc.).

State of Present Understanding

Many chemical and biological processes critical to trace gas exchange between seawater and the atmosphere can be affected either directly or indirectly by solar radiation and are consequently susceptible to changing radiation fields. Changes in the intensity and/or the spectral distribution of this radiation in the surface ocean or lower atmosphere will have an effect on the cycling of those trace gases controlled by photochemistry and/or biological processes.

Direct radiative effects on trace gas exchange between the surface ocean and lower atmosphere include:

- the photochemical production of important, atmospherically reactive trace gases such as COS (Zepp and Andreae, 1994; Weiss et al., 1995), CS₂ (Xie et al., 1998), CH₃I (Moore and Zafriou, 1994), alkenes (Ratte et al., 1993; 1998) and CO (Valentine and Zepp, 1993; Najjar et al., 1995);
- photo-oxidative loss of other trace gases like DMS (Kieber et al., 1996); and
- the photochemical breakdown of dissolved organic carbon in marine waters directly to CO₂ (Miller and Zepp, 1995), a process that has been estimated to be of similar magnitude to carbon fixed by new biological production (Johannessen, 2000; Mopper and Kieber, 2000).

Changes in oceanic biological processes in response to changing radiation fields or biological activity also affect the emission of marine biogenic halogens, which contribute to halogen budgets in both the stratosphere and the troposphere. Shorter-lived organic and inorganic

halogen compounds are also either emitted directly from the ocean (e.g. CH_2Br_2 , CHBr_3 , CH_3I), produced indirectly in the atmosphere via photochemical transformation of precursor species, or made by chemical processes involving sea-salt aerosol in the MABL (e.g. HCl , HBr , Br_2 , BrCl , Cl_2 , BrO , ClO , IO) (Platt and Moortgat, 1999). Heterogeneous photochemical reactions are also apparently involved in the release of reactive halogenated species (e.g. the “Bromine Explosion”, Wennberg, 1999).

Reactive halogen compounds (such as atomic Br and BrO originating in the ocean) can contribute to ozone destruction in the troposphere (Barrie and Platt, 1997), as exemplified by the polar “Tropospheric Ozone Holes” that occur during spring time in the Arctic and Antarctic boundary layers (Figure 5). It is evident that halogens change greenhouse forcing both directly (through the IR absorption of ozone) and indirectly via the change in tropospheric oxidation capacity, which controls the lifetimes and atmospheric abundances of greenhouse gases such as CH_4 and hydrochlorofluorocarbons.

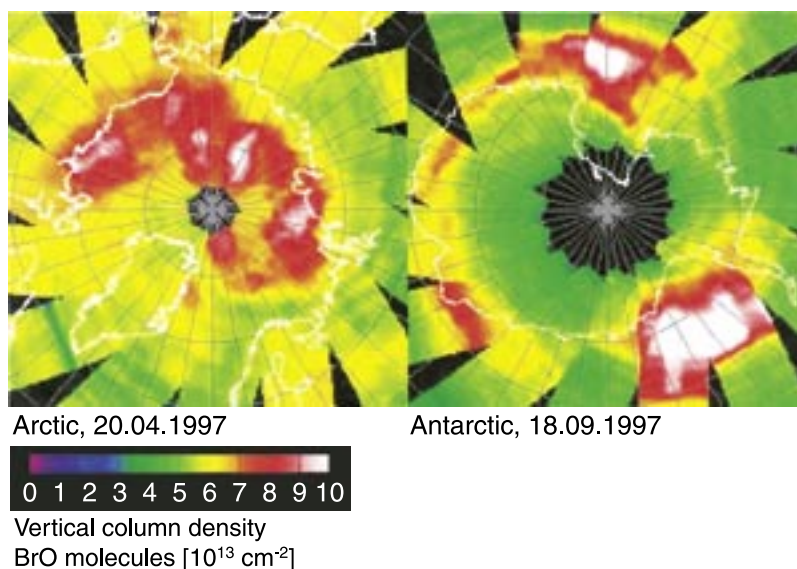
Some halogen species are powerful oxidants themselves. BrO and atomic Cl , for instance, may play an important role in the oxidation of DMS (Toumi, 1994). Since Cl atoms are roughly one order of magnitude more reactive than OH radicals, even low levels could have a large influence on the atmospheric lifetimes of many trace gases (Platt and Janssen, 1996) and selected hydrocarbons (Singh et al., 1996).

Currently, the organo-halogen compounds CH_3Br and CH_3Cl contribute about 25% of the equivalent chlo-

rine to the stratosphere and, consequently, contribute significantly to the loss of stratospheric O_3 (Solomon, 1999). An increase of only 0.5 pptv (5%) in the atmospheric burden of CH_3Br (perhaps as a consequence of climatic change) would reverse the current downward trend in the atmospheric burden of ozone-depleting gases. Thus, climate-driven changes in biogenic production of organo-halogens, their emission fluxes, or their transport by deep convection could significantly impact stratospheric O_3 .

The ocean is also a significant source of biogenic VOCs (Plass-Dulmer et al., 1995). C_2 and C_3 compounds and isoprene can be present in the MABL at concentrations high enough to react with a significant fraction of the OH and thus affect the oxidation capacity of the atmosphere. A myriad of heavier organic compounds, many of biological origin and surface-active, are found in the sea surface microlayer, where they may affect air-sea gas exchange rates (Focus 2). Condensable organic vapours (oxidised VOCs that were emitted from the ocean or adjacent land masses) may participate in the nucleation of new particles as well as in their growth. VOCs play a large role in modifying the ability of particles to serve as cloud condensation nuclei. As indicated in Activity 1.1, a significant amount of the organic material processed through the MABL is emitted from the ocean in association with sea-salt aerosols. Organics associated with sea salt react in atmospheric aqueous phases to produce both volatile and particulate products (Kawamura et al., 1996). Other sources of condensed organic material include primary processes that release biological aerosols, e.g. bacteria and cell fragments, to the atmosphere. Iden-

Figure 5. Satellite (Global Ozone Monitoring Experiment, GOME, on the ERS-2 satellite) observations of tropospheric BrO “clouds” in the Arctic and Antarctic. Total BrO column densities in the centre of the clouds exceed 10^{14} BrO molecules cm^{-2} . The clouds are associated with total loss of boundary layer ozone, occur only in spring time, and have a typical lifetime of one to a few days (Wagner et al., 2001). Reproduced by permission of American Geophysical Union.



tification of these organics and estimation of their fluxes has been impeded both by sampling artefacts (a significant amount may be volatilised from aerosols during sampling), and by analytical challenges arising from the large number of compounds (such as ill-defined humic-like substances) that are involved. In general, there is a lack of information on the sources and composition of organic material in marine aerosols, which inhibits our understanding of the effects of such organics on cloud properties, formation of precipitation and chemical transformation of aerosols.

The absorption of solar radiation by chromophoric (coloured) dissolved organic matter (CDOM) in the surface ocean initiates many indirect controls on trace gas cycles in the surface ocean, including:

- the photo-reduction of metals important for biological growth;
- the production of oxygen and organic radicals that alter surface ocean redox conditions and the bioavailability of trace nutrients (Activity 1.4) (Miller and Kester, 1994; Blough and Zepp, 1995);
- the photo-transformation of refractory dissolved organic carbon into molecules with altered microbial availability (Moran and Zepp, 1997; Mopper and Kieber, 2000);
- the breakdown of CDOM (photochemical fading) and consequent changes in inherent ocean optical properties that result in a deeper penetration of UV into the water column, as well as changes in photochemical rates that rely on CDOM absorbance (Vodacek et al., 1997; Nelson et al., 1998);
- Production of important trace gases such as COS and CO. Coastal areas may be particularly significant areas for production of these gases because of their high concentrations of CDOM.

UV radiation also causes direct damage to many organisms in the ocean with a large number of specific responses, for example, decreased photosynthesis in phytoplankton, DNA damage in bacteria and changes in the survivability of a suite of organisms ranging from viral cells to fish larvae. Together with increased visible radiation, UV can inhibit cellular processes such as N₂ fixation (Activities 1.4, 1.5), nutrient uptake, methane oxidation, and nitrification. A selection of review papers on these subjects is given in DeMora et al. (2000) and

Hessen (2002). It seems clear that changes in radiation will affect phytoplankton community structure, biological pigment distribution, and dissolved organic matter utilisation. Altered stress due to changes in light regime, together with photochemical alteration of redox chemistry and organic carbon constituents, are likely to provide drivers for changes in the role of biology in trace gas cycling and atmospheric exchange.

