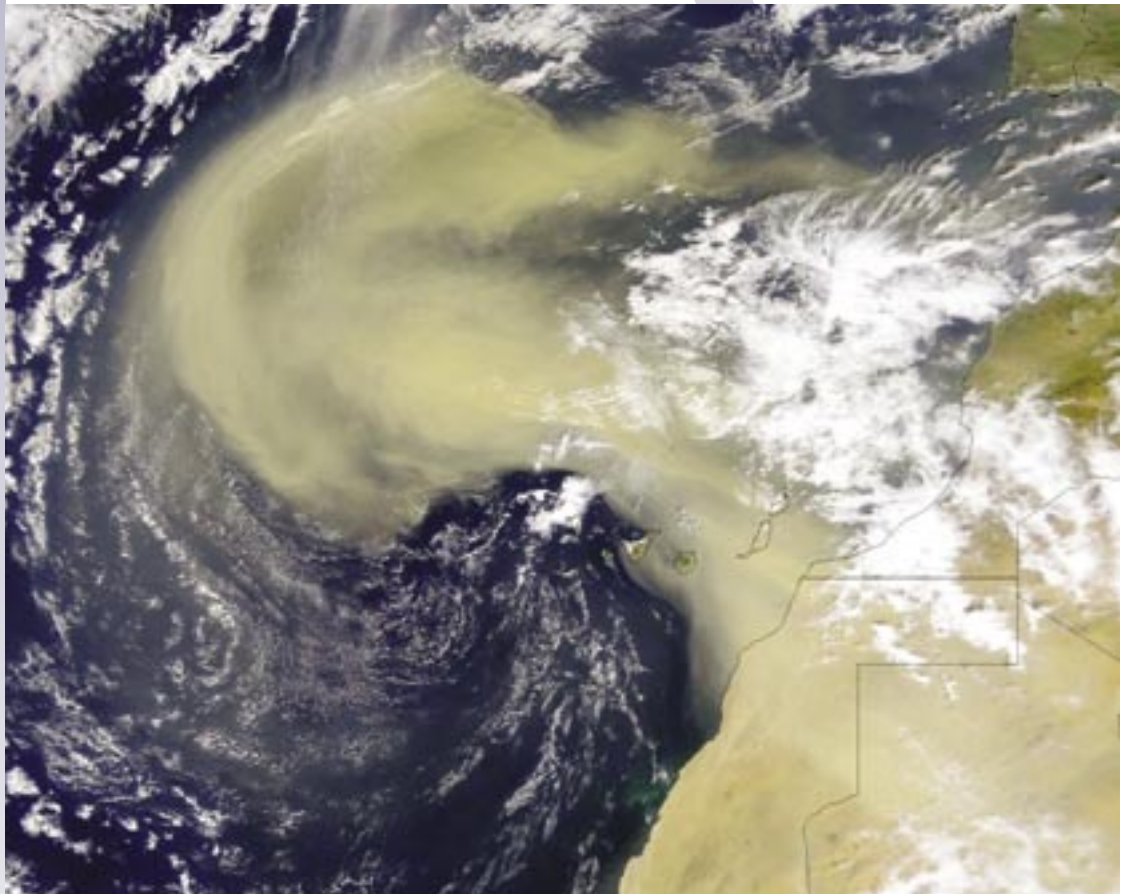




IGBP Report 50

The Surface Ocean – Lower Atmosphere Study



Science Plan and Implementation Strategy

Front Cover Image

A massive sandstorm blowing off the northwest African desert has blanketed hundreds of thousands of square miles of the eastern Atlantic Ocean with a dense cloud of Saharan dust. The massive nature of this particular storm was first seen in this SeaWiFS image acquired on Saturday, 26 February 2000 when it reached over 1600 km into the Atlantic. These storms and the rising warm air can lift dust 5000 m or so above the African deserts and then out across the Atlantic, many times reaching as far as the Caribbean where they often require the local weather services to issue air pollution alerts.

Provided by the SeaWiFS project, NASA/GSFC and ORBIMAGE

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Preface

The SOLAS Science Plan and Implementation Strategy sets out the scientific scope of SOLAS and outlines a strategy for addressing the major issues that are identified. Thus the Science Plan and Implementation Strategy forms the basis on which the project is being built. However, it cannot remain current for the 10 years envisaged for SOLAS in view of the fast moving nature of this area of research.

To ensure that SOLAS moves with the times, detailed Implementation Plans will be produced for each Focus. These will be regularly updated by the Focus Implementation Groups and are intended to complement this document. As they are produced, the Plans will be made available for download from the SOLAS website: www.solas-int.org.

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September 2003

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Executive Summary

SOLAS (Surface Ocean - Lower Atmosphere Study) is a new international research initiative that has as its goal:

To achieve quantitative understanding of the key biogeochemical-physical interactions and feedbacks between the ocean and the atmosphere, and of how this coupled system affects and is affected by climate and environmental change.

Achievement of this goal is important in order to understand and quantify the role that ocean-atmosphere interactions play in the regulation of climate and global change.

The domain of SOLAS is focussed on processes at the air-sea interface and includes a natural emphasis on the atmospheric and upper-ocean boundary layers, while recognising that some of the processes to be studied will, of necessity, be linked to significantly greater height and depth scales. SOLAS research will cover all ocean areas including coastal seas and ice covered areas.

A fundamental characteristic of SOLAS is that the research is not only interdisciplinary (involving biogeochemistry, physics, mathematical modelling, etc.), but also involves closely coupled studies requiring marine and atmospheric scientists to work together. Such research will require a shift in attitude within the academic and funding communities, both of which are generally organised on a medium-by-medium basis in most countries.

SOLAS deals with the following issues or Foci. Each Focus is divided into several Activities.

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 carbon uptake.

- Activity 1.1 Sea-salt Particle Formation and Transformations
- Activity 1.2 Trace Gas Emissions and Photochemical Feedbacks
- Activity 1.3 Dimethylsulphide and Climate
- Activity 1.4 Iron and Marine Productivity
- Activity 1.5 Ocean-Atmosphere Cycling of Nitrogen

Focus 2: Exchange Processes at the Air-Sea Interface and the Role of Transport and Transformation in the Atmospheric and Oceanic Boundary Layers

The objective in Focus 2 is to develop a quantitative understanding of processes responsible for air-sea exchange of mass, momentum and energy to permit accurate calculation of regional and global fluxes. This requires establishing the dependence of these interfacial transfer mechanisms on physical, biological and chemical factors within the boundary layers, and the horizontal and vertical transport and transformation processes that regulate these exchanges.

- Activity 2.1 Exchange Across the Air-Sea Interface
- Activity 2.2 Processes in the Oceanic Boundary Layer
- Activity 2.3 Processes in the Atmospheric Boundary Layer

Focus 3: Air-Sea Flux of CO₂ and Other Long-Lived Radiatively Active Gases

The air-sea CO₂ flux is a key inter-reservoir exchange within the global carbon cycle. The oceans also play an important role in the global budgets of other long-lived radiatively active gases, including N₂O and to some extent CH₄. The objective of Focus 3 is to characterise the air-sea flux of these gases and the boundary layer mechanisms that drive them, in order to assess their sensitivity to variations in environmental forcing.

- Activity 3.1 Geographic and Sub-Decadal
Variability of Air-Sea CO₂ Fluxes
- Activity 3.2 Surface Layer Carbon
Transformations in the Oceans:
Sensitivity to Global Change
- Activity 3.3 Air-Sea Flux of N₂O and CH₄

The Plan includes a description of the organisation and management of SOLAS and an outline of how it will be implemented.

Introduction

The Goal of SOLAS

SOLAS (Surface Ocean - Lower Atmosphere Study) is a new international research initiative that has as its goal:

To achieve quantitative understanding of the key biogeochemical-physical interactions and feedbacks between the ocean and atmosphere, and of how this coupled system affects and is affected by climate and environmental change.

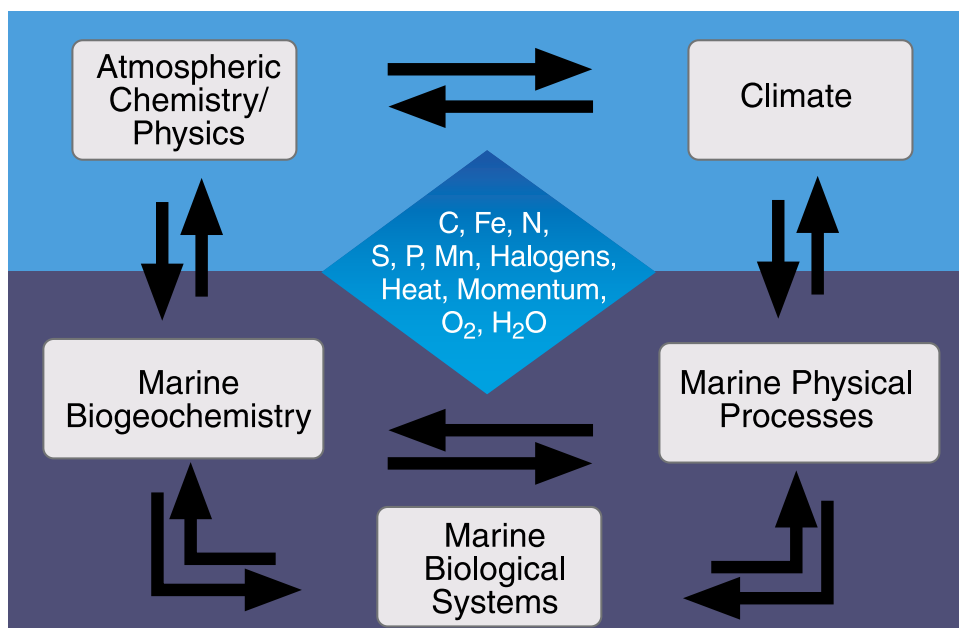
The scope of the study is illustrated in Figure 1 and described in detail in this Science Plan and Implementation Strategy. The Science Plan parts of this document are largely based on the results of the International SOLAS Open Science Meeting held in Damp, near Kiel, Germany in February 2000 which involved more than 250 scientists from 22 different countries. The International Geosphere-Biosphere Programme (IGBP), Scientific Committee on Oceanic Research (SCOR), Commission on Atmospheric Chemistry and Global Pollution (CACGP) and the World Climate Research Programme (WCRP) have approved SOLAS and are sponsors of it.

The SOLAS Approach

In this Plan we identify critical questions and hypotheses, as well as goals to quantify the rates and variability of various important processes. SOLAS will focus on important research issues that are not being emphasised by other projects and which require collaboration of atmospheric and marine scientists. It will concentrate on research that can be expected to produce results within a 10 year period, although some aspects will need to be continued beyond this timeframe.

The general approach to implementation is to assess the ambient situation as thoroughly as possible, identify the weak links in understanding, undertake laboratory work and focused field studies to resolve those issues, put the new understandings into process models, and test those models with carefully designed observations that bridge scales from the micro scale to the global. In many cases observations with high temporal and spatial resolution will be of great value for both process understanding and process model testing. It is clear that in some cases simultaneous observations with multiple platforms (ships, aircraft, buoys, satellites) will be required. The

Figure 1. The scope of SOLAS.



final step is to integrate this process understanding into diagnostic models which scale up to regional and global scales and can form the basis for modules in climate models.

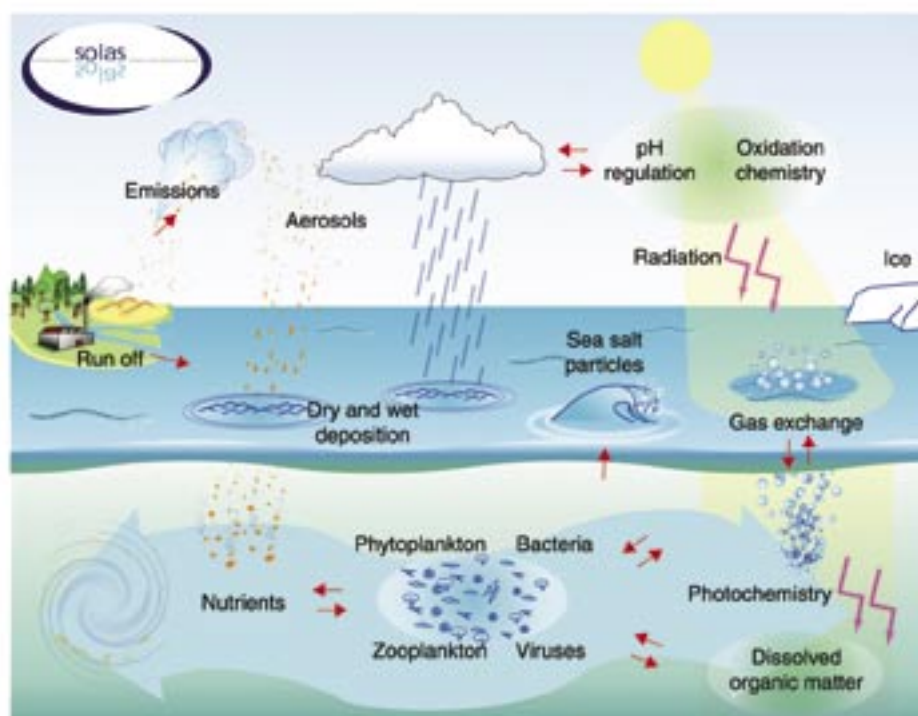
The key hypotheses under test in SOLAS will require numerical modelling studies for their systematic evaluation and quantitative assessment. Generally, SOLAS modelling activities will fall into three broad classes: (1) modelling as a key contribution to process studies, (2) modelling as a monitoring tool to integrate spatial and temporal scales, and (3) development of models and model components of SOLAS subsystems as parts of Earth System models.

Remote sensing data, mainly from satellite sensors, are expected to make a vital contribution to SOLAS. Satellites allow global observation of marine biogeochemical signatures (e.g. ocean colour, trace gases and aerosols), have good temporal coverage, and with 4-5 year missions, provide observations over an extended time period. In particular, satellite observations can put field experiments into a larger temporal and spatial perspective. A need will be to achieve coupling between field data, satellite observation, and models.

Many of the key questions in SOLAS can be addressed by time series studies that ideally should be conducted at strategic sites that are representative of large biomes or in regions that are likely to exhibit substantial interannual variability over large areas. Furthermore, these field investigations should be continued for at least several decades, in order to distinguish natural variability from that induced by human activities. Such observations, in combination with proxy records preserved in peat bogs, soil/dust deposits, firn, ice and lake and marine sediments, have clearly established the trends that are occurring in many individual components as well as in their gross budgets. They have also implicated human activities in many cases as the cause of change. In spite of their well recognised value, systematic, long-term, direct biogeochemical observations of the atmosphere are rather limited; for oceanic habitats they are indeed rare.