Our current understanding of the direct effects of radiation on atmospheric chemical and marine biogeochemical systems (particularly photochemical reactions related to trace gas exchange and climate feedbacks) is more advanced than that of the complex indirect effects that involve coupling biology, chemistry and physics. It may be that these indirect impacts are more significant than known direct effects. However, neither direct nor indirect effects are currently well quantified in relation to climate feedback and the effect of altered radiation regimes on trace gas exchange.

As indicated in Activity 1.1, another important effect of photochemistry in the marine boundary layer is aerosol formation by gas-to-particle conversion. These particles usually have diameters smaller than 1 µm. For example, DMS and organohalogens (O'Dowd et al., 2002) are oxidised and may produce new particles in the atmosphere. The chemistry of DMS is described in detail under Activity 1.3.

A related phenomenon is that of "particle bursts" - very rapid photochemical formation of ultra-fine particles observed in some coastal areas (Leck and Bigg, 1999; O'Dowd et al., 2002). Although the global significance of this effect is unclear, it provides a stringent test for theories of particle formation. Even ternary systems (H₂O, H₂SO₄, NH₃) appear to be unable to produce particles at a fast enough rate to explain the observations, and other condensable, but undetermined, species have to be invoked.

Major Issues that Require Resolution

- ▶ **What are the magnitudes of and controlling factors for trace gas fluxes between the surface ocean and the atmosphere?**
- ▶ **How is the oxidation capacity of the atmosphere affected by changes in the source of reactive halogen species (Cl, Cl₂, Br, BrO, IO, etc.) and the flux of biogenic VOCs from the ocean?** This includes both organic and inorganic halogen compounds. The nature of

the halogen release at the ocean-atmosphere and sea ice-atmosphere interfaces and from sea-salt aerosol is presently unclear.

- ▶▶ **Are the sea-surface microlayer, snow-covered ice and ice surfaces particularly active sites for photochemical interactions and trace gas emissions?** The microlayer (with enhanced levels of various materials and microorganisms) and snow and ice surfaces receive unattenuated solar radiation that will maximise photochemical reactions in direct contact with the atmosphere.
- ▶ **Do changing relations between water column structure, spectral quality and quantity of solar radiation reaching the ocean (related to clouds, atmospheric aerosols, etc.) and resulting penetration depth of radiation affect photochemical and biogenic trace gas cycles in the surface ocean?** Mixed layer depth, water transparency and spectral irradiance will affect cumulative biological exposure and depth of trace gas production, both important factors in nutrient exchange dynamics.
- ▶ **Will altered photo-dynamics of marine CDOM and changes in biological community structure affect trace gas cycles through changes in the inherent and apparent optical properties in the surface ocean?** Photo-oxidation is the main sink for CDOM in the surface ocean. In addition, CDOM is the main absorber of UV radiation, and biological particles both absorb (via photosynthetic pigments) and scatter (based on biological particle number, size, and light-scattering properties) solar radiation in the surface ocean. The quantity and spectral quality of radiation available for direct photochemical and photobiological reactions relate to trace gas exchange, where CDOM photodegradation is a source of trace gas emissions.
- ▶ **What are the mechanisms producing bursts of ultrafine particles that are sometimes observed in coastal and polar areas?** These particles (a few nm in size) are produced in the tidal zone at low tide by a photochemical mechanism, although the chemistry (compounds involved) and the mechanisms are poorly understood.

Specific Goals

- I. Quantify the contribution of reactive halogen species to the oxidation capacity in the marine boundary layer.
- II. Quantify the relationship between optical properties of the ocean surface layer, solar radiation intensity, and photochemical and biogenic cycles of climatically important trace gases.
- III. Develop heterogeneous (photo) chemical reaction mechanisms leading to halogen release at sea ice or snow surfaces and the sea surface microlayer. These mechanisms should be quantified well enough to establish the scale and magnitude of likely future atmospheric changes driven by these reactions.
- IV. Identify and parameterise the effect of changing photo-dynamics of marine CDOM and biological community structure on trace gas cycles.
- V. Quantify the nucleation and condensational growth of aerosols due to gas-to-particle conversion. Determine the relative contribution of gas-to-particle conversion to the marine aerosol population.

Promising Approaches and Implementation Strategy

As described in the Introduction, the general approach in SOLAS involves field and laboratory measurements which are then incorporated into and tested within computer models. There is a large separation of time scales between climate change issues and photochemistry and photobiology measurements (decades vs. nanoseconds). Consequently, great care must be taken in assigning significance to any trace gas exchange scenario because of the disparate time scales that must be critically addressed for all the approaches listed below. Collaborations with IGAC-II will be particularly valuable in this area.

To determine their controlling factors, trace gas fluxes must be measured with a much greater accuracy and temporal resolution than has been possible for most compounds to date. The development of chemical sensors that can operate at 1 Hz or faster is critical to be able to make direct flux measurements by the eddy correlation approach. Methods such as chemical ionisation mass spectrometry, which allow measurement of DMS at 25 Hz, will be needed to enable flux measurements by eddy

correlation. For compounds for which no fast analytical method can be developed, eddy accumulation and gradient approaches should be used. The goal is to measure fluxes on a time scale of 30 minutes or less, so that the response of fluxes to changes in the controlling factors (e.g. wind speed, bubble spectra, wave slope) can be clearly seen. Understanding of many important processes is currently limited by the accuracy of our flux measurements.

Concentration fields of organo-halogen gases (and other trace gases of interest to SOLAS, e.g. sulphur gases - Activity 1.3) are not adequately characterised in the surface ocean and lower atmosphere. Many of the halogen radicals are present at extremely low concentrations, so the development of sensitive analytical methods is necessary. Many more observations are needed to understand the spatial and temporal variability of halogen-containing compounds. Here satellite observations can be of great help with their ability to study large-scale structures. Understanding processes will require intensive field campaigns aimed at determining fluxes, the underlying physical, chemical and biological controls on them, and the subsequent atmospheric reactions that lead to oxidant and aerosol formation. Resources could be used more effectively by integration of such campaigns into Focus 1.

Continental outflows in the lower atmosphere should be exploited to study the influence of a changing chemical environment on the chemistry of the MABL and fluxes through it. Measuring the vertical profiles of O₃, CO, halogen compounds, VOCs, NH₃, and aerosol mass and size distributions in various regions would show the extent of the impact of emissions of these compounds and clarify the mechanisms of such impacts. Satellite measurements are also useful in estimating the areal distribution of gases (O₃, halogen oxides, NO₂, CH₂O, CH₄, and CO) in the lower troposphere, allowing us to test chemical transport models for these compounds (Figure 5). In addition near real-time data from satellites can support the planning of measurement campaigns. *In situ* measurement campaigns will be needed to calibrate these new satellite sensors.

The photochemical reactions of biogenic halocarbons and other important biogenic trace gases need to be studied in the laboratory under environmentally relevant conditions, considering all possible oxidants. Standards for the inter-comparison and intercalibration of light-normalised rates and photolysis frequencies should be developed, including an effort directed at radiation measurement methodology.

Laboratory studies are needed to determine fundamental photochemical and biological responses to solar radiative flux (especially the determination of photochemical quantum yields and biological weighting functions for use in models). These can then be compared with field studies under varying conditions of ozone depletion and cloud conditions (e.g. seasonal studies in the polar ocean areas) to verify and improve ozone depletion models. Methods for the measurement of CDOM absorbance in seawater at wavelengths greater than about 350 nm in the open ocean are needed for these efforts.

In addition, more field and laboratory work is needed to understand bursts of microparticles. Both chamber experiments and aerosol mass spectrometry show promise for improving our understanding of these nucleation phenomena. It is now known that several systems may participate in nucleation (sulphuric acid, condensable organics, sulphate, ammonium nitrate, and iodine compounds), so the scope of these studies needs to be inclusive.

Oceanic Lagrangian and transect studies that contrast mineral particles (e.g. as enhanced in river plumes) with biological particles (e.g. as enhanced in phytoplankton blooms) will provide insight into changing light fields and ensuing heterogeneous reactions as they affect the temporal evolution of trace gas processes, biological succession and feedbacks. Mesocosms will provide controlled radiation regimes together with specific mixed layer depths, particle loads, CDOM concentrations, etc. for the study of trace gas emissions.

Climate-driven changes in mixed layer depth relative to the depth of radiation penetration may alter the cumulative radiative exposure of both organisms and chemical constituents, affecting reactions and rates relevant to trace gas fluxes. Field sites to quantify the effects of changing radiation penetration should be located in areas of strong natural gradients of turbidity, colour and mixing. These might include river plumes, areas of ice melt, time series locations spanning storm mixing events, and longitudinal transects from coastal to open ocean regions. Conversely, calm marine regions could be studied over varying radiation regimes. Models based on these process rates will need to be tested using field campaigns in a variety of environments (high latitude, low latitude, oceanic, and coastal) to ensure an overall improvement in model predictions of future changes in the climatic effects of trace gas emissions.

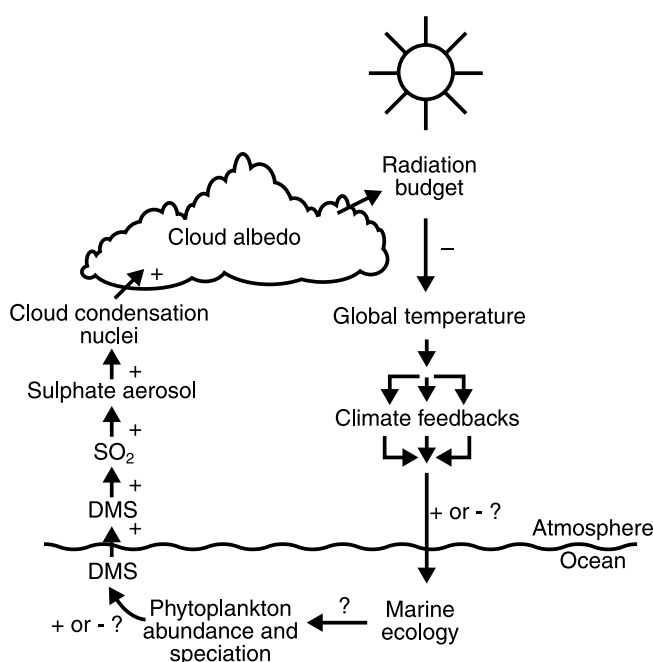
Activity 1.3 - Dimethylsulphide and Climate

Changes in dimethylsulphide (DMS) production by marine plankton can have a significant effect on climate by modifying aerosols and cloud albedo.

Introduction

In 1987, our understanding of the importance of air-sea exchange in regulating climate was dramatically changed by the publication of the CLAW hypothesis (named after its authors, Charlson, Lovelock, Andreae and Warren), as illustrated in Figure 6. This landmark paper postulated a feedback loop involving marine phytoplankton, sulphate aerosol formation, and cloud albedo that might stabilise the Earth's temperature. An increase in phytoplankton would cause an increase in DMS emissions to the atmosphere and raise atmospheric DMS concentrations, thereby increasing the rate at which sulphate aerosol (non-sea-salt sulphate - NSS) is formed. If this also increased the number concentration of cloud condensation nuclei (CCN), it should make clouds whiter, reflecting more sunlight back to space and

Figure 6. Mechanism by which marine algae may influence sulphate aerosol concentrations and the albedo of clouds, possibly feeding back to stabilise climate (Reprinted from Andreae, 1990, after Charlson et al., 1987, with permission from Elsevier Science).



cooling the Earth. Other sulphur gases emitted from the oceans (e.g. COS, Activity 1.2) are important sources of sulphate aerosols in the stratosphere. Understanding this highly coupled ocean-atmosphere system through interdisciplinary research is one of the important objectives of SOLAS. Some parts of this work will require collaboration with projects such as CLIVAR, IGAC-II, GLOBEC and IMBER.

State of Present Understanding

Whilst some of the CLAW linkages have been demonstrated, for instance NSS and cloudiness at Cape Grim correlate with the seasonal cycle of DMS fluxes (Ayers et al., 1991; Boers et al., 1994), all of the necessary steps have not been quantified well enough to determine whether the CLAW feedback loop actually exists. The palaeoclimate record is one of the few means for testing this overall scheme, but it has yet to produce a definitive answer (Legrand et al., 1991; Saltzman et al., 1997), because of uncertainties in the relationship between marine productivity and ice core MSA (methane sulphonic acid, a product of DMS oxidation that is preserved in ice cores). SOLAS activities may, in fact, be useful in calibrating MSA as a proxy for DMS fluxes and their relationship to marine productivity. In addition, the role of sea-salt particles as a source of CCN is largely unknown (Activity 1.1), and it has been suggested that the concentration of sea salt was underestimated in the original CLAW paper (Blanchard and Cipriano, 1987).

Process studies in algal blooms have established a general linkage between phytoplankton and DMS levels, but these studies have not quantified the long term natural variability in DMS concentrations in many marine areas. While it is clear that some taxonomic groups typically contain orders of magnitude more of the DMS precursor dimethylsulphoniopropionate (DMSP) than others, the reasons for these differences are not well understood. DMS emissions represent a small part of the total food web cycle of DMSP and further study of this cycle is required, since small changes in DMSP cycling could produce disproportionate changes in DMS emissions. Changes in UV-B radiation that depend on column

ozone levels in the atmosphere can also affect DMS production through ecological shifts (Activity 1.2).

The emission of DMS to the atmosphere depends on wind speed, temperature, seawater DMS concentrations, and possibly other factors. DMS concentrations in the surface ocean reflect the balance of biogenic sources and losses from ventilation, photolysis, and bacterial consumption. These interactions are not currently well quantified. For instance, the two most frequently used models for estimating DMS ventilation fluxes can differ by up to a factor of two (Nightingale et al., 2000b). SOLAS Focus 2 outlines approaches for reducing those uncertainties.

The atmospheric chemistry of DMS is still poorly known. It is clear that OH reacts with DMS by both OH addition and hydrogen-abstraction pathways, and that SO₂ and MSA are among the major products. The relative amounts formed by each mechanism are believed to be a function of temperature, which may explain the different product distributions observed in polar and equatorial regions. However, neither laboratory nor field experiments have yet been able to quantify rate constants for the entire suite of reactions that follow OH attack (Davis et al., 1999). It is also known that NO₃ and halogen radicals (e.g. BrO) can react with DMS, but the importance of these mechanisms is even less well known.

Some fraction of the SO₂ is oxidised homogeneously by OH (the only pathway that can cause the nucleation of new particles), while the rest may be dry deposited back to the ocean's surface, oxidised on existing particles in clouds, or oxidised on short lived sea-salt particles. Changes may be counterintuitive, for example if conditions that create higher DMS concentrations are accompanied by stronger winds (and thus more airborne sea salt to consume SO₂), it is possible that less new sulphate aerosol will be formed. On the other hand, as many global change scenarios currently assume, higher winds may result in more atmospheric DMS and more NSS aerosol.

The factors controlling homogeneous nucleation have been studied extensively since 1987, and significant progress has resulted. One scenario (Raes, 1995) suggests that new aerosol particles are primarily formed in the (largely particle-free) free troposphere, after which they are entrained into the MABL and grow by condensing the products of gas-phase DMS oxidation. However,

measurements near Macquarie Island found growth rates of nanoparticles to be larger than sulphuric acid condensation could explain (Weber et al., 1998). This prompts the question “Do condensable organics help embryonic particles grow large enough to nucleate cloud droplets?”

The relationship between particle number concentration (CN, or condensation nuclei) and cloud droplet number concentration (CDN) is also poorly known. The CLAW authors postulated an increase in CCN (cloud condensation nuclei, a subset of activatable CN), but thousands of observations have failed to establish a precise relationship between CCN and CDN (Chuang et al., 1999). In part, this is due to our inability to specify updraft velocities in clouds, but there are more serious problems. Cloud chamber-type CCN instruments may not mimic the kinetics of activation in clouds, a cloud's condensable water supply, or the impact of soluble gases (e.g. HNO₃, MSA, organic acids); all of which play critical roles in activation of particles to cloud droplets. This may explain why the range of observed CDN/CCN ratios spans more than an order of magnitude.

Finally, although it is well established that clouds with more particles have a higher albedo, the optical impact of various types of clouds is still poorly constrained. Higher droplet concentrations may also change the lifetime and extent of clouds by reducing precipitation. The observation of “anomalous absorption” in clouds is another issue that could limit our ability to predict cloud albedo and its dependence on aerosols. The ultimate question is: What would be the impact of these cloud property changes on phytoplankton and photochemical processes (Activity 1.2)? This is the final link that closes the hypothesised CLAW feedback loop.

Major Issues that Require Resolution

- » **What factors control the flux of DMS to the atmosphere?** We need to quantify the relationship between different types of plankton, their growth rates, and DMS production. We also need to understand DMS loss by biological and abiotic processes in the surface ocean, and how the emission of DMS to the atmosphere varies with changing chemical and physical conditions (Focus 2), as well as how these processes may vary in the future. It is essential that we learn how to use phenomena observable by satellite for scaling up to the regional and global scales.