Considering the very considerable resources required to set up and maintain time series measurement sites, wherever possible they should address the goals of several SOLAS Foci/Activities and be shared with other projects (e.g. IGAC, IMBER, GEWEX). They should also build on the results of the current time series stations. Since SOLAS has a strong emphasis on process-

Figure 2. Diagram to illustrate the domain of SOLAS, its interdisciplinarity and the main operative processes.



driven research, it may well be that it is not the obvious main sponsor for time series studies. In this situation it will be the responsibility of the SOLAS Implementation Groups to specify their long-term measurement needs for both satellite and ground-based routine observations and for them and the SOLAS SSC to support the efforts of those mandated to make the measurements.

The ethos of SOLAS is to use the disciplines of biology, chemistry, physics, etc. to study biogeochemical interactions in the ocean-atmosphere system. In achieving this goal, these disciplines are not principally to be advanced in their own right, but should be seen as tools to pursue the larger aim. So, for example, SOLAS will not carry out research to study for its own sake the physics of air-sea exchanges of heat and momentum, but will and must use the best physical knowledge available, together with that from other disciplines, to quantitatively address the issue of how matter is exchanged across the air-sea interface.

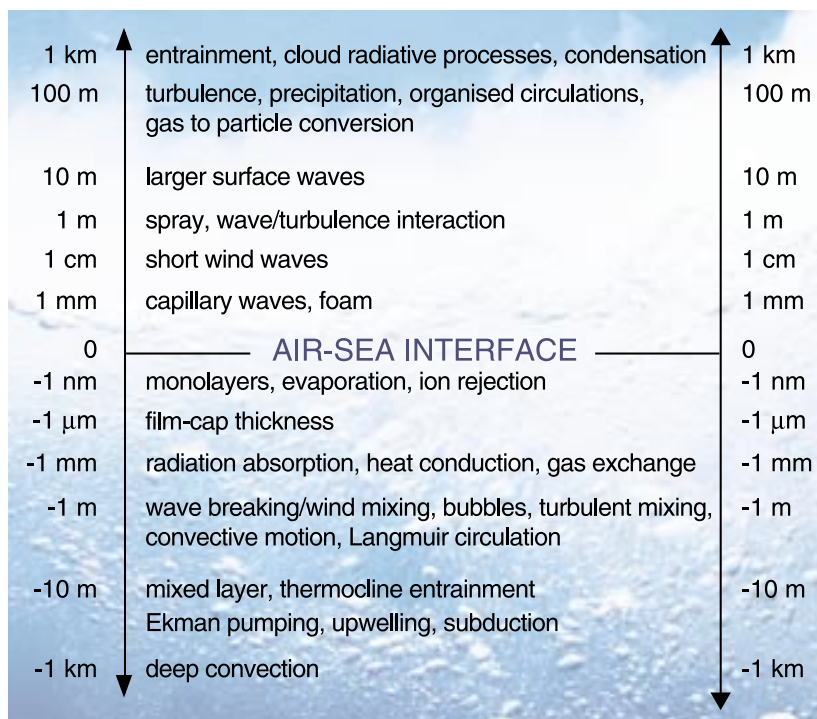
The Domain of SOLAS

SOLAS will focus on research topics of linked ocean-atmosphere interactions at a multitude of space and time scales in each medium. This focus results in an unavoidable

able mismatch in time and space scales of processes (and hence measurement needs) because atmospheric transport is more rapid than oceanic circulation. A distinctive feature of the ocean surface and surrounding air and water boundary layers is the progressive change in scale and progressively greater interdependence of different processes as the interface is approached. Processes that might be usefully explored in isolation at depth/height, must be considered with a host of competing and interacting effects close to the interface. The scales of the interacting phenomena become smaller and start to overlap, and the nonlinear interactions increase in strength as the interface is approached.

The interdisciplinary nature and broad domain of SOLAS are illustrated in Figure 2. The vertical domain of SOLAS is focussed on processes at the air-sea interface and includes a natural emphasis on the atmospheric and upper-ocean boundary layers, while recognising that some of the processes to be studied will, of necessity, be linked to significantly greater depth/height scales (illustrated in Figure 3). The atmospheric boundary layer can be functionally defined as extending to the top of the boundary-layer clouds (typically to about 1 km). The

Figure 3. Vertical scales of processes important for air-sea exchange.



upper-ocean boundary layer functionally includes the actively mixed or euphotic zone (typically 100-200 m).

In the horizontal dimension, SOLAS research can be focussed anywhere over the ocean, extending into coastal areas and estuaries, as well as ice covered areas. Coastal ecosystems are characterised by higher primary production than open ocean systems, with associated high rates of carbon burial that are significant to the global carbon budget. In addition, coastal seas are dominant marine sources of some trace gases globally (e.g. nitrous oxide (N₂O), carbonylsulphide (COS), methane (CH₄)) and are important production sites for almost all trace gases. Coastal research is spread across the whole of the SOLAS research agenda and will be linked to the LOICZ programme. Likewise, processes that occur at ice edges and in ice covered seas are important for emission of trace gases such as DMS and organo-halogens, and each focus in SOLAS includes important research in these regions.

In the temporal domain SOLAS will need to be concerned with a continuum, from the past through the present to the future. Measurements of oceanographic and climatic indicators of past ocean and atmospheric chemistry and climate will be needed to determine how a variety of factors related to air-sea interactions varied in relation to one another in the past. Long term, regular observations at important sites are needed to provide understanding of interannual to interdecadal variability of important global processes. Models need information from both palaeo indicators and from studies of present-day processes, in order to develop an ability to predict environmental variability and the responses of global systems to the effects of human perturbations. Models also provide capabilities to extrapolate measurements up and down across scales and to integrate data from different sources. Model studies conducted in parallel with experimental and observational studies will allow a systematic evaluation and qualitative assessment of the different hypotheses emerging from the data. The necessity of involving both palaeo and modelling expertise in SOLAS illustrates the need for strong cooperation between SOLAS and the Past Global Changes Project (PAGES) especially its International Marine Global Changes Study (IMAGES), and the Global Analysis, Integration, and Modelling (GAIM) Task Force. Data assimilation techniques, similar to those being used at numerical weather prediction centres and developed by GODAE for oceanographic applications, will be

required to handle the complex and disparate data sets generated by SOLAS field campaigns with many different platforms (e.g. ships, aircraft, satellites).

The chemical domain of SOLAS will include all natural elements (and their compounds) that play an important role in biogeochemical cycling (e.g. C, N, O, P, S, Group 1 and 2 elements, halogens, Fe, Mn and other trace metals and metalloids). Some inert gases and low chemical reactivity substances (lanthanides, natural and anthropogenic radionuclides), as well as a variety of persistent organic pollutants (POPs), will also be included in SOLAS, but only where their study can yield information useful in elucidating the ocean-atmosphere behaviour of biogeochemically and/or climatically active elements.

Societal Relevance

SOLAS can contribute to our understanding of the important role that the ocean-atmosphere interface plays in relation to issues relevant to society, including climate change, air quality, and the health of the ocean. For each of these topics, SOLAS will seek to develop collaborative research with related international projects. Likewise, the International Human Dimensions Programme on Global Environmental Change (IHDP) and SOLAS can work together to identify societal issues and important human drivers of changing biogeochemical fluxes, for example with respect to ethical, legal and financial implications of the research.

The Montreal and Kyoto Protocols marked a change in attitude within the international policy community to the issues of global change related to ozone and atmospheric carbon dioxide, respectively. Ozone depletion and greenhouse gas emissions are increasingly recognised as threats to the quality of human life, the global economy and natural ecosystems. Such threats require close observations and forecasts. As a practical matter, nations must plan to meet the commitments made in these agreements. Transparent and accountable verification of greenhouse and ozone-depleting gas sources and sinks is required. Within its area of research, SOLAS will help to better quantify the global emissions of these compounds and thereby address major societal needs.

However, at present, the political imperative is running well ahead of scientific knowledge. For example, from models that interpret atmospheric and marine measurements of CO₂, we know that the Northern Hemisphere

land biota is taking up 1-2 PgC (petagrammes of carbon, 1 PgC = 1 GtC) of atmospheric CO₂ per year, and the global ocean a similar amount. But beyond this understanding, little scientific consensus exists as to where (which continent or ocean) or why (what processes are responsible) these sinks exist, or their variability on seasonal to decadal time scales. A second example of knowledge gaps is related to aerosols, which are now recognised as having a significant, but very poorly quantified, effect on global climate change. However, their generation, chemistry and fate have received relatively little attention. Without a substantial maturing and deepening of our knowledge about this complex aerosol system, scientists will be unable to provide the verification techniques and forecasts of future trends that will be required. Similar arguments apply to ozone depletion where, in spite of the success of the Montreal Protocol, ozone recovery is being delayed by the continued increases in brominated gases and CFC (chlorofluorocarbon) replacements and, potentially, by global warming. This perturbation must be evaluated within the context of the large scale and uncertain air-sea exchange of biogenic halogen gases (Br, Cl, I). A further example is the case of proposals to fertilise large parts of the open oceans with iron in order to enhance the oceanic sink for CO₂; an issue for which proposed industrial application is running substantially ahead of scientific understanding. All these topics, together with many others, are major basic scientific issues in the SOLAS programme, the results of which will form the sound foundations for policy making in the coming years.

Simulations of future climate are only now beginning to incorporate the biological and chemical feedbacks that may arise as the atmosphere-ocean system changes in response to climate and other environmental forcing. These simulations give divergent predictions, depending on which feedbacks are included and how they are modelled. Substantial changes in “natural” sources and sinks of climatically active gases are possible, indeed probable, once climate change effects become obvious. CO₂ is the most closely studied example, but dimethylsulphide (DMS) and other chemically active trace species such as organo-halogens may also have important effects, little addressed to date. These deficiencies lead to uncertainties in the timing and magnitude of global change effects by many decades, the social and economic implications of which are clearly profound. Adaptation strategies are highly dependent on the time scales of change. SOLAS is designed to address these issues, with the purpose of

substantially reducing the uncertainties in our predictions of the timing and effects of future global and climate change.

SOLAS and the Global Carbon Cycle

SOLAS cannot address all issues related to the ocean’s present and future role in the global carbon cycle. Rather, it will address an important subset of carbon cycle issues that are compatible with its overall goals, domain and technical approaches. These topics can be summarised as:

- Quantification of the present-day exchange of CO₂ and carbon-related properties between the atmosphere and the surface ocean.
- Understanding of surface-layer ocean processes that can change the future air-sea flux of CO₂, with potential implications for altered sequestration of carbon within the ocean.

SOLAS will focus on providing a description of the contemporary geographical and temporal structure and variation of air-sea CO₂ fluxes, as well as mechanistic understanding of surface-layer processes that determine these fluxes, both now and in the future. This should include a strong emphasis on continental margins where forcing and fluxes can be particularly large. SOLAS is not the appropriate home for a global-scale pCO₂ measurement system, but its work will help guide the development and progress of such a programme, which the SOLAS SSC will strongly support. The limited SOLAS objectives above will provide a foundation for broader global carbon cycle science activities in the Global Carbon Project (GCP), particularly for the evaluation and parametrisation of processes in the models required to predict future ocean carbon sequestration.

Interdisciplinarity and Integration

More than is usually the case, meaningful developments in SOLAS will depend on research that is not only interdisciplinary, but also involves closely coordinated field studies in which the different research components are combined so as to produce comprehensive data sets.

Achieving understanding of processes that occur at the ocean-atmosphere interface will require an enhanced level of cooperation in planning and execution of research among many different disciplines in the environmen-

tal sciences. The success of SOLAS will depend on the effectiveness of such cooperation and ability to integrate measurements and analyses of many different types.

These challenges require some educational efforts, such as summer schools, to bring together young and established researchers for the mutual exchange of ideas and experience, and from countries with developed and developing science bases. (The first SOLAS Summer School was held in 2003 in Corsica). In addition and most importantly, research involving the coherent study of linkages between environmental compartments (in the case of SOLAS, atmosphere and oceans) will require a shift in attitude within the academic community and research funding agencies, both of which are generally organised on a medium-by-medium basis in most countries. Bridging such barriers is vital because knowledge of atmosphere-ocean interactions is key to understanding climate and other global changes.

Added Value and Legacy

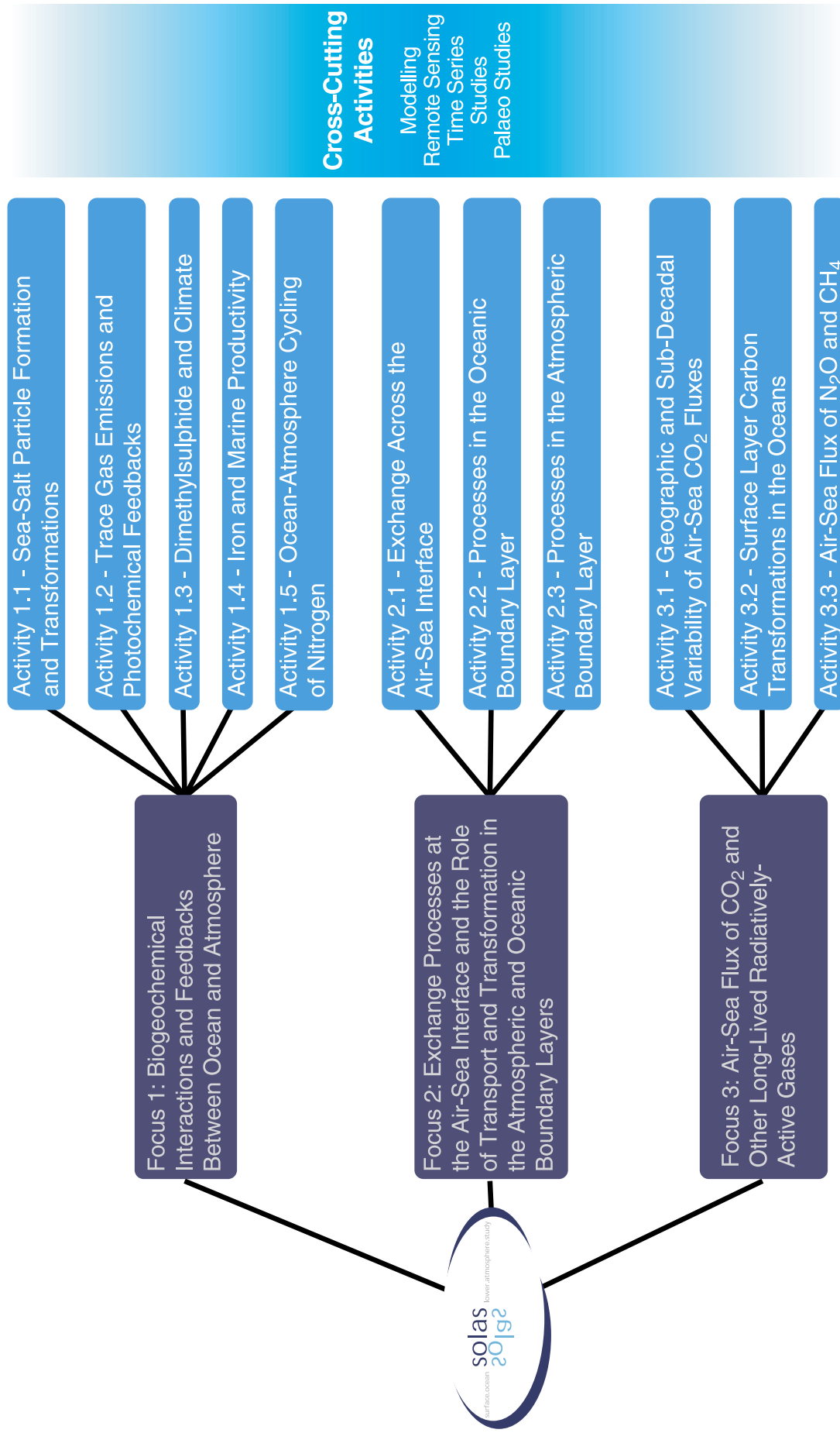
As is the goal of many international projects, SOLAS will add value to the research in its area of interest by activities such as: answering broad questions that individual nations cannot address alone; coordinating large-scale international activities, encouraging multi-investigator studies and avoiding unnecessary duplication of effort; establishing a common data policy to allow sharing of results between investigators; synthesising and publicising the results obtained in the project; carrying out data and model intercomparisons; standardisation of methodologies; testing models against new and existing data sets.