- ▶ **What fraction of atmospheric DMS will eventually form SO₂, MSA and sulphate aerosol and will this lead to higher particle number concentrations?** It is particularly important to know the absolute amount and size distribution of sulphate aerosol formed from SO₂ and DMS, which requires that we have accurate rates for all the competing reaction pathways including dry loss of SO₂. We are far from a quantitative understanding of the relationship between sulphate formation and particle number concentration. There is the potential for interaction with IGAC-II on this issue.
- ▶ **What are the relationships between CN, CCN and CDN concentrations, and will changes in CDN have a significant radiative impact?** Our current uncertainty in these relationships is at least an order of magnitude. An increase in CDN may both decrease droplet size and extend cloud lifetime.

Specific Goals

- I. Quantify the impact of competing biotic and abiotic processes on DMS emissions to the atmosphere, so that the flux to the atmosphere under a variety of environmental scenarios can be calculated.
- II. Quantify the DMS and SO₂ (from biogenic, volcanic and anthropogenic sources) reaction pathways so that their relative impacts on marine particle size and number concentrations can be modelled.
- III. Quantify the relationships between DMS, CCN, and CDN concentrations well enough to support the needs of diagnostic climate models.

Promising Approaches and Implementation Strategy

Integrated studies of both marine and atmospheric processes will allow confirmation of relationships that extend beyond either medium. For example, as a phytoplankton bloom evolves or wind speed changes, do these changes produce the expected responses in atmospheric DMS and sulphate aerosol concentrations, and cloud albedo? SOLAS will quantify the processes from food-web driven DMS production to cloud albedo using integrated ocean-atmosphere field experiments. The WCRP research community is more qualified to address

the radiation aspects of the atmosphere-to-ocean part of the feedback loop. SOLAS will work closely with them on this aspect of the cycle. Similarly, linkage between SOLAS Activities 1.2 and 1.3 will address feedbacks on DMS production due to radiation changes. SOLAS will be responsible for integration of these various component activities into assessment of the entire CLAW hypothesis.

Predicting seawater DMS concentrations requires models of DMS-plankton relationships, which are still in their infancy due to the lack of integrated process understanding, including the interactions among phyto, zoo, bacterio, and viro plankton, and the impacts of temperature, nutrient supply, light, and other environmental factors (Liss et al., 1997; Gabric et al., 1998). Collaboration with GLOBEC and IMBER will be especially useful for this work. Studies at ocean time series sites will be particularly valuable. Both laboratory and field studies in a variety of environments, the latter using Lagrangian approaches involving patches of water marked with a tracer, are needed to support the development of adequate process models. These studies will often extend beyond DMS to include trace gases considered within Activities 1.1 and 1.2.

DMS fluxes need to be measured directly by eddy correlation (Focus 2) to improve the parameterisations used in atmospheric models. Fluxes need to be measured along gradients of (and simultaneously with) the many potential controlling factors. Detailed research on the mechanisms of sea-air gas exchange (the objective of Activity 2.1) is critical for improving the calculation of DMS fluxes to the atmosphere. In order to quantify the long term spatial and temporal variability in DMS fluxes, it will be useful to identify appropriate proxies for DMS concentrations that can be sensed from satellites. This will require specific laboratory work including the application of molecular biological techniques.

Quantifying the processes by which some fraction of atmospheric DMS is converted to sulphate aerosol requires both laboratory kinetic work and precise ambient time series measurements of atmospheric sulphur species, oxidants, intermediates, and products. Since many state of the art instruments cannot be run in a monitoring mode, intensive process studies will be required initially in the simplest possible equatorial and polar regions. ("Simple" here implies both understandable boundary layer dynamics and the absence of nearby anthropogenic sulphur sources).

While process models will be essential for integrating the observations, existing marine sulphur models contain so many unverified assumptions that modelling alone is unlikely to improve our understanding. Process studies that are directed at quantifying the major atmospheric loss processes for SO₂ are critical. We need to close the atmospheric sulphur budget in Lagrangian experiments (Huebert and Lenschow, 1999) that involve direct eddy correlation measurements of both DMS and SO₂ surface fluxes, so that we have as few unconstrained variables as possible. Conducting these experiments under a variety of wind and cloud conditions will help quantify heterogeneous loss to sea-salt particles and cloud droplets. Lagrangian microphysical studies of particle formation and growth in simple environments are also needed to resolve the relationship between sulphate formation and particle number. Studies of air with enhanced SO₂ (from volcanic or pollution sources, or deliberately added) may be useful in revealing particle formation mechanisms in the troposphere. Many of these tasks would benefit from close collaboration with IGAC-II.

Extensive laboratory and fieldwork is required to resolve the relationship between aerosol number and cloud droplet number concentrations before we can confidently model the change in CDN that will accompany a change in particle number. Focused *in situ* microphysical, optical, and remote satellite measurements will be needed to quantify the impact on the net radiation budget of a change in CDN. Intensive studies of natural (e.g. volcanic plumes or smoke from large fires) or intentional perturbations could help to achieve process understanding by generating data sets that can constrain our integrated models of the SO₂-to-albedo parts of the system. We need to characterise both the CCN upon which cloud droplets form and the extent to which the number of CCN is changed as DMS emissions change. While it is a challenge to design intra programme experiments, collaboration with GEWEX, CLIVAR and SPARC will be vital for the cloud physics and radiative transfer parts of this activity.

It is clear that some multi nation, multi platform experiments will be required to resolve important questions regarding the fate of DMS. SOLAS is well suited to plan and coordinate such experiments. To increase the benefit from the substantial costs of these experiments, they should be designed to answer questions from several SOLAS Activities.

Ultimately, coupled marine biological and chemical transport diagnostic models are the tools that will be used for predicting regional and global DMS fluxes and their effects on climate. However, the forecasts of these models can be no more realistic than the descriptions of processes in the models. Simultaneous observations from both air and water are essential to support tests of the models of this complex set of processes.

Palaeo studies also offer promise for testing our understanding of the global ocean-atmosphere system through changes in climate. The MSA record in ice cores can be compared to changes in productivity obtained from ocean sediment records to constrain the long term changes in DMS fluxes. Thus, our improved understanding of DMS exchange will be very useful for challenging our understanding of marine productivity, ocean dynamics, and transport related to past climate changes.

Activity 1.4 - Iron and Marine Productivity

Natural and anthropogenic changes in climate and global biogeochemistry will alter the atmospheric input of aerosols containing iron and other essential trace metals to the ocean, which may cause changes in planktonic productivity and food web structure, resulting in altered carbon partitioning and biogenic air-sea gas fluxes.

Introduction

One of the most significant recent advances in oceanography was the experimental demonstration of the importance of iron supply in regulating key biogeochemical interactions and feedbacks between the ocean and atmosphere (Martin et al., 1994; Coale et al., 1996; Boyd et al., 2000), together with the recognition that a primary transport path for iron found in the ocean is through atmospheric mineral aerosol (dust). The limiting role of iron for many classes of pelagic organisms is at first glance surprising because iron is one of the most abundant elements in the Earth's crust. However, the oxidation conditions of upper ocean seawater and the inorganic chemistry of iron result in rapid precipitation of iron, reducing it to very low dissolved concentrations in surface seawater (Johnson et al., 1997). Recognition of the scarcity of iron and evaluation of its sources were dependent on advances in both analytical marine iron chemistry (Landing and Bruland, 1987) and early global syntheses of aeolian dust and iron deposition rates (Duce and Tindale, 1991).

State of Present Understanding

Phytoplankton growth in surface waters is limited by the supply of light and by the availability of various nutrients including nitrogen, phosphorus and iron. It is now clear that iron from terrestrial sources can play a role in biological activity in all pelagic regions of the global ocean. Especially in high nutrient, low chlorophyll (HNLC) regions, such as the sub arctic Pacific Ocean, the equatorial Pacific Ocean and the Southern Ocean, iron availability can be the major factor regulating primary productivity (De Baar and Boyd, 2000). It is also possible that other trace metals delivered to the oceans primarily from the atmosphere, such as Mn, Co, and Zn, may influence primary productivity under some circumstances in some regions, and there will be an interaction with nitrogen deposition (Activity 1.5).

Nitrogen fixation by cyanobacteria in oligotrophic regions (where N supply is probably limiting production) may also be limited by iron availability (Falkowski et al.,

1998; Berman-Frank et al., 2001), although this is controversial (Tyrrell, 1999) since such cyanobacteria have a relatively high Fe requirement. This controversy has important consequences for understanding the ocean's past and future roles in regulating the concentration of atmospheric CO₂. The relative roles of phosphorus, iron, and mixed layer physics in the regulation of large-scale nitrogen fixation in the tropical ocean, and the feedbacks between these factors, are some of the major unresolved issues in Earth System Science (see also Activity 1.5). Recently, several lines of evidence have suggested that nitrogen fixation in both the subtropical Atlantic and Pacific oceans has increased in the past two decades. In the North Pacific Ocean large-scale, low frequency physical changes in the mixed layer have been proposed as the causal mechanism (Karl, 1999), while in ocean regions downwind of major dust-generating areas, such as the tropical Atlantic Ocean and Caribbean Sea, increased iron deposition by dust from the African Sahel is thought to increase nitrogen fixation rates (Falkowski et al., 1998). An explosion of information about the molecular biology, photophysiology and distribution of oceanic N-fixing organisms is taking place. Regional and global estimates of nitrogen fixation are primarily model-based (Gruber and Sarmiento, 1997) and suggest that nitrogen fixation is one of the dominant sources of "new" nitrogen to the ocean (i.e. that from sources other than internal recycling within the ocean) (Jickells, 2002).

In general, the highest atmospheric concentrations of dust over marine areas are found in the Northern Hemisphere e.g. over the tropical North Atlantic Ocean, the northern Indian Ocean including the Arabian Sea, and the western North Pacific Ocean (e.g. Duce and Tindale, 1991). However, the pattern and magnitude of delivery of dust containing iron varies dramatically with season, vegetation and soil aridity in the source area (Mahowald et al., 1999). It also depends on natural climate variability, human land disturbance, local and regional-scale weather and global atmospheric circulation. Changes in atmospheric inputs of dust will likely impact phytoplankton processes and, thus, in turn alter the exchange of climatically important trace gases between the atmo-

sphere and oceans (Activities 1.2 and 1.3), providing potential climate feedbacks. In addition, an increase of biogenic particles in surface water may modify the heat balance between ocean and atmosphere.

Accurate measurement, and even estimation, of dust deposition to the ocean is very difficult. The total input of iron to the ocean from the atmosphere has been estimated at between 15 and 100 Tg yr⁻¹, a figure that is both uncertain and very variable from year to year. Although this may appear to be a substantial quantity, it is distributed very unevenly, with lowest deposition to ocean regions remote from land (these approximately correspond to the HNLC areas). Further, only a small fraction (perhaps 0.8-2.1%, Jickells and Spokes, 2001) of the amount of total deposited iron is soluble in seawater. The iron is primarily bound in the aluminosilicate matrix of the mineral aerosol, a form that cannot be utilised by primary producers. Iron solubility is pH dependent so interaction with sulphur dioxide, other acidic gases, and particles from anthropogenic and marine biogenic sources (see Activities 1.2 and 1.5) may change the solubility of iron in mineral aerosol. Some studies have observed soluble Fe(II) in aerosols, and its formation is postulated to occur via photochemical reduction of Fe(III) hydroxides, probably involving organic matter. However, details of the chemistry and photochemistry of iron in aerosols and cloud droplets (Activity 1.2) are minimal to date (Jickells and Spokes, 2001). High ionic strength solutions, possibly low pH solutions, and alternating wet and dry cycles during cloud formation and evaporation could enhance the solubilisation of iron. In addition, changes in halogen radical chemistry could alter the oxidative capacity of the MABL, thus influencing the speciation of iron. Iron and other trace metals can catalyse oxidation and halogen cycling reactions in the atmosphere (Brandt and Van Eldik., 1995; Sadanaga et al., 2001). These reactions link this activity directly to Activities 1.1, 1.2 and 1.3 and provide further potential feedback mechanisms within the CLAW hypothesis (Activity 1.3) (Zhuang et al., 1992).

We currently know relatively little about the fate of dissolved iron in the surface ocean. While insoluble oxide/hydroxide-containing particles likely form with Fe(III), they may not sink rapidly out of the euphotic zone. Some iron is scavenged by pre existing surfaces such as phytoplankton. The remaining dissolved iron can be measured and is found to occur in the pico to nanomolar concentration range. These extremely low levels explain why iron can be a limiting nutrient for micro

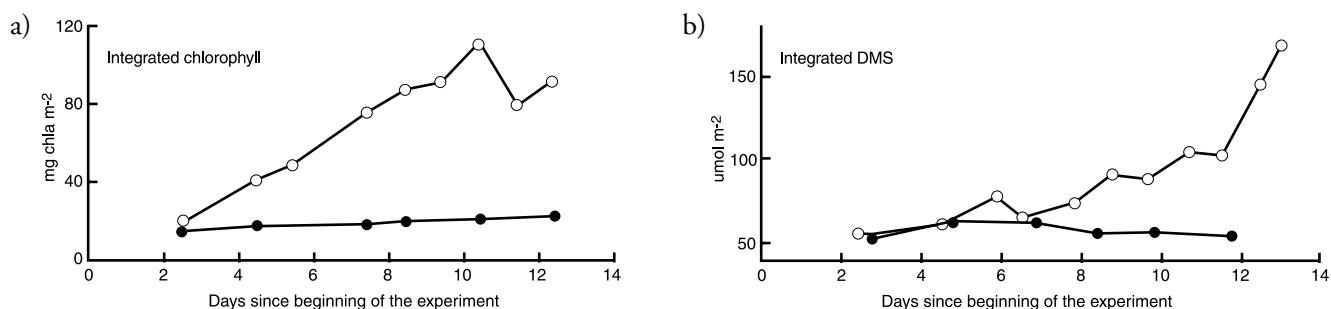
organisms (both bacteria and phytoplankton). Of the measurable iron in seawater, more than 99% is organically complexed with natural organic ligands that are part of the dissolved organic material in the oceans (Rue and Bruland, 1997). However, we know little about the chemical form, sources or sinks of the ligands (Lefevre and Watson, 1999), although they are apparently released by phytoplankton (Boye and Van Den Berg, 2000). Various ideas have been proposed for how micro organisms acquire the iron they need, including production of siderophores bound to cell surfaces and photochemical production of Fe(II) (Activity 1.2), both of which would enhance iron transport into the organisms (e.g. Wells et al., 1994). The ground breaking Fast Repetition Rate Fluorometer (FRRF) analyses made in the IronEx1 and 2 studies (Martin et al., 1994; Coale et al., 1996) have established that the ambient pico and nanoplankton adjust their photochemical efficiency to iron availability within hours (Kolber et al., 1994). This line of analysis needs to continue, focusing on the response of individual functional groups of phytoplankton.

In situ iron addition experiments in two of the HNLC regions (Martin et al., 1994; Coale et al., 1996; Boyd et al., 2000) have found that, at least over the short time scales of the experiments (e.g. Figure 7):

- variations in the magnitude and pattern of iron delivery have the potential to change the absolute level of primary productivity and the structure of the pelagic food web;
- added iron results in CO₂ drawdown;
- added iron results in changes in the aquatic concentrations of trace gases as a result of alterations in productivity and phytoplankton species composition; and
- there are important feedbacks relating to atmospheric chemistry and climate (Activity 1.3). Recent modelling efforts have led to significant new insights into iron supply, cycling and demand in the ocean (e.g. Archer and Johnson, 2000; Fung et al., 2000).

These pioneering iron addition experiments and water column analyses in HNLC regions have confirmed that low iron availability impacts productivity and food web structure. However, many biogeochemical issues remain unresolved. Particularly important from the SOLAS perspective are those relating to exchange of gases with the atmosphere (Focus 2, Activities 1.2 and 1.3).

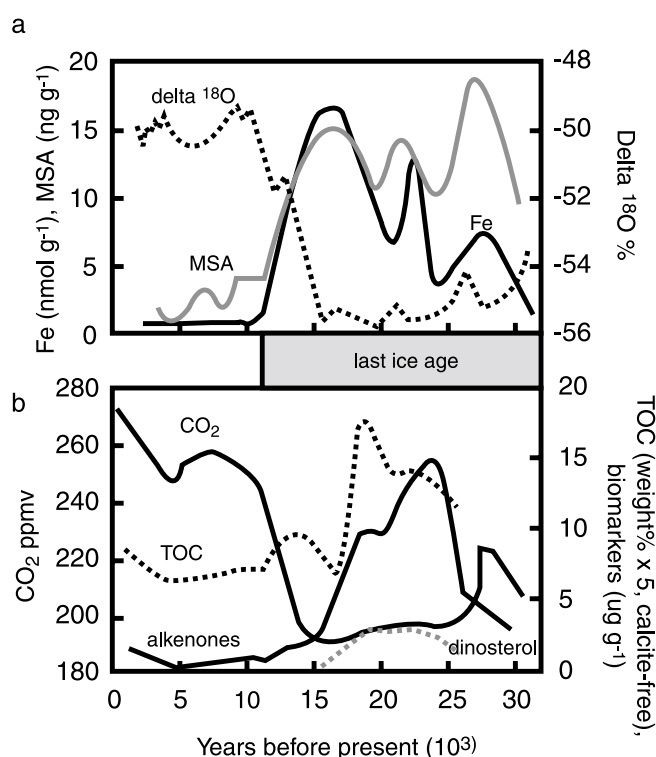
Figure 7. Measurements during the SOIREE experiment in the Southern Ocean showing dramatic increases in a) chlorophyll in the iron fertilised area (open circles) compared to the unfertilised area (dark circles); and b) aqueous dimethylsulphide (DMS) in the iron-fertilised area (open circles) compared with the unfertilised area (dark circles) (Boyd et al., 2000). Reprinted with permission from Nature, Macmillan Magazines Limited.