Specifically, SOLAS will add value by improving process understanding in both the surface ocean and the lower atmosphere, as well as the mechanisms of exchange between them. This will lead to improved parameterisation of air-sea transfer rates and processes within both fluids. In turn, this will feed into better models for upscaling local results to regional and global scales. Finally, the improved understanding of biogeochemical interactions between atmosphere and ocean to be achieved in SOLAS will be vital components in the construction of Earth System models of various degrees of complexity. A current example is the strong involvement of SOLAS in the SCOR/IGBP Fast Track Project 'Global Iron Connections', which will produce an integrative assessment of the global iron cycle.

The Structure of the SOLAS Science Plan and Implementation Strategy

SOLAS consists of 3 Foci, each containing several Activities, as shown in Figure 4. In the main part of the Plan, the Activities are introduced and a review of the present state of understanding is presented. This leads to definition of the major issues requiring resolution, which have been classified in terms of essential (▶▶) and complementary (▶); these are followed by a statement of the specific goals of each Activity. Finally, promising approaches to tackling the identified issues are discussed, together with a strategy for implementation. The Plan concludes with a description of the organisation and management of SOLAS.

Figure 4. The structure of SOLAS.



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.

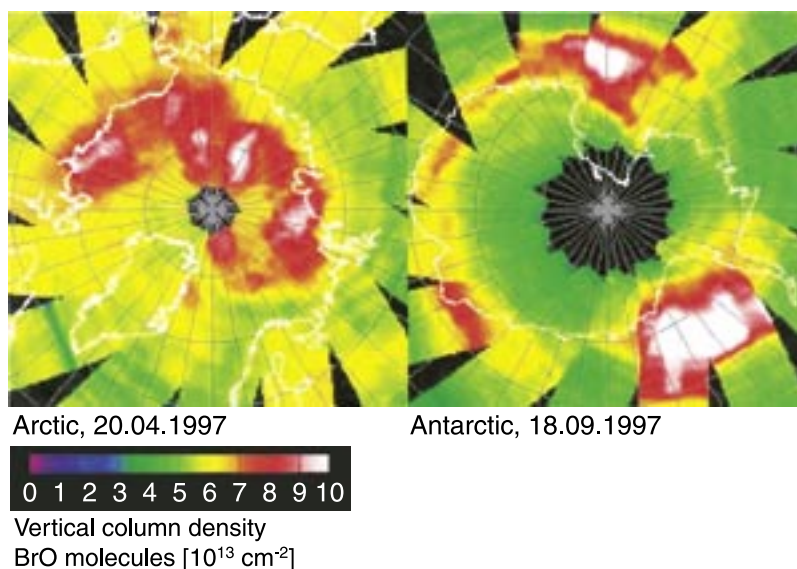
Some halogen species are powerful oxidants themselves. BrO and atomic Cl , for instance, may play an important role in the oxidation of DMS (Toumi, 1994). Since Cl atoms are roughly one order of magnitude more reactive than OH radicals, even low levels could have a large influence on the atmospheric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

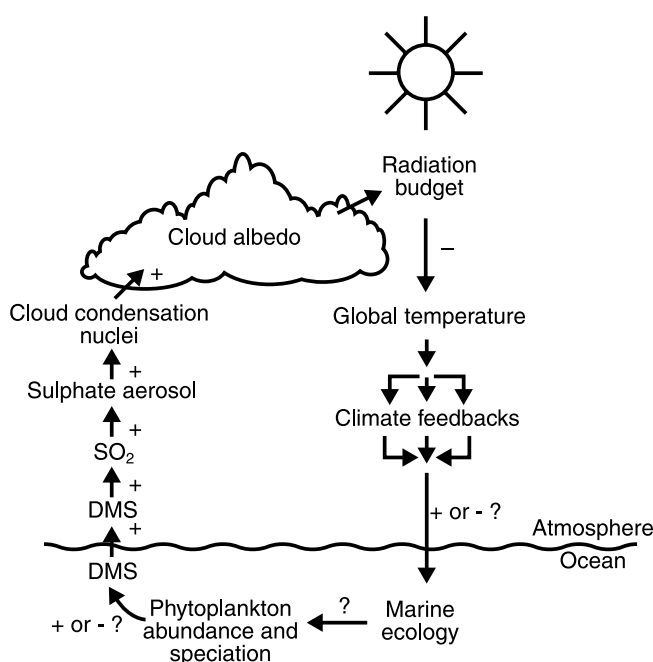
Activity 1.3 - Dimethylsulphide and Climate

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

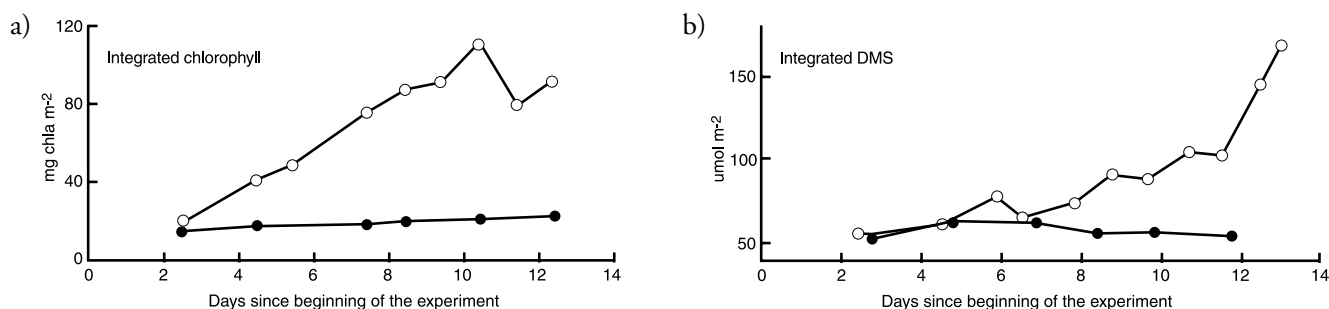
organisms (both bacteria and phytoplankton). Of the measurable iron in seawater, more than 99% is organically complexed with natural organic ligands that are part of the dissolved organic material in the oceans (Rue and Bruland, 1997). However, we know little about the chemical form, sources or sinks 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).

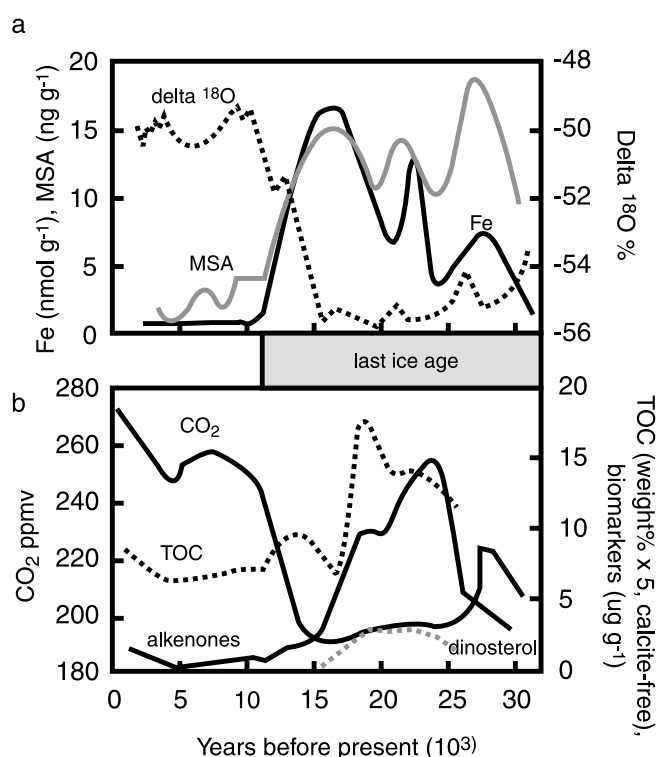
Figure 7. Measurements during the SOIREE experiment in the Southern Ocean showing dramatic increases in a) chlorophyll in the iron fertilised area (open circles) compared to the unfertilised area (dark circles); and b) aqueous dimethylsulphide (DMS) in the iron-fertilised area (open circles) compared 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.

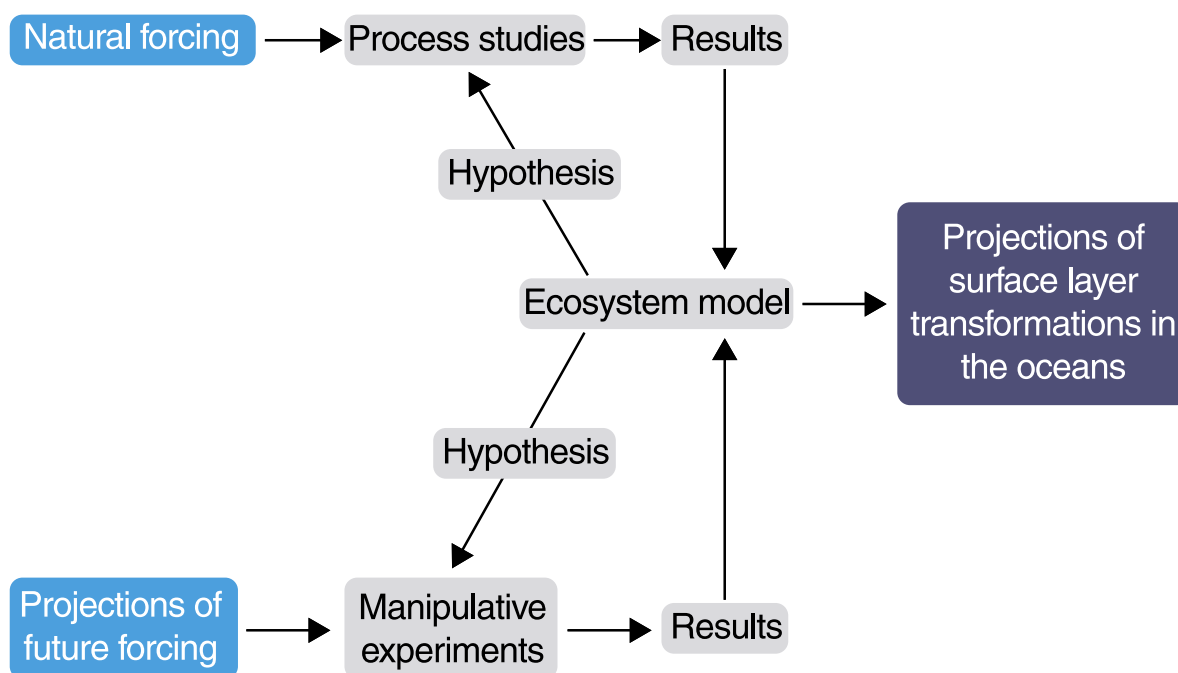
It should be kept in mind that the upper ocean inorganic and bio-inorganic chemical processes, as well as the biological responses to iron deposition, are exceedingly complex and difficult to recreate under controlled laboratory conditions. In recent years, the international biogeochemical research community 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.

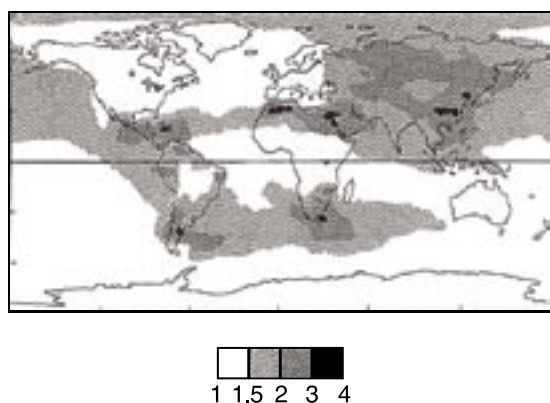
While we have a rudimentary understanding of the present atmospheric deposition patterns of inorganic

[†] 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.

Focus 2: Exchange Processes at the Air-Sea Interface and the Role of Transport and Transformation in the Atmospheric and Oceanic Boundary Layers

The objective of Focus 2 is to develop quantitative understanding of processes responsible for air-sea exchange of mass, momentum and energy to permit accurate calculation of regional and global gas and aerosol fluxes. This requires establishing the dependence of these interfacial transfer mechanisms on physical, biological and chemical factors within the atmospheric and oceanic boundary layers, and the horizontal and vertical transport and transformation processes that regulate these exchanges.

Our understanding of mass (gases, liquid and solid particles) transfer in the ocean-atmosphere system is less well developed than that for the exchange of physical quantities (heat, momentum, and moisture). This discrepancy neatly defines the remit of Focus 2 of SOLAS, i.e. to improve quantitative understanding of the exchange of gases and particles – an important component of this advancement being the utilisation and development of existing understanding of physical exchanges.

The primary motivation for developing improved knowledge of mechanisms underlying air-sea exchange is that it is essential for the interpretation of larger-scale biogeochemical and physical processes and feedbacks. Hence, the development of models with credible prognostic capability within the context of changing forcing is required. The large range of scales associated with the mechanics of air-sea exchange (from micrometre to mega metre) necessarily requires such models to be idealised, so that unresolved processes have to be parameterised. The critical issue is that unless these parameterisations are adequate and well founded, the models will have limited skill and predictive capacity with respect to climate or other environmental change. A primary milestone in SOLAS will be the development of models for air-sea fluxes, including the exchange of gases and aerosol particles, founded on sound physical and biogeochemical principles. Such improvement requires quantitative measurements of the exchange (including wet and dry deposition) of mass (gases, aerosols and water vapour), momentum, and energy (including heat) across the air-sea interface, as well as the biogeochemical and physical parameters that characterise the interface and drive the processes. Simultaneous study of the physics and biogeochemistry of the air-sea interface will lead

to improved understanding of the fluxes of momentum and energy. SOLAS aims to significantly improve the parameterisation of air-sea exchange processes, thus allowing, for example within Foci 1 and 3, more accurate estimations of regional and global flux fields, including their spatial and temporal variability.