From the historical ice record, significant increases in dust delivery to the ocean took place during the last glacial maximum. This appears to be correlated with reduced atmospheric CO₂ (Broecker and Henderson, 1998), enhanced concentration of atmospheric sulphur species, and increased ocean productivity, as shown in Figure 8 (Turner et al., 1996). Similar palaeo signals of dust fluxes are recorded in marine sediments (Rea, 1994). These observations do not, of course, prove a link between atmospheric iron supply and climate change, but they do suggest palaeo records can contribute to evaluating the significance of altered dust deposition on ocean biogeochemistry over long time scales. The palaeo record provides valuable information on natural variability to be compared and contrasted to more recent records from time series measurements, *in situ* process studies and models. It is expected that future climate change will impact desert areas and the global wind field, altering soil moisture, particle size and hence the emission flux of mineral aerosols. Similarly, atmospheric circulation, transport pathways and the deposition of aerosol iron to the ocean will likely be affected, leading to significant changes of the types outlined above.

In ocean areas close to large dust sources, the high flux of dust may even act as a scavenging agent for suspended particles and particle reactive species in seawater, thereby decreasing rather than increasing iron concentrations (Jickells, 1995).

Figure 8. Changes in various ice core and marine sediment parameters between the Holocene and the end of the last ice age. a) delta¹⁸O (a temperature proxy), Fe and MSA (an atmospheric oxidation product of DMS) from Antarctic ice cores. b) CO₂ from the Vostok ice core; TOC (total organic carbon), alkenones and dinosterol (proxies for surface ocean productivity) in a sediment core from the eastern tropical Pacific Ocean (Turner et al., 1996). Reprinted with permission from Nature, Macmillan Magazines Limited.



Major Issues that Require Resolution

- ▶ **What are the ecological and physiological effects of atmospheric iron deposition on the phytoplankton community in terms of productivity, nitrogen fixation rates and species composition, and what impact do these effects have on trace gas emissions and CO₂ exchange with the ocean?** While the impact of iron on productivity has been recognised, many issues remain, including the significance of ecological effects in terms of species response, community structure, etc., and feedbacks such as production of DMS and halogenated compounds. The magnitude and controls on nitrogen fixation rates are very poorly understood.
- ▶ **What is the temporal and spatial variability of the atmospheric transport and deposition of dust to the ocean, and how are these altered by climate changes?** Understanding these variabilities is critical for determining the global importance of iron fluxes to the ocean.
- ▶ **What controls the chemical transformation of iron in aerosols and how would anthropogenic and natural changes in climate affect the speciation, solubility and bioavailability of iron in surface waters?** While changes in aerosol pH, photochemistry, cloud processing etc. can alter the speciation of iron (which will in turn affect the solubility and availability of iron and other micronutrients for marine bacteria and phytoplankton), little is currently known of the heterogeneous phase chemistry of mineral aerosols in the atmosphere.
- ▶ **What is the chemistry and biochemistry of iron in surface seawater?** The chemical speciation of iron and complexing with organic ligands in surface seawater are critical to understanding its solubility and bioavailability.

Specific Goals

- I. Predict the temporal and spatial patterns of iron deposition flux to the world oceans and how this will change in the future.
- II. Quantify bioavailability of iron in mineral particles after transformations in the atmosphere and seawater.
- III. Predict the change of planktonic composition

and food web structure caused by changing iron deposition fluxes.

- IV. Quantify the effect of iron deposition flux on the carbon and biogas flux to and from the ocean.

The sensitivity of marine systems to iron and other essential trace metals deposition varies considerably. SOLAS research will identify the most sensitive areas and work to reduce the uncertainties in those that have the greatest impact on climate change predictions.

Promising Approaches and Implementation Strategy

The deposition of dust to the oceans is controlled by a variety of factors, including wind speed and rainfall patterns in arid areas thousands of kilometres upwind, hemispheric-scale atmospheric circulation patterns, removal and processing by frontal systems and clouds, etc. Remote sensing from space can now follow dust plumes from the deserts to the oceans, but it is to date of limited quantitative value and supplies little information on the altitudes of dust plumes. Because so much dust is deposited in inaccessible regions, we must rely heavily on deposition models that need to be thoroughly tested against observations. These observations should include both atmospheric and surface ocean measurements of mineral mass concentrations, particle size distributions, iron speciation, mineralogy, and the concentrations of related compounds (sulphate, nitrate, organics) that might be involved in solubilisation or complexation reactions, so that the ability of the models to simulate each of these can be assessed. Studies of the entire dust history from its source to its deposition will be required to resolve the factors controlling dust transport and deposition and here, IGAC-II, ILEAPS and the new IGBP Land project will be important partners. Interactions with PAGES will be valuable in these studies since ice core records of dust provide a key test of the links between dust and climate, as will interactions with scientists doing historical GCM runs.

Two types of laboratory studies will be needed to address the bioavailability and impacts of atmospheric iron and other biologically essential trace metals. On one hand, laboratory studies simulating heterogeneous aerosol/gas/liquid interactions can lead to advances in describing the cycling and solubilisation of dust aerosol and iron, while field measurements using new instrumentation

such as aerosol mass spectrometers will provide details about the composition of ambient aerosol mineral particles (Activity 1.1). On the other hand, controlled field studies, conducted both on land and at sea and involving interdisciplinary approaches, can provide valuable information on the chemistry and biochemistry of iron in seawater and how it is taken up by microorganisms. Studies of the fundamental physiology of phytoplankton and the role of iron and other trace metals as trace nutrients for photosynthesis, nitrogen fixation and trace gas production will be essential.

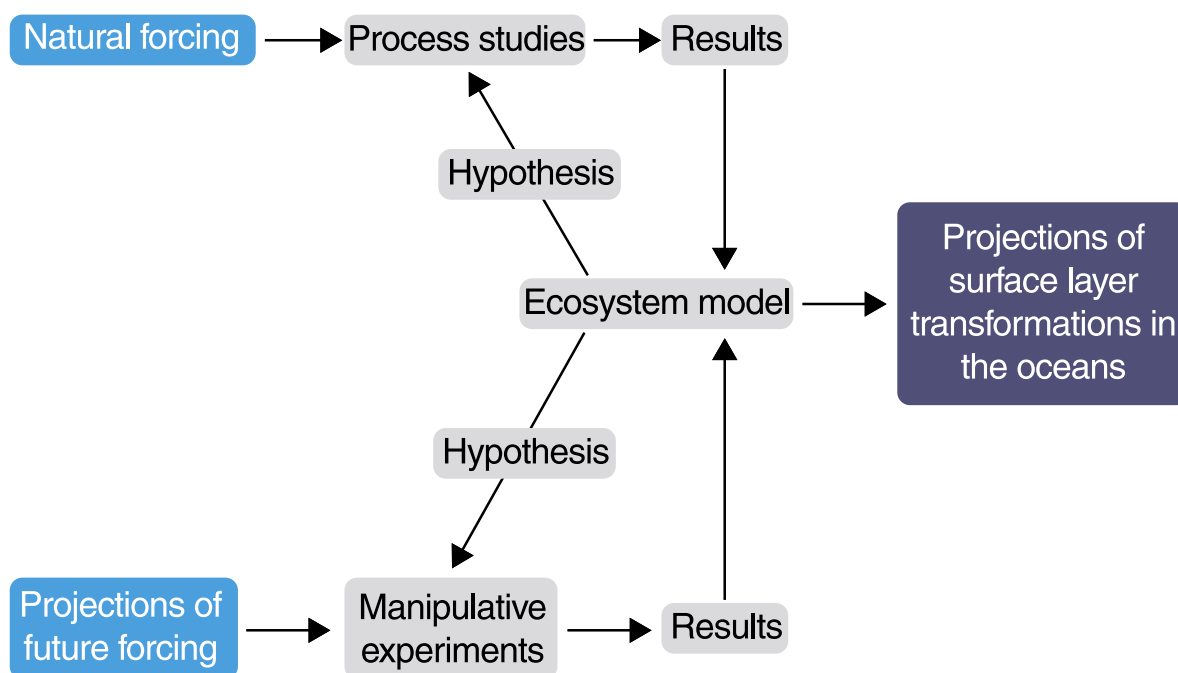
It should be kept in mind that the upper ocean inorganic and bio-inorganic chemical processes, as well as the biological responses to iron deposition, are exceedingly complex and difficult to recreate under controlled laboratory conditions. In recent years, the international biogeochemical research community has gained considerable experience with natural (Young et al., 1991) and experimental *in situ* iron (or dust) addition experiments (Martin et al., 1994; Coale et al., 1996; Boyd et al., 2000) designed to reproduce the target chemical and biological interactions and feedbacks. SOLAS, recognising

such *in situ* work presents logistical, as well as scientific difficulties, will encourage a mix of both simulated (using multiple forms of iron) and natural addition experimental studies that will be followed for longer periods of time and in larger areas than possible up to now.