Traditionally, parameterisations of the air-sea fluxes of momentum, heat and moisture have been based on dimensionless transfer coefficients (e.g. the drag coefficient for wind stress), whereas gas flux parameterisations have been based on vertical transfer velocities. Aerosol production and dry deposition are generally parameterised in terms of wind speed or friction velocity. An essential objective of the implementation activities of Focus 2 will be the harmonisation of these approaches, both in field studies and in theoretical/modelling studies. For example, Figure 11 depicts the processes that influence the transfer of gases and aerosols across the air-sea interface. A strategy of SOLAS is to quantify all processes controlling air-sea exchanges. The goal is to accurately measure air-sea fluxes on small spatial and temporal scales and to extrapolate to regional and global scales. This will be achieved by air-sea flux studies, common boundary layer studies and satellite and modelling activities.

The efforts needed to develop understanding of the myriad of processes shown in Figure 11 have been divided into three Activities. Activity 2.1 concentrates on processes controlling transfers at the air-sea interface, while Activities 2.2 and 2.3 deal with processes affecting these exchanges in the oceanic and atmospheric boundary layers, respectively. The list below shows the aspects of air-sea exchange that are considered in each Activity.

Activity 2.1

- Ocean surface roughness
- Microlayer surfactants
- Rain effects
- Thermal stability
- Radiation mediated effects
- Air-sea gas transfer and sea ice

Activity 2.2

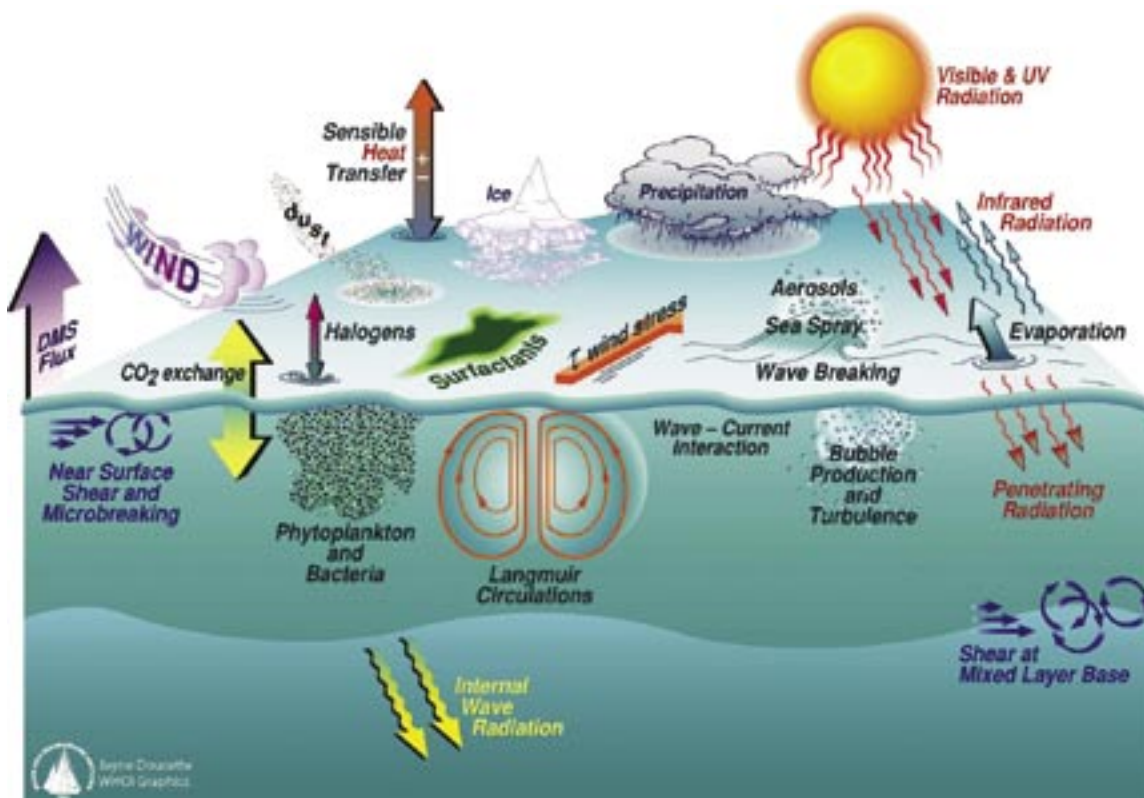
- Bubble plume dynamics
- Factors controlling surface ocean trace gas concentrations
- Upper ocean transport

Activity 2.3

- Atmospheric boundary layer properties
- Sea-spray production
- Deposition to the sea surface
- Cloud processes
- Atmospheric heterogeneity and entrainment

The three Activities of Focus 2 must be developed within a common strategic framework in order to maximise the benefit for this Focus and optimise cooperation and collaboration between oceanographic and atmospheric studies. An important goal of this Focus of SOLAS is to learn enough about the exchange mechanisms so that straightforward measurements of mean quantities can be used to infer air-sea exchange on regional and global scales, and to provide the basis for improved parameterisation of air-sea exchange in models at these scales. This goal will require a coordinated programme of comprehensive observations, experiments and modelling. The modelling should include a focus on small-scale studies of transport across the air-sea interface. It should include turbulence resolving models as well as larger-scale modelling of mesoscale transport extending throughout both the oceanic and atmospheric boundary layers, and should extend across the top of the marine atmospheric boundary layer and the bottom of the oceanic boundary layer. In the atmosphere, the effects of boundary-layer clouds on transport, wet deposition, and chemical transformation also need to be considered.

Figure 11. Processes in the surface ocean and lower atmosphere responsible for the exchange of mass, momentum and heat. Image: US SOLAS.



Activity 2.1 - Exchange Across the Air-Sea Interface

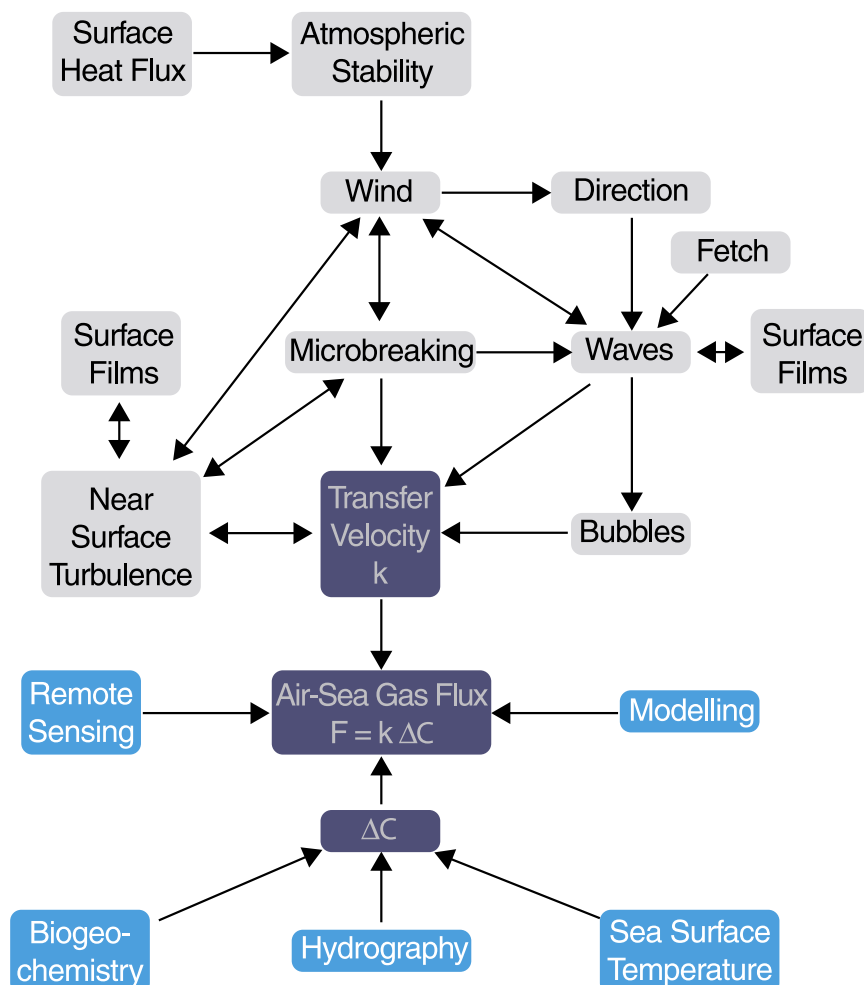
Understanding physical and biogeochemical processes near the air-sea interface is critical for predicting the air-sea exchange of gases and aerosol particles and determining how these processes will affect and be affected by global change.

Introduction

Material transport across the air-sea interface is viewed as turbulent transfer across the two fluid boundary layers and the interface separating them. Rates of transfer across the coupled boundary layers are controlled by a myriad of processes (Figure 12). The rate of turbulent transfer in the atmospheric and oceanic boundary layers determines the atmospheric transport rates away from or to the interface, which in turn, are determined by surface roughness, buoyancy forces and wind speed. In the surface ocean, vertical transport is also dependent

on turbulence. Close to the surface this turbulence is intermittent and thought to be greatly enhanced in the presence of breaking waves. Breaking waves introduce bubbles in the oceanic surface layer that enhance gas transfer and mediate primary aerosol production. Organised circulations (Langmuir circulation and convective motions) contribute to the transfer to and from the oceanic surface layer, and nocturnal cooling and mixing can redistribute near-surface properties downwards over several tens of metres. It is important to account correctly for the air-sea transfer of heat and momentum, as these properties are critical to the struc-

Figure 12. Key components to be measured to understand and extrapolate air-sea gas transfer to global and regional scales.



ture and evolution of the boundary layers, and hence the transport of mass to and from the interface.

Across the microscale interface, where viscous effects are important, transfer occurs by molecular or conductive transport. *In situ* (possibly catalysed) chemical reactions may significantly modify fluxes for some species. The nature and behaviour of this interface can be affected by the presence of surface-active chemicals produced by photochemical and biological processes (Activity 1.2). Surfactants can significantly dampen waves at high wave numbers and thus affect wave slope spectra, and at low wind speeds they can suppress near-surface turbulence. Thus, the behaviour and properties of these processes need to be measured and understood for development of adequate transfer models.

At lower wind speeds, the transfer of heat and water vapour (buoyancy fluxes) at the sea surface will strongly influence transport near the interface, and rain impacting the sea surface generates turbulence, entrains bubbles, and creates splash droplets. In addition, the thermal anomaly at the sea surface associated with heat transfer (the “cool skin effect”) can also influence gas fluxes through the dependence of gas solubility on temperature.

To help focus research on key aspects of such a wide ranging topic, simulations that test model sensitivity to air-sea exchange can be used. For example estimates of the oceanic CO₂ uptake can differ by as much as 30 to 50%, assuming the same wind field and different parameterisations of the gas exchange as a function of wind speed (Wanninkhof et al., 2001; Takahashi et al., 2002). Another example is the variation in radiative forcing that varies by a factor of three depending on the emission strength of sea spray (Houghton et al., 2001).

State of Present Understanding

The study of the exchange of physical quantities in the atmosphere-ocean system has been ongoing for several decades, and is a mature discipline with many impressive achievements. The processes by which exchanges take place are well studied theoretically, in the laboratory and at sea, and boundary-layer models have been successfully deployed. SOLAS will utilise these firm foundations in its continuing studies of the air-sea exchange of gases and particles. Despite what has been achieved, there are still many uncertainties in the estimation of the exchange of physical quantities, particularly so in high and low wind speed regimes, with implications for

weather prediction and climate applications. Joint efforts by the physical and mass flux communities should lead to mutual benefits in resolving such issues and advancing understanding of gas and particle fluxes across the sea surface.

Within the SOLAS domain, modelling and formulation of large-scale gas exchange rates as a function of environmental conditions and forcing are not well developed. The models are generally idealised, heuristic, and incomplete. A widely used formulation incorporates a quadratic function of wind speed (Wanninkhof, 1992), but the empirical underpinning is weak, particularly at high wind speeds. Field measurements have suffered from both a high degree of uncertainty and the difficult challenge of obtaining direct observations near the interface at high sea states, making the evaluation or parameterisation of empirical relationships difficult. Moreover, although gas exchange rates can be correlated with wind speed, other properties that characterise the degree of turbulence near the interface more directly might be better suited for parameterisation of the gas exchange rate (e.g. mean square wave slope), especially if they can be measured over large scales.

Basic surface renewal models have provided useful guidance in determining the quantitative relationship between fluxes of properties with differing molecular diffusivity, and have been supported by dual tracer release experiments (Nightingale et al., 2000b). Schmidt number (ratio of viscosity to diffusivity) dependence of gas exchange rates has also been determined under low to medium wind speed conditions. It is not yet clear how well this formulation works under high wind conditions in the presence of bubbles.

Ocean surface roughness

There is increasing evidence that the air-sea gas transfer velocity strongly correlates with ocean surface roughness or the mean square slope of short wind waves (e.g. Jähne et al., 1987; Bock et al., 1999). Even in the presence of surface films the relationship between the transfer velocity and the surface roughness appears to remain valid, since the surface films may also reduce roughness.

It is currently unclear why surface roughness correlates with the gas transfer velocity. It has been shown, both theoretically and experimentally, that short wind waves support a significant part of the total momentum flux as form drag (e.g. Makin and Kudryavtsev, 1999; Uz et al., 2001). However, it is believed that short wind waves

do not directly contribute to the air-sea gas flux. Instead, waves appear to enhance surface renewal and resulting gas/heat transfer by microscale breaking, wave-current interaction, and other physical processes (e.g. Melville et al., 1998; Zappa et al., 2001).

Microlayer surfactants

Laboratory measurements of the role of surfactants have proven to be more useful in elucidating the fundamental physicochemical mechanics of gas exchange than for direct extrapolation to environmental conditions (e.g. Asher et al., 1996; De Leeuw et al., 2001). Studies in annular wind tunnels showing a dependence of wave slope and gas exchange rates on the amount of synthetic and natural surfactants (e.g. Frew, 1997, Figure 13) have provided useful insights into underlying processes. However, field measurements using the dual tracer technique in the IronEx II study showing no dependence of transfer velocity on changing algal pigment concentrations (a proxy for surfactant concentrations) (Figure 14) appear to contradict these findings (Nightingale et al., 2000a). More work, both in the laboratory and in the field (e.g. Bock et al., 1999) is clearly needed to address this issue.

Figure 13. Transfer velocity (k_w), a parameter that quantifies the kinetics of gas exchange, as a function of time measured in an annular laboratory tank for a series of seawater samples collected on an inshore (Narragansett, RI - Station A) to offshore (Bermuda - Station F) transect. Scale at the right indicates measured k_w values relative to those obtained for clean distilled water ($k_w(\text{clean})$). As the experiment progressed k_w generally decreased as surfactant material accumulated at or near the water surface (Frew, 1997).

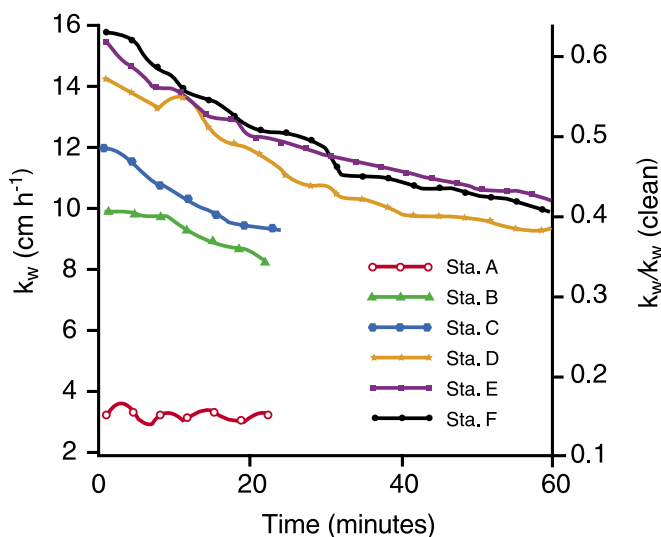
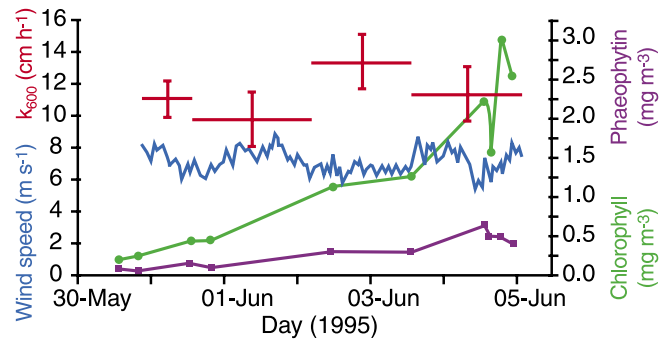


Figure 14. Air-sea gas transfer rates during the development of an open ocean algal bloom in IronEx II. Estimates of the gas transfer velocity normalised to a Schmidt number of 600, k_{600} (red), plotted against time, together with wind speed from the two nearest TAO buoys (blue), chlorophyll (green), and phaeophytin (mauve), showing no dependence of k_{600} on increasing algal pigments (Nightingale et al., 2000a). Reproduced by permission of American Geophysical Union.



Rain effects

Laboratory experiments and preliminary field studies show that raindrops falling on the water surface can significantly enhance the rate of air-water gas exchange, which increases systematically with the kinetic energy flux to the water surface supplied by the raindrops (Ho et al., 1997; 2000). The enhancement in air-water gas exchange by rain is dominated by the production of turbulence and secondary motions, while rain-generated bubbles contribute a smaller portion (0 to 20%) to the total gas exchange, depending on rain rate, raindrop size, and gas solubility.

At low wind speeds and rain rates, rain falling on the ocean surface is likely to suppress air-sea gas exchange by creating a layer of lower density that is slowly mixed with the saline water below. However, at moderate wind speeds and rain rates, wind-induced mixing is likely to disperse any potential stratification. At present, a quantitative relationship between wind speed and the breakdown of stratification is lacking.

Thermal stability

Thermal stability at the air-sea interface is extremely important in controlling momentum and heat fluxes between the ocean and atmosphere, and also plays a critical role in air-sea gas exchange. Observational stud-

ies need to be developed with a focus on quantifying the influence of thermal stability on air-sea gas exchange. Thermal stability may be especially important at high latitudes where significant CO₂ uptake occurs and large areas of thermal instability exist.

Radiation mediated effects

Radiative transfer, which is affected by atmospheric composition, plays a role in oceanic heat transport. There are complicated feedbacks between the radiative transfer and biological and chemical processes in the surface ocean. For example, the absorption depth scale of shortwave radiation depends on water transparency. At lower wind speeds the differential heating of near-surface water can lead to density-driven stratification and, consequently, to higher stability. Increased biological production leads to decreased transparency, which further decreases the depth of solar penetration and increases the magnitude of that thermal stability. Stabilisation, in turn, inhibits nutrient replenishment via vertical transport. These conditions might be expected to favour plankton adapted to high light and low nutrient levels, which may affect trace gas emissions (Activity 1.2 and 1.3). The thermal stratification leads to higher surface temperatures, which in turn can enhance sensible and latent heat losses to the atmosphere, a potentially destabilising feedback. Particularly at high latitudes, stability can also be affected by haline stratification. At low latitudes, evaporation can lead to changes in salinity-driven stratification.

Air-sea gas transfer and sea ice

A similarly difficult problem concerns air-sea exchange in regions covered or under the influence of sea ice. Sea ice can provide a direct cap for gas exchange, but can also act more indirectly by altering the wave field and the related turbulence in the oceanic and atmospheric boundary layers. Experiments most likely to contribute to the solution of this latter problem include geochemical balances and flux measurements in the marginal ice zone and extending beyond the sea ice edge. Studies in the Southern Ocean (Weddell Sea) using dissolved oxygen and ³He balances (Hohmann et al., 2003) indicate that knowledge of the gas transfer rates in the presence of sea ice is critical to correctly estimate gas fluxes in such regions.

Major Issues that Require Resolution

- ▶ **What is the quantitative dependence of gas and aerosol air-sea fluxes on such factors as wind speed, wave state, turbulence**

level, stratification, temperature, salinity, insolation, humidity, precipitation, sea ice cover, bubble population, the skin effect, and microlayer surfactants? It is evident that exchange rates depend on a variety of environmental factors that are not simply related to wind speed. In the case of gas exchange, this is illustrated by the fact that the observations show broad scatter around the most widely used formulations of gas exchange rates, which depend on wind speed alone (Liss and Merlivat, 1986; Wanninkhof, 1992). Another example of uncertainty is our poor knowledge of the transfer rates for wind speeds larger than 15 m s⁻¹. The situation for primary aerosol is even more cumbersome, with an uncertainty of an order of magnitude in the production rate.

- ▶ **What is the sensitivity of climate and ecological models to air-sea gas and aerosol fluxes?** Model simulations that test their sensitivity to air-sea exchange will help to guide the evolving experimental activities on these processes within SOLAS.

Specific Goals

- I. Predict gas and aerosol exchange rates for commonly observed environmental conditions. This requires determination and quantification of the processes that control mass exchange rates. The errors of these exchange rate estimates should be comparable to those for fluxes of momentum, heat and moisture.
- II. Quantify the sensitivity of models used in SOLAS to a range of gas flux and primary marine aerosol radiative forcing scenarios spanning at least twice the range of uncertainties determined from known measurements.

Promising Approaches and Implementation Strategy

Field measurements of gas exchange rates traditionally have been determined by geochemical mass balance techniques applied on a variety of scales. These range from local dye-release experiments, through radon disequilibrium determinations, to global and regional-scale radiocarbon uptake estimates. Comparison of these measurements remains challenging because of differing scales and scope, but a successful model of air-sea exchange must satisfy all these diverse constraints. Moreover, a

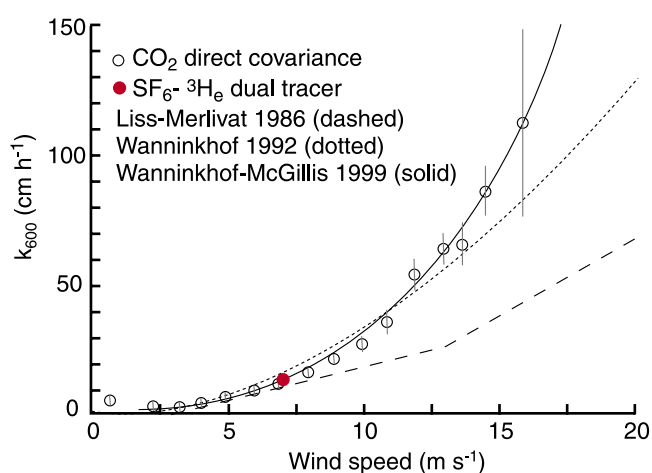
well designed observational programme should span as broad a range of space and time scales as possible, in order to provide robust calibration and validation of air-sea exchange models.

Direct measurement of air-sea fluxes of gases and aerosol particles is very difficult, especially in the open ocean at higher wind speeds. Given this difficulty it would seem especially important that gas and aerosol transport be measured at the same time and with the same temporal and spatial resolution as the crucial parameters describing the quantities and processes that mediate the transport. This requirement suggests the need for more comprehensively integrated studies than have usually been attempted or found practical in the past. Important steps in this direction have recently been made in studies in the southern North Sea (Jacobs et al., 2001) and North Atlantic Ocean (McGillis et al., 2001b, Figure 15), in which micrometeorological and purposeful tracer approaches have been applied in tandem with important ancillary measurements. Such experiments may be viewed as proto-SOLAS studies.

Direct eddy correlation measurements from aircraft of the air-sea flux of dimethylsulphide (DMS) are now possible, as has been demonstrated in the DYCOMS-II programme. The development and testing of analytical instruments capable of resolving frequencies of 1-10 Hz in biogenic gas concentration measurements in the atmosphere should be considered a very high priority (Activity 1.3). These direct flux measurements can be made on the same time (20-30 min) and spatial (tens of km) scales as changes in the physical forcing processes.

Direct eddy correlation measurement of aerosol fluxes has been demonstrated by Nilsson et al. (2001). However, improvements are required, in particular, for size resolution and chemical speciation, as a matter of high priority. Other promising new techniques are aircraft measurements to establish the role of fetch in aerosol fluxes (Reid et al., 2001) and application of transport models (Vignati et al., 2001). Key unifying factors used for parameterisation of the sea-spray source function should be based on micrometeorological and oceanographic parameters, which include wind speed and wind speed variability, thermal stability, wave steepness, water temperature, bubble concentrations and spectral shape, and surface tension. Simultaneous measurement of bubble and sea-spray size distributions, covering a variety of atmospheric and oceanographic conditions, in combination with techniques to derive the sea-spray

Figure 15. Transfer velocity (k) determined by eddy correlation (direct covariance) in GasEx-98 and one k measurement obtained using the SF_6 - ^3He dual tracer pair, all plotted against wind speed. Also plotted are some widely used parameterisations of k versus wind speed (McGillis et al., 2001b). Reprinted with permission from Elsevier Science.



source function using methods described above, provide a promising approach to better parameterise the production of sea-salt aerosol.

Implementation of Activity 2.1 should include the following items:

Laboratory experiments

Process studies

- Influence of wave breaking and bubbles involving a variety of gases with different physical properties (Schmidt number, solubility) providing parameterisations of gas transfer rates and physical insight into the contributions of various processes (De Leeuw et al., 1999; De Leeuw et al., 2001).
- Effects of surfactants on wave breaking, bubble bursting and consequences for gas transfer and for the chemical composition of aerosols, with emphasis on aerosol composition and contribution of organics.
- Detailed studies on bubble-mediated aerosol production mechanisms from single bubbles and bubble plumes, including the relative

importance of film and jet droplet production and, using visualisation techniques, spume droplet production by direct tearing. Of special interest is the production of very small sea-spray droplets observed both in the field (Nilsson et al., 2001) and in the laboratory (Mårtensson et al., 2003).

Development of parameterisations

- Effect of breaking wave properties on bubble plume types and resulting aerosol production.

Technology development

- Development and testing of instrumentation and experimental techniques for application during open ocean deployments.

Field experiments

The following field experiments need to be undertaken using both proven and innovative methods in a variety of conditions:

- Continued development of new methodology and techniques for direct flux measurements using (relaxed) eddy correlation measurements for gases and aerosols, including techniques providing information on chemical composition (De Leeuw et al., 2003; Nilsson et al., 2003).
- Comprehensive intercomparison of flux measurement techniques in single experiments in representative environmental conditions.
- Deployment of geochemical and micrometeorological techniques for measurement of gas and aerosol fluxes during campaigns at several locations selected for characteristic oceanographic, biological and micrometeorological properties.
- Long-term measurements of these parameters at a selected number of well chosen sites, covering a wide range of environmental (micrometeorological, oceanographic, biological, geographic) conditions, to study the various influences as well as seasonality. This activity will be planned and carried out cooperatively with ongoing programmes responsible for long term sustained observations and where possible will use the same locations as other parts of SOLAS.

Modelling

Parameterisations of air-sea transfer processes are used in various kinds of models such as meteorological, climate (GCM) and local and regional-scale chemical transport models. For instance, sea-spray source functions are used in GCMs to estimate the top-of-atmosphere, global-annual radiative forcing due to sea salt, which amounts to -1.51 to -5.03 W m^{-2} for low and high emission values, respectively. This uncertainty will be addressed by SOLAS studies of the parameterisation of sea-spray production. The interaction between the modelling communities (as users of the parameterisations from the SOLAS air-sea exchange studies) and the experimentalists will provide input on the required accuracy and limitations of the results that can be expected from SOLAS in the next decade.

Important modelling and other numerical activities in Activity 2.1 include:

- Parameterisation of transfer velocities and fluxes across the air-sea interface to provide an optimum description of the various processes for application in models.
- Modelling the interface processes for gas transfer and aerosols (e.g. aerosol deposition, spume droplet production, bubble bursting processes).
- Inverse modelling to determine sources and sinks at the air-sea interface, using assimilation of surface observations and satellite derived data (aerosols, gases, surface characteristics) in chemical transport models. This activity will be developed in collaboration with CLIVAR, WGCM and WGNE.
- Development of parameterisation of k as a function of satellite-derived data such as wind stress and surface roughness (Glover et al., 2002).

Activity 2.2 - Processes in the Oceanic Boundary Layer

Understanding upper ocean boundary layer physical and biogeochemical processes that regulate changes in near surface concentrations and air-sea exchange of gases and materials is critical for determining how such exchanges and processes will affect and be affected by global change.

Introduction

The upper ocean is intermittently mixed and re-stratified through the combined effects of wind, surface buoyancy fluxes and penetrating radiation. Mixing reduces vertical property gradients close to the air-sea interface. In the oceanic boundary layer, upper ocean circulations combine with *in situ* biogeochemical transformations to control exchanges with the atmosphere. Wind mixing, wave action and current shear represent a constantly changing input of kinetic energy in space and time. Moreover, the temporal response of the upper ocean to this changing input is also subject to the Earth's rotational effects, which introduce additional length and time scales. Biogeochemical transformations have a further set of distinctive time scales that are, in general, not matched to the physical scales. It is the combination and interaction of these different and interdependent processes that produce the spatially and temporally varying properties within the ocean surface layer.