A general strategy of SOLAS for designing manipulative experiments would include not only the natural or imposed forcing on an ecosystem but would also consider the possible projections of future forcing, as suggested by regional and global climate models, in its design. Such a strategy would promote dialogue and interaction between experimentalists, large-scale observationalists and modellers (Figure 9).

SOLAS will pay special attention to the impact of dust deposition on those biological functional groups involved in trace gas emissions, N₂ fixation and CO₂ ocean exchanges. In addition, an obvious impact of enhanced iron availability will be carbon export from the oceanic boundary layer (Activity 3.2) and ultimate carbon sequestration. The study of these processes will require close collaboration with IMBER.

Figure 9. General strategy of SOLAS for the design of manipulative experiments.



Natural dust deposition events can be studied in different oceanic regions depending on whether the goal is to understand dust deposition and dissolution processes (e.g. N. Atlantic, Mediterranean - frequent events), and/or the biological consequences of such processes (e.g. N. Pacific - strong but episodic events in an iron limited regime). Recent work suggests that using surface water dissolved aluminium and iron measurements offers an indirect means of estimating dust deposition to the remote ocean integrated over relatively long time scales (Measures and Vink, 2000). Adding proxy atmospheric observations such as these and enhancing the type of upper ocean observations at existing time series sites, as well as increasing the number of such sites in different biogeochemical provinces, will be critical.

Exploitation of natural dust addition “experiments” is now feasible. Improved satellite measurements and dust transport models can be used to direct ships and aircraft to sites of anticipated atmospheric dust deposition events, allowing detailed process studies of the ecological and biological response to them. Ships can measure both the detailed geochemical and biological processes, while aircraft measure the variability within the dust event, the emissions of biogenic gases like DMS, and their impact on oxidants, aerosols, and clouds. Such experiments require close collaboration before, during and after the experiment between experimentalists and modellers.

In addition, marine observing systems such as autonomous buoys (Bishop et al., 2002) offer the opportunity to study the ecological effects of dust inputs that are not dependent upon serendipitous arrival of ships at the time of deposition events. It would be necessary to add instrumentation that can make observations of dust aerosols, iron and other relevant parameters to these buoys.

Global dust distributions are best obtained by satellite observations. However, field campaigns will be required to more specifically define the spatial and temporal variability of dust and other aerosol component concentrations, for which land, mooring and ship based studies will be required. These measurements can be used to calibrate and test models of dust distributions and to ground truth satellite observations. Work is also required on converting atmospheric concentrations into deposition fluxes, an area of work discussed in Activity 2.3.

Activity 1.5 - Ocean-Atmosphere Cycling of Nitrogen

Increased atmospheric deposition of fixed nitrogen[†] species to both pelagic and coastal oceans can significantly change phytoplankton activity, resulting in alteration to air-sea fluxes of climatically important gases and aerosol particles.

Introduction

Significant quantities of nitrogen species are delivered from the land to the ocean via the atmosphere (Jickells, 2002). Much of this atmospheric nitrogen is from anthropogenic sources (primarily the combustion of fuels and the utilisation of fertilisers), and it is subject to future changes, both in amount and geographical distribution, depending on population and industrial growth in various regions. Delivery of atmospheric nitrogen to coastal regions in Europe and North America is estimated to have increased by 50% to 200% during the past 50 years (Paerl, 1995). This deposition increases pressure on coastal ecosystems already stressed by a wide range of other human activities. A comprehensive study of these interactions will require collaborations between SOLAS, LOICZ and IGAC-II.

There is also growing concern about the increasing input of human-derived nitrogen species to regions of the pelagic ocean where nitrogen is the limiting nutrient, such as the subtropical gyres of the North and South Pacific oceans. While estimates suggest that, at present, atmospheric nitrogen accounts for only a few percent of the annual new nitrogen delivered to surface waters in these regions, the atmospheric input to the ocean is highly episodic, often coming in large pulses extending over only a few days (e.g. Spokes et al., 2000). Such pulsed deposition has the potential to create a different impact on primary production and phytoplankton ecology than comparable chronic inputs. Overall, the deposition of fixed nitrogen from the atmosphere may increase phytoplankton production in open ocean and coastal waters, leading to changes in CO₂ exchange and the emission of other climatically important trace gases (see Activities 1.2, 1.3). In nitrogen-poor regions of the surface ocean, nitrogen fixation by marine bacteria may act to relieve nitrogen stress. This process requires sig-

nificant amounts of iron (Activity 1.4) and is inhibited by the addition of fixed nitrogen.

State of Present Understanding

Atmospheric wet and dry deposition includes several familiar biologically active inorganic nitrogen species – nitrate, nitrite, and ammonium. In addition, atmospheric organic nitrogen deposition may be a substantial fraction of the total nitrogen flux to the pelagic ocean (Cornell et al., 1995). This organic nitrogen is known to be biologically active but its sources and chemical form are not well known (Cornell et al., 2003).

Atmospheric nitrogen gases emitted as gases from terrestrial sources (NO, NO₂, NH₃) are converted to water soluble species (e.g. HNO₃) and/or interact with sea-salt aerosol (Activity 1.1) in coastal areas, a process that alters deposition rates and releases halogens (Activity 1.2). This makes the coastal zone an area of particularly dynamic and complex atmospheric nitrogen chemistry within a region of complex meteorology (Activity 2.3). Nitrogen fluxes in coastal regions cannot currently be predicted well enough to provide appropriate advice on anthropogenic nitrogen emission strategies to environmental managers. In addition, there are emissions of other radiatively important trace gases from coastal zones, such as DMS, N₂O and CH₄ (Activities 1.3 and 3.3), that are also susceptible to anthropogenic perturbations by N deposition.

The air-sea exchange of ammonia in the marine environment depends on both the atmospheric concentrations of ammonia and ammonium, and the surface seawater ammonium concentration and pH. In coastal waters, the direction of the air-sea flux is uncertain and likely to vary substantially in space and time. Further offshore it is believed that the ocean represents a source of ammonia gas to the atmosphere. This ammonia gas acts as an important base within the atmosphere and couples to the CLAW hypothesis (Activity 1.3) with the formation of ammonium sulphate aerosol.

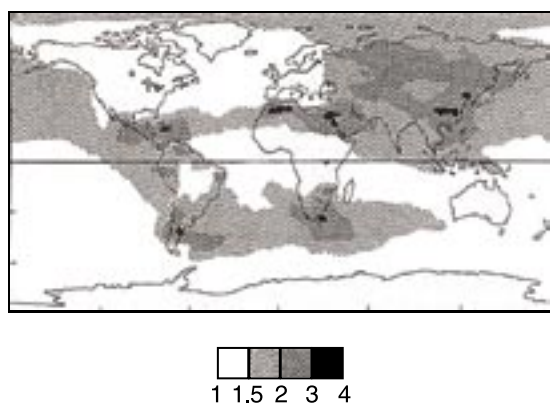
While we have a rudimentary understanding of the present atmospheric deposition patterns of inorganic

[†] Since N₂ gas is only utilised by a limited group of specialised bacteria (Activity 1.4) and is never biolimiting, we exclude it from consideration here and only consider fixed nitrogen, meaning all inorganic and organic forms of nitrogen apart from N₂ gas. For simplicity we refer to these collectively as nitrogen.

nitrogen to the ocean, the primary locations and relative amounts of atmospheric nitrogen inputs to the ocean may change in the future. Galloway et al. (1994) have evaluated in a modelling study the fixed nitrogen generated in 1980 from human activities such as energy production (primarily as nitrogen oxides) and fertiliser use, and compared it with the estimated additional fixed nitrogen that will be produced in 2020 as a result of human activities. Developed regions of the world are predicted to show relatively little increase in the fixation of nitrogen over this time period, while rapidly developing areas will contribute significantly to increased human-derived atmospheric fixed nitrogen fluxes. Both energy production (nitrogen oxides, and ultimately nitrate) and fertiliser (ammonia, urea) will drive this increase. For example, Asia is predicted to account for ~40% of the global increase from energy-derived fixed nitrogen with ~87% of that from fertiliser. Figure 10 shows the ratio of the estimated deposition of oxidised nitrogen in 2020 to the values for 1980. Increases in deposition from 1.5 to 3 times, and in some limited areas up to 4 times, are projected to occur over large areas of the coastal and pelagic ocean. This estimate does not include possible changes in ammonia and organic nitrogen fluxes. These large projected increases lead to the possibility of regional biogeochemical impacts in coastal and pelagic ocean areas.