The ocean-atmosphere interface, which exerts a primary, short-term control over exchange across it, is influenced by the interaction between processes occurring on short time scales and longer-term controls that regulate the nature of the oceanic boundary layer. Transport and transformation of properties within this layer are important determinants of air-sea exchange processes on diurnal through seasonal time scales. Moreover, they exert fundamental controls on the character and overall rates of biogeochemical processing within the upper layers, which in turn play a role in modifying the characteristics of the interface itself. Although the boundary layer is most conveniently defined in physical (circulation and mixing layer) or biological (euphotic zone) terms, we are also concerned with the coupling of the boundary layer to deeper layers. This coupling is important, particularly with regard to the return of remineralised nutrients and the subsequent regulation of biological productivity and trace gas production. It is through this pathway that significant climate feedbacks may occur.

State of Present Understanding

Bubble plume dynamics

At higher wind speeds the interface is disrupted to a progressively greater extent. In the water, bubbles can be formed after wave breaking and penetrate some distance beneath the surface. The downward penetration and evolution of bubble plumes are controlled by a combination of wave action, organised fluid motion (circulation cells and vortices) and turbulence, by the presence of surfactants and particles and by bubble buoyancy. Thus, bubble spectra are highly variable and evolve strongly after the initial wave breaking process (Leifer and De Leeuw, 2001), which has consequences for the bubble-mediated processes of gas transfer and sea-spray aerosol production. Under increasing hydrostatic pressure, the transfer of gases across the bubble-water interface is controlled by physico-chemical transport across yet another interfacial layer, the properties of which evolve and are modified by surfactants and micro particles. The gaseous composition of the bubbles therefore evolves in a complex manner along their individual trajectories. Depending on sea state and biogeochemical factors, varying fractions of the bubble population are forced into solution, whereas the remainder rise to the surface and escape. Thus, bubbles are a unique and potentially important extension to the air-sea interface, particularly for relatively insoluble gases.

Factors controlling surface ocean trace gas concentrations

The gas concentration in the surface ocean is controlled by physical, chemical, and biological processes. For a chemically and biologically non reactive gas, the mixed layer concentration is determined by advection, entrainment from below, and exchange across the air-sea interface. Even in this simple case, it is presently difficult to quantify the effects of air-sea exchange on trace gas concentrations. This is especially important with high wind speeds when the air-sea exchange is proportionally higher. There may also be subsequent supply from below the mixed layer which also increases under high winds.

The prominent mesoscale structures visible in satellite images are a dominant characteristic of ocean variability and doubtless play a crucial role in material transport. The formation of mesoscale eddies and fronts is determined by the response of internal dynamical processes in the ocean to large-scale wind and buoyancy forcing. Fronts represent important boundaries between different water properties and can be associated with significant cross-isopycnal mixing and vertical motions, producing enhanced biological response. High resolution numerical modelling of frontal structures reveals that ageostrophic motions and associated isopycnal frontal slumping result in substantial vertical and diapycnal nutrient exchange, which appear to support enhanced production (Mahadevan and Archer, 2000; Nurser and Zhang, 2000). That, in turn, may result in enhanced levels of trace gases. Mesoscale eddies have also been strongly implicated as mechanisms for productivity enhancement by eddy heaving (McGillicuddy et al., 1999). Recent sub mesoscale biogeochemical modelling of upper-ocean processes exhibits significant enhancement of biological production over that in coarser resolution models, indicating the importance of small-scale (~ 1 km) motions.

Upper ocean transport

Horizontal gradients of physical properties in fronts also feed back to air-sea exchange. For example, differences in surface water temperature modify atmospheric stability and hence create a corresponding wind response, along with the local surface divergence field that modulates the wave field and resultant air-sea transport. Different cloud and fog conditions can further modify the surface buoyancy flux and photosynthetically available radiation on either side of the front, the latter with important biological consequences. The presence of phytoplankton (and other particulate materials) affects the depths over which penetrating radiation is absorbed, influencing the thermal stability of the upper ocean.

To the extent that nutrient availability controls the biological emission of gases, surfactants and certain primary particles, it is essential to quantify horizontal and vertical near surface gradients of nutrients. Outside the tropics, seasonal mixing plays a major role in nutrient renewal during winter. Wind mixing and surface buoyancy flux tend to dominate the stratification in spring and summer, providing constraints on the biological response. It might be expected that reduced wind mixing over the summer season would limit the nutrient input, decreasing carbon uptake and air-sea transfer of CO_2

and other gases. However, in the subtropics, the summer time accumulation of photosynthetic oxygen and DMS and the drawdown of CO_2 , despite the clear vertical separation of the nutrient-depleted euphotic zone from the pycnocline nutrient pool below, belies this simple view. Geochemical mass balance analyses reveal that a substantial fraction of annual production may occur during this summer period, indicating that models must include and delineate between other sources of nutrients, both from physical processes (e.g. frontal exchanges and eddy heaving) and from nitrogen fixation by cyanobacteria; photochemical inhibition of biological degradation may also play a role.

In the stratified tropics, the reflux of aphotic zone remineralised nutrients to the euphotic zone must occur via turbulent mixing across the pycnocline or from wind-induced upwelling. The former is especially significant near the equator, where large shears are generated by the strong zonal currents. Tropical upwelling characteristically results in regions of abnormally high nitrate concentrations spreading away from the equator, probably where the micronutrient iron, supplied by the same processes, has already been used up by the phytoplankton. The biological and biogeochemical characteristics of such regions may well be unique in their behaviour and response to change in forcing.

Transport and mixing processes in coastal regions can differ in many ways from the open ocean. Stratification will be enhanced where there is freshwater input from rivers and may be dominated by salinity rather than temperature. Tides can greatly enhance mixing throughout the water column in shallow shelf seas. Interaction between the surface layer and the seafloor can lead to significant geochemical effects. The diversity and range of biological response is far greater in coastal waters. Moreover, human influence on the ocean is most extreme in coastal waters, where agricultural and other pollutants, delivered by surface runoff, atmospheric inputs, and groundwater discharge, lead to profound changes in the chemistry, and biological production and respiration. Although the areal extent of the coastal ocean is small relative to that of the world ocean, its importance is disproportionate because of its proximity to population centres and the magnitude of the changes that occur in these waters. Thus, the mechanisms that lead to transport between coastal and offshore areas have a particular significance for modification of offshore waters, influencing in turn the air-sea exchange that

occurs over much larger areas. This is a research topic where strong interaction with LOICZ will be mutually beneficial.

Major Issues that Require Resolution

- ▶ **How do physical transport and biogeochemical processes in the upper ocean regulate near-surface concentrations of biogeochemically important materials (e.g. nutrients, O₂, CO₂, DMS)?** Understanding processes controlling near-surface concentrations is a central requirement for determining air-sea exchange. Determination of near-surface concentrations may require consideration of the coupling of the surface layer of the ocean to water masses below the thermocline, as well as horizontal gradients caused by processes associated with mesoscale features such as eddies and fronts.
- ▶ **How does the generation and evolution of surface ocean bubble fields control the production of primary marine aerosols and affect gas transfer?** Marine aerosols that are generated from bubbles will be controlled by the physical behaviour and chemical composition of the surface ocean bubbles. Organic and inorganic materials accumulate on bubble surfaces. These materials are concentrated in both film and jet drops of surfacing bubbles. Gas transfer is augmented by bubbles, causing unknown degrees of supersaturation and turbulent mixing.

Specific Goals

- I. Accurately measure gradients of gases within the upper ocean and their variability. Develop a dynamic coupled biogeochemical - upper-ocean mixed layer model with time resolution of less than 10 minutes and vertical resolution near the surface of the order of 1 m, capable of *inter alia* 'predicting' near-surface concentrations and gradients of salinity, nutrients, O₂, CO₂, DMS, NH₃, DIC, DOC and Fe species, with contemporary process formulations.
- II. Develop parameterisations of bubble generation and subsequent aerosol generation dependent on wind speed (and sea state, where available).

Promising Approaches and Implementation Strategy

Biogeochemically important substances including CO₂, DMS, Fe species, and nutrients are taken up, transformed and/or released in the surface ocean on short time scales by chemical processes (e.g. photochemical transformation) and by phytoplankton, zooplankton and bacteria. Because there are many outstanding gaps in our knowledge of these processes, and it is an active area of research, it will be essential to focus on specific material cycles.

The importance of very small-scale processes in driving upper ocean biogeochemical activity requires the development of very high resolution numerical models, and the concomitant observational programme to design, parameterise and test them. Numerical experimentation is an important activity because it reveals the importance and interrelationship of process scales. Critical tests of model validation include not only the simulation of macroscopic behaviour and evolution, but also small-scale variability and statistics of physical properties and biogeochemically important species. A number of strategies, some applicable across all SOLAS Foci, need to be employed.

Consideration should be given to the development of the next generation of sensors suitable for deployment on floats, towed devices, autonomous vehicles and moorings. This requirement cuts across all activities proposed in SOLAS, but is especially important to Focus 2 because of the requirement for sensor response (and stability) spanning a range of 10⁻¹ s (10 Hz) to perhaps 10⁸ s (~3 years).

These approaches will benefit from fieldwork such as:

- Studies of physical forcing (advection, upwelling, vertical exchange within the surface mixed layer and across the thermocline).
- Measurement of diagnostic tracers (e.g. ³He, O₂/Ar ratios).
- Time series measurements (both by repeat stations and moorings) of biogeochemically important elements and compounds (nutrients, oxygen, carbon, sulphur compounds).
- Optical bubble measuring systems deployed from buoys.

- Remote sensing for regional and global scale integration, and studies of interannual and decadal-scale variability (e.g. chlorophyll, biomass, sea surface temperature).

Modelling activities at different levels of complexity are needed. They should be able to reproduce today's ocean dynamics, as well as capture alteration in upper ocean circulation due to climate change. We need to develop:

- An idealised and appropriately parameterised upper ocean boundary layer model that adequately mimics the behaviour of today's ocean and is skilful at predicting mass transfer in the oceanic boundary layer.
- A numerical model that correctly incorporates the relevant physical and biogeochemical processes and their dependencies on changing environmental variables.

At higher wind speeds the challenge of making useful measurements of near-surface and interfacial processes increases. Recently, lightly built floating sensors that follow the surface, even at high wind speeds, have been used to derive finely resolved temperature profiles, bubble size distributions and related properties in the oceanic surface layer. Acoustical methods have proved especially helpful in the study of wave breaking and in delineating bubble distributions. High frequency sonars provide remote detection of bubble distributions. Bubbles may then be used as tracers of the near-surface flow field, as they become organised and transported by Langmuir circulation and other coherent motions. Sonars may also be used to observe the penetration depth of bubbles, while acoustic Doppler methods lead to direct measurement of the velocity field. The sound radiated by breaking surface waves allows detection of their presence, breaking intensity and motion across the ocean surface. Bubbles ring with a high quality factor at resonance, giving an acoustical signature that can be used to infer their size distribution. This property is exploited in sensors that track changes in bubble size distributions with depth and time. The size distribution depends on the prior life history of the bubbles, from their formation in breaking waves, through turbulent mixing, advection and loss by buoyancy and dissolution. Measurements of bubble sizes in the context of these processes provide a sensitive diagnostic basis for exploring the detailed physics of the upper ocean boundary layer. Optical techniques to measure the evolution of

bubble plumes and the bubble size distributions using multiple cameras have been explored in wave tanks (De Leeuw and Leifer, 2001; Leifer and De Leeuw, 2001), and contrasted with 'background' bubble size distributions that are generally measured in the open ocean. Oceanic measurements of bubble size distributions show a wide variety of concentrations and shapes (De Leeuw and Cohen, 2001).

Activity 2.3 - Processes in the Atmospheric Boundary Layer

Understanding atmospheric boundary layer physics and biogeochemical processes is critical for predicting the air-sea exchange of gases and particles and in determining how such exchanges and processes will affect and be affected by global change.

Introduction

The lower atmosphere, specifically the boundary layer, links processes occurring at the air-sea interface to the rest of the atmosphere. To quantify the vertical transport and fate of gases and particles in the atmosphere, it is necessary to understand the physical and chemical mechanisms involved. In general, the atmospheric boundary layer is more difficult to observe over water than over land. Although there are important differences, model parameterisations often use values derived from measurements over land. Problems can be expected particularly in coastal regions due to the change in surface properties at the land-sea transition. Not surprisingly, the greatest observational difficulties arise at high wind speeds. Gas and particle transport may be especially important under these conditions because of the increased role of sea spray (see Activities 1.1, 1.2 and 1.3). The air-sea transports described here represent a sensitive part of the coupling between the ocean and atmosphere. Changes in climate variables, such as temperature or wind speed, will produce feedbacks through this coupling. Thus, understanding these processes is essential to the development of reliable predictions of the effects of global change.

Transport of energy, momentum and mass in the atmospheric boundary layer is achieved through a variety of processes. Wet and dry deposition, sea-spray dynamics and atmospheric heterogeneity are all important factors to consider. Trace species are incorporated into cloud droplets by condensation and coagulation, and diffusive (Brownian) capture to droplets. Therefore, the size spectra and associated hygroscopic properties of cloud condensation nuclei are critical in controlling the microphysical, chemical, and optical properties of clouds, which in turn affect chemical processing, wet deposition and boundary layer turbulence.

State of Present Understanding

Atmospheric boundary layer

Large-scale atmospheric circulation generates small-scale motions through shear instability, primarily due to

frictional drag in the boundary layer. These smaller-scale motions are described as turbulent eddies that fill the boundary layer. Their vertical motion dominates the vertical transport of momentum and scalar properties. Near the surface, turbulent viscosity varies rapidly with height. In contrast to the upper ocean boundary layer, effects due to passage of fronts and storms rarely allow Ekman spirals to develop. Convective effects, due to heat transport at the interface, can effectively mix the boundary layer to mid level, which is therefore commonly known as the mixed layer.

A useful concept for explaining boundary layer properties is the Monin-Obukhov (M-O) similarity theory, based on the argument that the structure of turbulent flow in the surface layer is governed by mechanical and thermal forcing. The balance between these two components results in a length scale, the M-O scale (L), determined by the relative strength of mechanical versus thermal forcing, with the sign determined by the direction of the buoyancy flux. The similarity hypothesis is that the turbulent characteristics, when appropriately normalised, can be expressed as a universal function depending on the parameter $\zeta = z/L$, where z is height above the surface. This scaling approach has proved successful in many atmospheric experiments and is widely accepted by the atmospheric community.

Under stable stratification ($\zeta > 0$), vertical transfers are suppressed and the boundary layer may be very shallow (of the order of metres). M-O parameterisation for this case often gives unsatisfactory results. However, the more common case over the ocean is that of near neutral stratification (particularly at higher wind speeds), or unstable stratification ($\zeta < 0$). In this case the boundary layer can be considered to consist of three layers: a near surface region or wave boundary layer (of the order of metres) where wave effects are important, a “constant flux” layer (of the order of tens of metres), and a mixed layer (of the order of hundreds of metres to 1-2 km).

The mixed layer may extend upwards to the main inversion and may also be capped by a layer of shallow cumulus or stratocumulus clouds. A typical overall depth for

the cloud topped marine boundary layer is approximately 1000 m. A particular feature of the marine atmospheric boundary layer (compared with that over land) is that the effects of cloud top evaporation and cloud radiative processes are of similar or even greater magnitude to the effects of the surface fluxes. Thus, the cloud layer may become decoupled from (or only intermittently coupled to) the near-surface mixed layer, suppressing vertical transfer into the cloud layer. While detailed investigation of most of these boundary layer processes is beyond the scope of SOLAS, their effects on the exchange of gases and particles must be considered.

Sea-spray production

When bubbles reach the water surface, they burst and produce two types of drops. Film drops are produced by the film cap opening and are only produced by bubbles larger than about 1200 μm . The number of film drops produced has been reported to be 100-1000 per bubble (Blanchard, 1963). The opening bubble leaves a hole at the water surface from which a vertical jet rises. In the air the jet breaks into up to six droplets that are called jet drops. The number of jet drops depends on the bubble size; bubbles larger than 1700 μm produce no jet drops, the smallest bubbles produce about six jet droplets (Spiel, 1997). High wind speeds ($> 9 \text{ m s}^{-1}$) lead to the formation of spume drops by direct tearing from the wave tops (Monahan et al., 1986; Marks, 1990). This enhances the effective surface area for exchange of constituents that are transferred across the air-water interface. Film, jet and spume droplets are collectively referred to as sea-spray aerosol.

The rate at which the sea surface produces spray droplets is roughly estimated as the third power of the 10 metre wind speed, U_{10} . Andreas and DeCosmo (1999) estimated that when U_{10} exceeds 20 m s^{-1} , the surface area of the airborne spray above a unit area of sea surface is equal to 10% of that unit area. In other words, at high winds, spray rapidly increases the effective surface area of the ocean and, therefore, should enhance the exchange of any constituent or property normally transferred across the air-sea interface. A further spray-producing process is the formation of spume, which creates droplets that are typically larger than 20 μm . Both rain drops and spume striking the surface can produce splash droplets (Andreas et al., 1995). Spume droplets account for most of the spray volume flux but are deposited more rapidly than the smaller drops typical of bubble bursting. Small droplets can be dispersed throughout the boundary layer and can act as cloud condensation nuclei.

Evaporation of spray can influence humidity and temperature profiles because at high wind speed, when the surface area of sea-spray aerosol is strongly enhanced, the particles provide a large area for evaporation and heat transfer as well as chemical reactions. Sea spray will also carry with it the enhanced concentrations of biological and chemical constituents of the air-sea interface, including gases (Activities 1.1, 1.2 and 1.3). Sea spray therefore serves as a medium for transporting these properties up into the boundary layer and ultimately into the free atmosphere.

Sea spray also plays other roles in the marine boundary layer. It dehydrates into sea-salt aerosol (a major component of marine aerosol) and, thus, contributes to climate forcing either directly by scattering incoming sunlight (e.g. Haywood et al., 1999), or indirectly by providing CCN and thereby affecting the optical properties of marine clouds (Ghan et al., 1998; Murphy et al., 1998). Relative to bulk seawater, the bubbles from which most spray droplets and sea-salt aerosols originate are also concentrated in marine surfactants and, consequently, enhance the air-sea fluxes of particulate organic matter (Blanchard and Syzdek, 1972; Macintyre, 1972; Duce and Hoffman, 1976; Blanchard, 1983). Spray is known to influence the transfer of halogens such as chlorine and bromine from the ocean to the atmosphere where they undergo chemical reactions that result in gas-phase halogen atom production. Gas-phase Br and Cl may play a critical role in O_3 dynamics in the marine boundary layer (Sander and Crutzen, 1996; Erickson et al., 1999) (Activity 1.2). Sea-salt particles are hygroscopic and provide a large volume of reactive medium in and on which atmospheric chemical transformations can proceed. These multiphase chemical processes significantly impact the cycling of other important atmospheric constituents including ozone, S and N compounds, and hydrocarbons (e.g. Sander and Crutzen, 1996; Ravishankara, 1997; Keene et al., 1998; Erickson et al., 1999; Galbally et al., 2000).

The magnitude of the sea-spray effect as a function of wind speed, however, is a subject of heated debate. The main reason that such diverse opinions can exist is our uncertainty in the so called spray generation function, which is the rate at which droplets of a given size are produced per unit area of sea surface. For any given wind speed and droplet radius, the spray generation functions available in the literature range over six orders of magnitude. Since modelled spray effects generally

correlate linearly with this function, such a range means that modelled spray effects are fraught with uncertainty. Andreas (2001) has reviewed the available spray generation functions to look for some consensus. On applying theoretical tests and indirect evidence, he discarded as unrealistic many of the reported spray generation functions and, finally, recommended four as the most plausible. These four agree within half an order of magnitude. Recent determinations of the sea-spray generation functions, using various techniques based on new approaches, are within similar uncertainty limits (Schulz et al., 2003). Andreas and DeCosmo (1999; 2001) used one of these seemingly reliable functions (Andreas, 1998), to construct a spray signature from the turbulent surface fluxes of sensible and latent heat measured during HEXOS (DeCosmo, 1991). In their analysis, the spray-mediated enthalpy flux could be roughly 10% of the total turbulent flux for 10 metre winds above 12 m s^{-1} .

Deposition to the sea surface

Atmospheric inputs to the ocean occur via both wet and dry deposition. The latter includes dry deposition of aerosols as well as gas exchange (Activity 2.1). To describe deposition with sufficient accuracy for planned SOLAS modelling activities, the parameterisation of both wet and dry deposition needs to be improved.

Atmospheric wet and dry particle deposition is a major pathway by which trace nutrients such as iron, nitrogen and phosphorous are delivered to the surface ocean. Consequently, reliable estimates of deposition rates are essential for predicting the response of marine biota to global change and associated feedbacks. In addition, atmospheric deposition rates of species such as SO_4^{2-} , NO_3^- , NH_4^+ and Al provide useful constraints on emission fluxes of precursors (SO_2 , NO, NH_3 , and crustal dust, respectively) in upwind source regions, as well as related information concerning transformation rates and atmospheric lifetimes. Thus, these fluxes (particularly multi year time series of wet deposition via precipitation) are widely used to construct budgets and to parameterise and evaluate global chemical transport and climate models. However, the limited spatial and temporal extent of available deposition measurements, coupled with large uncertainties in the magnitudes of these fluxes, seriously constrain the reliability of existing models. The relative importance of dry versus wet deposition varies considerably over time and space, and among species. Furthermore, in some regions, occult deposition via cloud and fog water could also contribute significantly to the total flux.

Reliable quantification of wet deposition requires accurate measurement of both the chemical composition of incident precipitation and the precipitation rate. Using state of the art sampling, storage, and analytical procedures, many species of interest in precipitation can be accurately measured. However, reliable, multi year data records have been generated at relatively few marine locations (e.g. Galloway et al., 1982; Moody et al., 1991; Galloway et al., 1993). In contrast to the accurate measurements of the chemical composition of incident precipitation, quantification of the amount of precipitation that falls is often uncertain. Precipitation in marine regions is sampled on islands, in the coastal zones of continents and from ships at sea. Islands and coastal locations frequently exhibit strong spatial gradients in wet deposition owing to local orographic, heat island and land-sea-breeze effects, and/or other perturbations of local wind fields. In addition, the motion of ships at sea generally precludes reliable water flux measurements. Finally, the water collection efficiencies of gauges vary somewhat as functions of their inlet geometry and wind velocity. Consequently, regional wet deposition fluxes are considerably less certain than corresponding measurements of precipitation composition.

Currently, the most reliable approach for estimating the dry deposition of particles to the ocean surface requires measurements of size-resolved aerosol composition (and inferred density), and the corresponding wind speed, relative humidity and temperature. Deposition fluxes are then calculated based on a model originally developed by Slinn and Slinn (1980), or improved variants thereof (e.g. Williams, 1982; Hummelshøj et al., 1992), which consider gravitational settling, impaction, and Brownian diffusion as a function of particle size both above and within the laminar sublayer at the ocean surface. The generation of such intensive input data is limited to short-term field experiments and, consequently, no long-term data records based on this approach have been produced. There are currently no techniques for accurate direct estimation of dry deposition fluxes. Research is required to improve estimates of dry deposition velocity, as well as to develop novel techniques for direct estimation of dry fluxes (Activities 1.4 and 1.5).

Alternative approaches have been used to infer dry deposition rates from measurements of the chemical composition of aerosol sampled in bulk and “average” or “representative” deposition velocities. However, the dry deposition fluxes of many particulate species of

interest (e.g. NO_3^- , SO_4^{2-} , Fe) are typically dominated by larger aerosol size fractions (e.g. Huebert et al., 1996; Turekian et al., 2001), which vary greatly over space and time. Consequently such approaches are very uncertain. Micrometeorological (e.g. Sievering, 1987) and inferential (e.g. Meyers et al., 1998) techniques have been employed to estimate the dry deposition fluxes of finer-fraction (less than 2 μm diameter) aerosol constituents over continents. To our knowledge, however, such approaches have not been successfully deployed in marine regions, nor have they been extended to the larger aerosol size fractions that typically dominate the dry deposition of many species to the ocean surface. The most reliable estimates of particulate dry deposition in marine regions are uncertain by a factor of at least two and probably more.

Cloud processes

Changes in clouds are also a large uncertainty in global climate predictions, mainly because the relative anthropogenic contribution to the global cloud condensation nuclei (CCN) budget is unknown. Anthropogenic CCN increase cloud droplet concentrations and reduce cloud droplet sizes, compared with natural background CCN concentrations. Material is further transferred within clouds by droplet coalescence. Coalescence rates depend on droplet sizes and concentrations, which are in turn determined by the CCN spectra.

The increased number and reduced size of cloud droplets associated with anthropogenic CCN reduce the efficiency of coalescence and thereby reduces precipitation. The resulting increases in cloudiness and associated albedo have a net cooling effect on global climate. Variability in cloudiness affects boundary layer processes, including air-sea mass and heat exchange and surface ocean photochemistry (Activity 1.2). There is still considerable uncertainty in our understanding of how air-sea exchange affects the development of CCN, including the magnitude of the CCN ocean source and the role of dry and wet CCN deposition.

Within the cloud layer, chemical reactions occur in association with cloud droplets. CCN derived from the sea surface modify the cloud droplet concentrations and hence the cloud albedo, as well as the potential to form precipitation. Precipitation from boundary layer clouds (as well as deep convection and higher cloud layers) acts to scavenge particulates and gases from the sub cloud layers and return them to the sea (Activity 1.1).

Atmospheric heterogeneity and entrainment

Transfer of particulates and gases from the atmospheric boundary layer upward to the free troposphere occurs at atmospheric fronts and in regions of deep convection. At atmospheric fronts, the entire boundary layer may be displaced upward by a denser air mass and so become separated from the sea surface. In deep convection boundary layers, air may be transported to the upper troposphere and detrained at the cloud edges. Both processes tend to be accompanied by precipitation, which may remove particulates and gases.

Entrainment at the top of the atmospheric boundary layer transfers particulates and gases from the free atmosphere downward into the boundary layer. This process is more efficient for a cloud topped boundary layer.

Several scales of horizontal variability exist in the marine atmospheric boundary layer (MABL). The primary transport modes that occur in the MABL are thermals and longitudinal rolls, both of which scale with the depth of the MABL, which is of the order of a kilometre. Thermals are the primary response of the MABL to buoyancy excess at the surface and efficiently mix the MABL through vertically coherent motions that increase in size with height (Lenschow and Stephens, 1980). Longitudinal rolls, quasi-2D counter-rotating roll vortices approximately aligned with the mean wind, are generated by a combination of buoyancy and shear (Etling and Brown, 1993). Both of these coherent structures can generate horizontal variations in the wind vector and scalar concentrations from a few hundred meters to a few kilometres over a horizontally homogeneous surface. In addition, there are mesoscale variations in the MABL generated by a variety of other processes, such as synoptic (weather) disturbances, cloud-driven convection and gravity waves that can generate variations on scales of kilometres to tens of kilometres. Clouds are particularly important since they not only directly generate velocity and scalar fluctuations, but also indirectly affect air-sea exchange through precipitation, changes in radiation exchange, processing of trace gases and aerosols by cloud droplets, and efficient venting of the MABL into the overlying free atmosphere (with compensating input of overlying air into the MABL). Non linear interactions in the atmosphere cause forcing introduced at these scales to cascade down into ever smaller scales giving a spectral continuum down to dissipation scales of a centimetre or less.

As a result, in order to make direct measurements of turbulent transport in the MABL, it is necessary to resolve the turbulent eddies over a wavelength region of a few metres to several hundred metres near the surface. For practical flux measurements, this means averaging lengths of a few kilometres near the surface to a few tens of kilometres in the middle of the MABL. At the other end of the spectrum, it is necessary to resolve eddies as small as a couple of metres near the surface and a couple of decametres in the middle of the MABL.

Major Issues that Require Resolution

- ▶▶ **What is the impact of primary marine aerosol on the chemical composition and physical properties of the marine atmospheric boundary layer?** Measurements of sea spray remain too limited to draw definite conclusions, especially at higher wind speeds. We need to establish the source function for spray, which is currently very uncertain (Andreas and DeCosmo, 1999; Schulz et al., 2003). The most urgent requirement in this context is improved and more extensive measurements of sea spray at higher wind speeds.
- ▶▶ **What are the important chemical and physical interactions in the marine atmospheric boundary layer, such as interaction of particles and gases with clouds?** Aerosols generated at the sea surface may be transported to such a height that they provide CCN, leading to the enhancement of clouds. DMS gas released from the ocean through the sea surface undergoes both chemical transformation and physical transport leading to the enhancement of sulphate aerosol concentrations and CCN (Activity 1.3).
- ▶ **What is required to improve parameterisations of the wave boundary layer?** The MABL differs from its terrestrial counterpart primarily by the presence of surface waves, making the use of terrestrial measurements to infer surface fluxes over the ocean questionable. It is highly desirable to attempt flux measurements in the wave boundary layer to test and improve flux formulations based on observations conducted over land.
- ▶ **Are there significant modifications of the atmospheric boundary layer in coastal regions?** For onshore winds, sea state and wave breaking may be significantly modified by the shallow depth and the effects of tidal currents. Offshore winds may carry particulates and gases

originating from the land out over the ocean. The surf zone provides an immediate source for sea-spray aerosol, available for chemical reactions (Activity 1.1). At the land-ocean interface there will be a significant change in surface roughness and ζ at the coast, and an internal MABL will form within the advected terrestrial boundary layer. Such effects will be significant within the first 10-100 km of the coast, with the effects of the developing sea state extending tens of km or more (Geernaert and Astrup, 1999; Zagar et al., 2003)

Specific Goals

- I. Determine a quantitative algorithm describing the generation of sea spray as a function of wind speed and sea state to within a factor of two, up to wind speeds in excess of 20 m s^{-1} .
- II. Quantify the DMS flux from the surface ocean to the atmosphere and the transport of sulphur compounds through the MABL to permit modelling of temporally and spatially varying generation of CCN from DMS outgassing (with Activity 1.3).
- III. Improve atmospheric surface layer models for gases and conduct coupled ocean-atmospheric boundary layer studies for gases and material.
- IV. Perform studies in the surf zone to an offshore distance of 10-100 km to estimate gradients in sea-spray aerosols, surface roughness, and boundary layer stability. This goal can be achieved through underway airborne or ship transects, and/or a series of platforms.