Many nations have set ambitious goals for reducing coastal eutrophication in order to minimise impacts on coastal ecosystems arising from changes in the phytoplankton abundance and species composition, as a result of increased nutrient inputs. Such management plans

Figure 10. Ratio of the estimated deposition of reactive nitrogen to ocean and land surfaces in 2020 to that in 1980 (adapted from Galloway et al., 1994 and Watson, 1997).



often focus on river inputs, but need to include consideration of atmospheric nitrogen deposition. Societal emissions of contaminants and nutrients may alter coastal ecology with large-scale impacts on CO₂ uptake, as well as trace gas cycling and related atmospheric chemistry. Important and sensitive ecosystems such as coral reefs and intertidal areas may be particularly vulnerable to these effects when combined with other aspects of global change.

Major Issues Requiring Resolution

- ▶ **What impacts will deposition of fixed nitrogen (coupled to other factors associated with global change) have on surface ocean ecosystems and on the emissions of ammonia and other climatically important gases from the oceans?** Ammonia emissions are particularly important because they affect the formation and the acid-base balance of aerosol particles in the atmosphere. Studies need to recognise that marine ecosystems respond simultaneously to a wide variety of nutrients (N, P, Si, Fe, and light) and contaminants that may be delivered from the atmosphere or from other sources,

Specific Goals

- I. Quantify the temporal and spatial variability of atmospheric transport and deposition of fixed oxidised and reduced nitrogen to marine systems. To be valuable to marine modellers these fluxes need to be known to a factor of 2 over relevant time and space scales. Since iron deposition can alter N₂ fixation rates, these studies need to be linked to those of Activity 1.4.
- II. Determine the atmospheric deposition and (in the case of organic nitrogen) bioavailability of nitrogen to the oceans. Deposition rates are very sensitive to aerosol particle size. Atmospheric reactions significantly alter nitrogen aerosol particle size and these processes need to be quantified and incorporated in regional and global deposition models (Focus 2).
- III. Describe the ecological impacts of changes in the deposition of atmospheric fixed nitrogen on euphotic zone marine systems and on the resultant air-sea exchange of climatically important gases. It is likely that the nature of impacts will be fundamentally different in coastal and open ocean systems. Even the direction of change in trace gas emissions is currently uncertain.

This will require the development of coupled atmosphere/ocean N models, which will need to be interfaced with dust transport and deposition models (Activity 1.4).

In terms of surface ocean biogeochemical carbon models, the relevant space scales are ocean biogeochemical provinces, but for coastal environmental managers spatial resolution on scales of tens of kilometres is required. Time scales of relevance are days to weeks in the water column, relevant to phytoplankton growth, but much shorter in the atmosphere, related to atmospheric reaction rates.

Promising Approaches and Implementation Strategy

This Activity will need to be supported by laboratory studies of heterogeneous atmospheric chemical reactions involving nitrogen compounds in the gas, aerosol and liquid phases (see Activities 1.1 and 1.2). New instrumentation such as aerosol mass spectrometers allow much better characterisation of the size and composition of aerosol nitrogen species (e.g. the relative importance of ammonium nitrate, calcium nitrate, sodium nitrate and nitrate held within mixed aerosols). Organic nitrogen characterisation will probably require new instrumentation.

It is hard to demonstrate that sampling is representative when measuring nitrogen wet and dry deposition rates. This makes determining the controls on deposition particularly difficult. The first step, then, is to try to quantify N deposition rates. For wet deposition, this may involve wet-only collectors on islands, ships or buoys, augmented with remote sensing of the intensity and distribution of precipitation, to scale the local collections to a larger area. For dry deposition, there is a need for the development of new methods to augment the usual measurement of size-fractionated concentration distributions that are then multiplied by estimated dry deposition velocities, plus extension of the concentration database to describe the global distribution of fixed nitrogen in the atmosphere. Coastal regions may receive larger deposition fluxes, but open ocean studies, possibly in association with those of iron (Activity 1.4), are still needed. Ice core studies can help define the pre-industrial atmospheric N deposition to provide a baseline against which to assess the scale of human perturbation. Studies of N isotopes (coupled to the dissolved oxygen distribution in the ocean), can help to describe the relation between productivity and nitrification-denitrification in the ocean to better constrain the N

cycle and global atmospheric chemistry of N. Studies of N isotopes in phytoplankton remains in marine sediments in collaboration with PAGES can then offer a means of reconstructing changes in the ocean and atmospheric N cycle.

These traditional approaches have large unknowns, however, so an independent approach is needed for testing their estimates. Budget approaches such as Lagrangian experiments provide independent constraints by looking for closure among the apparent source and removal terms. These can be combined with modelling studies. The factors controlling deposition can be identified only after we are able to measure reliably the fluxes on a time scale of hours or less. Thus again the SOLAS approach involves laboratory process studies whose results are incorporated into computer models that are then tested against field measurements.

SOLAS should encourage a series of both natural and intentional *in situ* N addition experiments similar to successful iron addition studies mentioned earlier. These would be used to determine the biological response in terms of productivity, species composition, diversity, export and yield of grazers. Interaction with GLOBEC and IMBER will be valuable. The nitrogen deposition experiments will require much larger quantities of nitrogen to be delivered than the quantities of iron used in the *in situ* iron experiments. A way to circumvent this problem will be to use mesocosm bags. With careful attention to potential artefacts from enclosure, this approach shows promise in requiring less N and offering greater possibilities for replication of treatments.

The quantification of biogeochemical interactions and feedbacks such as emission of climatically relevant gases (Activities 1.2 and 3.3), the impact of pH on NH_3 emissions, and the effect of Fe on N_2 fixation (Activity 1.4) will also be essential components of such experiments. Many of the concerns and design considerations of an *in situ* iron addition experiment will apply to such *in situ* nitrogen experiments. A variety of inorganic fixed nitrogen and organic nitrogen compounds will need to be used in these experiments. Potentially, the ideal venue for such nitrogen deposition experiments is existing time series sites that are located in subtropical gyres, where fixed nitrogen supply is a key limit on primary production. There are serious technical issues to be resolved before mesocosm experiments can be done in the open ocean. The time series projects have existing logistic

infrastructure that could be deployed and the time series records would serve as excellent controls. Resulting from these studies, new mechanistic understanding will need to be incorporated into and evaluated within surface ocean biogeochemical models.

The development of autonomous buoys will greatly aid in the monitoring of phytoplankton growth parameters during intentional manipulations or natural nitrogen deposition events. Development of buoys capable of aerosol sampling for N species may also be valuable. These instruments should be used to support the inversion of satellite data and to test models of N deposition. Satellite observations now provide a viable approach for studying NO₂ transport (and its subsequent loss) to the marine environment that can be used to test chemical transport model forecasts of anthropogenic nitrogen deposition patterns. Considerable progress will still be required in modelling so as to include reactions of nitrogen species with sea salt (Activity 1.1), as well as ammonia and organic nitrogen effects on fixed nitrogen deposition. This combination of laboratory and field studies, coupled with modelled and remotely sensed data, should make it possible for full scale “natural experiments” to be conducted in an area where episodic nitrogen deposition occurs.

In the case of coastal regions, this activity will require collaboration with LOICZ scientists in order to comprehensively determine the impacts of the deposition of atmospheric inorganic and organic nitrogen on ecosystem dynamics. As in Activity 1.4, special attention should be paid to the impact of nitrogen deposition on those biological functional groups involved in trace gas emissions, N₂ fixation and CO₂ ocean exchanges. Collaboration with IOC/SCOR GEOHAB scientists will greatly enhance our understanding of the dynamics of possible harmful and noxious algal blooms resulting from changes in natural nitrogen deposition.