Promising Approaches and Implementation Strategy

Particle flux approaches

There is still a poor understanding of the mechanism of production of atmospheric sea-salt particles, their distribution and residence times as a function of wind speed, and their role in affecting aerosol radiative forcing and the chemical properties of the marine atmosphere (Activity 1.1). A collection of wind speed dependencies presented by Gong et al (1997) shows concentrations varying by more than an order of magnitude. Direct measurements of fluxes of particles to and from the sea surface are not possible because there is sea-spray production at the

surface as well as deposition of particles of other origins, which current techniques cannot separate with the frequency required for micrometeorological measurements.

Presently used models are based on a combination of laboratory measurements and empirical relations of whitecap coverage (Monahan and O'Muircheartaigh, 1986), or evaluation of the balance between production and removal (Smith et al., 1993), which works only for super-micron droplets. Promising new techniques are aircraft measurements of atmospheric column loading with increasing fetch (Reid et al., 2001), application of transport models (Vignati et al., 2001), direct covariance measurements (Nilsson et al., 2001), and parameterisations based on laboratory experiments (e.g. Mårtensson et al., 2003). Results from these techniques appear to converge to within one order of magnitude. This is similar to bubble size distributions, which are the major source of sea-spray aerosols at moderate wind speeds. Existing source function parameterisations are based on wind speed or friction velocity, with water temperature and atmospheric stratification effects taken into account for whitecap cover and water temperature in laboratory experiments. At elevated wind speeds, production of spume drops by direct tearing of wave tops is, so far, an unresolved issue as regards its importance in relation to bubble-mediated production of sea-salt particles.

Scavenging of atmospheric gases and aerosols to the liquid phase occurs both within and below clouds. If their liquid phase turns into precipitation, wet deposition can occur. The scavenging depends on aerosol size and type, and water availability. Wet deposition fluxes can be estimated from knowledge of rainwater concentrations and precipitation amounts over the ocean. As the latter are not well known, SOLAS will work with GEWEX to improve their estimation. In modelling studies, wet deposition is usually described by a scavenging ratio, which attempts to parameterise the scavenging process. This parameterisation requires improvement or, alternatively, a more fundamental description within models.

Micrometeorological approaches (also see Activity 2.1)

Until recently, only a few atmospheric measurements have been attempted to directly measure air-sea gas fluxes. Earlier attempts to apply micrometeorological techniques to measure air-sea gas flux, particularly CO₂, led to much controversy in estimating even the order of

magnitude of the oceanic flux (Broecker et al., 1986). Because of the lack of confidence in direct flux measurements, parameterisations for air-sea gas exchange were based on indirect techniques, leading to the development of models combining sea surface measurements of concentration with parameterisations for the gas exchange rate. (Liss and Merlivat, 1986; Watson et al., 1991; Wanninkhof, 1992; Wanninkhof and McGillis, 1999; Nightingale et al., 2000a) However, there are no data sets that are adequate to confirm a single relationship for air-sea gas exchange.

Several advances in micrometeorological techniques for gas flux measurements address the concerns related to oceanic applications (Fairall et al., 2000). Advances in atmospheric gradient and covariance measurements have decreased the time scale for flux measurement to sub-hour; this being particularly true for the ocean-atmosphere direct covariance method for CO₂ (Donelan and Drennan, 1995; McGillis et al., 2001b), and the gradient method (Dacey et al., 1999; McGillis et al., 2001a) and direct covariance (Mitchell, 2001) for dimethylsulphide (DMS). Problematic issues for air-sea gas flux measurements by micrometeorological techniques include: (1) contamination of the measurements from motions of mobile measurement platforms such as ships and aircraft, (2) errors from flow distortion induced by flow around the measurement platform, and (3) inadequate gas sensor sensitivity and frequency response. Progress has been made in addressing these problems (Fairall et al., 2000), but considerable work remains.

The most direct method of measuring surface fluxes of atmospheric gases is by the eddy correlation or covariance technique. The flux is given by the average of the instantaneous product of the quantity whose flux is to be measured with the vertical velocity. Although the covariance technique is the standard for measurement of air-sea physical fluxes, there are limitations to its applicability. For example, it may not be possible to measure fluctuations in a trace species with sufficient time response to resolve all the contributions to the flux. One alternative is to measure average differences in the quantity with height, and relate this to the flux by flux-gradient relationships derived from turbulence similarity theory. Other similarity relationships relate variances of scalar quantities to their surface fluxes. A further refinement is to consider only high frequency variances and use the inertial subrange hypothesis to estimate fluxes. This is especially attractive from a ship to obvi-

ate the need to make corrections for lower frequency ship motions. These techniques, described, for example, by Lenschow (1995), rely on empirically determined formulations to estimate the flux.

Another approach to measuring trace species fluxes is to use conditional sampling techniques. In these the species is collected in two or more reservoirs. In the eddy accumulation technique, the species is collected in one reservoir if the vertical velocity is positive, and in another if it is negative, at a rate that is proportional to the magnitude of the velocity. The flux is proportional to the difference in mass between the two reservoirs, divided by the collection time. In relaxed eddy accumulation, the collection rate is held constant, and the flux is proportional to the standard deviation of the vertical velocity multiplied by the concentration difference and a scaling parameter that is empirically determined.

In principle, the above approaches can also be applied to quantify air-sea exchange of aerosols. However, most measurement techniques for aerosol composition as a function of size lack adequate temporal resolution. In addition, super-micron diameter sea-salt aerosols that dominate the particulate deposition fluxes of many species cannot be sampled quantitatively from most aircraft. Consequently, vertical distributions and deposition fluxes of particulate material over the ocean are very poorly constrained.

Atmospheric inverse modelling approaches

Air-sea exchange fluxes of carbon isotopes occur mainly due to the fact that the carbon isotopic compositions of surface ocean waters are not in equilibrium with the atmosphere (surface waters are enriched in ^{13}C in tropical and mid latitude oceans, but depleted in high latitude oceans, relative to the atmospheric compositions). The oceanic isotopic fluxes have previously been estimated from *in situ* atmospheric and oceanic measurements using air-sea gas exchange models and monthly average winds (Wanninkhof, 1992; Wanninkhof and McGillis, 1999; Gruber and Keeling, 2001), or predicted from ocean biogeochemistry models (Heimann and Maier-Reimer, 1996; Murnane and Sarmiento, 2000). The regionally aggregated isotopic fluxes can also be estimated by inverse modelling of atmospheric observations of $^{13}\text{C}/^{12}\text{C}$ ratios of atmospheric CO_2 , which does not require the use of an air-sea gas exchange model. The atmospheric inverse calculations thus provide an independent estimate of the carbon isotopic fluxes and a check on estimates based on oceanic measurements or ocean models.

Atmospheric signals resulting from fine-scale surface fluxes are dispersed and homogenised by diffusion processes (entrainment, synoptic-scale eddies, meridional circulations). The atmosphere integrates surface fluxes in space and time, while persistent spatial and temporal patterns can occur in the atmosphere over a long period of time (e.g. from 1 hour to a season). Atmospheric measurements of CO_2 and other trace gases can be combined with transport (advection and diffusion) modelling to derive their surface fluxes averaged over space and time. Observations and inverse modelling of atmospheric CO_2 transport yield useful information related to the global distribution of terrestrial and oceanic carbon dioxide sources and sinks.

The spatial resolution of an inverse calculation for air-sea exchange is presently limited by spatial coverage. Oceanic and terrestrial biogeochemistry models have been used to prescribe the spatial distribution of surface fluxes at a resolution of about 100 km. The air-sea gas transfer velocity used in an ocean model thus represents an average over a horizontal scale of about 100 km. Understanding of the physical and biological processes controlling air-sea exchange is needed to scale gas exchange measurements on a tower, ship, or other platform to a 100 km grid size.

Global inverse calculations are further limited by transport modelling. The strength of the Hadley Circulation in a GCM, for instance, is dependent on the representation of diabatic processes including radiative transfer, deep convection and its drag on zonal winds. A recent tracer transport model intercomparison revealed that a major transport error is caused by the parameterisation of turbulent mixing in the MABL and entrainment of free tropospheric air into the planetary boundary layer (Denning et al., 1999). Measurements of transport are lacking in the MABL. These should be incorporated into long-term tower or ship based observational programmes. The combination of surface flux measurements and measurements of the MABL height and mixed layer thickness has proved to be the most useful in evaluating planetary boundary layer transport models at some forest sites on land (Bakwin et al., 1990; Davis et al., 1997), and should also be applicable over the sea.

Process study approaches

Process studies should include measurements from a combination of fixed observation sites (e.g. towers) and mobile platforms (e.g. ships and aircraft). The advantages of fixed sites are that long time series can

be obtained over particular locations, corrections for platform motions are not needed, and there are generally less stringent sensor time response requirements. The advantages of mobile platforms are the ability to measure over many different regimes, including remote areas, well behaved turbulence statistics can be obtained in a shorter period of time and averaged over an area, and, in the case of aircraft, the ability to resolve the vertical and horizontal structure throughout the atmospheric boundary layer and above.

Field studies should be conducted on the transport of particulates within the atmospheric boundary layer to determine the degree of turbulence, and hence, the extent to which M-O scaling applies. The relationship between the surface roughness lengths for particulates and the sea state is still unknown. It is generally considered to depend on wave age, but other factors, such as the presence of swell or the mean wave slope, may have a significant effect and should be explored in the field. Rather than classifying measurements only on the basis of the wind speed, it will be important in SOLAS to also determine roughness length and the sea state.

Process studies are needed on transport in the atmosphere from the air-sea interface through the entire atmospheric boundary layer, including entrainment across the boundary layer top, and to cloud-driven mixing and processing (including aerosol production, scavenging and heterogeneous reactions). Organised motions in the MABL, such as longitudinal rolls, cloud-driven mesoscale circulations, and synoptic-scale variations, should be investigated. Measurement campaigns to determine vertical turbulent transports in the atmospheric boundary layer over the ocean should employ DMS as a convenient tracer, because vertical gradients of DMS above the immediate surface boundary layer can now be measured reliably from airplanes (Activity 1.3).

Measurements in high wind speeds should be made using self contained air-deployed sensor technology. LIDAR techniques can be used to study formation of aerosols by breaking waves and surf, and subsequent transport of the aerosol plume in a developing internal boundary layer. Measurements should also include the chemical composition and hygroscopic properties of marine aerosols as a function of size and altitude.

SOLAS process studies should also be conducted in the atmospheric boundary layer of coastal regions. The coastal zone is very heterogeneous and this creates chal-

lenges for sampling its unique physical and biogeochemical properties that SOLAS will need to understand.

Numerical weather prediction (NWP) approaches

NWP models are tested against observations, and parameterisations are tuned to give skilful predictions, providing insight into the parameterisation of air-sea exchange processes. The plans of the European Centre for Medium-Range Weather Forecasts to extend NWP to running real time Earth System Models, with an ocean biogeochemistry component, are a promising avenue of interdisciplinary research and should be encouraged. Integrating satellite ocean colour and aerosol data into NWP is also a key challenge in which SOLAS would be a willing partner.

Integration, Assimilation and Scaling Up in Focus 2: Remote Sensing and Modelling

A major challenge for SOLAS is to integrate and parameterise the small-scale process-oriented studies carried out in Focus 2, such that they can be applied to larger-scale studies and especially in regional and global models used for predicting the future behaviour of the Earth System. The key tools by which this scaling up will be accomplished are remote sensing and modelling for the assimilation and objective mapping of observations to larger scales.

Remote Sensing for Focus 2

Satellite measurements are ideally suited for upscaling information from integrated process studies. Satellites presently can provide measurements of a wide variety of environmental parameters such as precipitation, wind speed and direction, sea state, sea surface temperature, chlorophyll concentration, turbidity, atmospheric aerosols and gases, and eddy energy. Using information from process studies, derived quantities such as types of phytoplankton (e.g. harmful algae blooms, coccolithophores), primary and export productivity, and gas transfer velocities can be estimated. However, their resolution is insufficient to resolve the processes on the smaller scales that control air-sea exchange. Notwithstanding, it is probable that the scales of variability influencing regional gas flux estimates can be captured with satellites. Such satellite measurements also provide a context for point measurements and are crucial for extrapolation from these to regional and global estimates, either through coupled models or empirical parameterisations. Sampling resolution for preferred locations can be improved significantly by using aircraft, geostationary platforms or by combining data from several satellites measuring similar parameters at different overpass times. The acknowledged limitations in quality of remotely sensed measurements, such as wind speeds at extreme low and high values, characterisation of aerosols, depth penetration of optical measurements, and uncertainty in atmospheric correction, are offset by the large quantity of data which allows data assimilation procedures to be applied so as to strengthen models. Satellite-derived data products are improving greatly with the development of new sensors, improved calibration/validation efforts, and a better understanding of the retrieved signals and retrieval techniques. Earth observation with optical instruments which are limited to cloud-free areas are augmented with instruments performing similar measurements with cloud penetration techniques (e.g. active microwave). Novel uses of the remotely acquired information may prove more fruitful than simple use of standard products. New applications are more likely to

occur if field programmes explicitly incorporate remote sensing. For instance, it may be possible to develop local, real time, vicarious calibrations using *in situ* observations in conjunction with several satellite data sets to develop new satellite data products. Additionally, local *in situ* observations may be of use in characterising the variability and biases of the satellite observations, such as winds or SST, in order to provide a statistical basis for carrying out sensitivity studies and probability estimates using remotely sensed data sets.

Remote sensing observations can provide data when *in situ* sampling is not feasible. Remote sensing methods are the only way to sample globally in short time frames. Similarly, they can be used to supplement temporal sampling efforts at fixed sites by providing a spatial context, such as regional variability, to local point measurements. Thus, satellite measurements are critical for extrapolating to global, regional or basin scale analysis or modelling efforts, and complement intensive field programmes.

Empirical relationships are not the only result of coincident field and remote sensing measurements. By using multi-sensor approaches and/or coincident process studies, an improved understanding of controlling parameters and processes is feasible. This results in part from the advantage of expanding the spatial-temporal sampling frame. By obtaining measurements from the interdisciplinary suite of sea viewing sensors, progress can be made to compensate for missing field sampling and identify necessary improvements to the experimental design, as well as to provide insight into additional remote sensors that may be developed for future science support.

Ongoing efforts to quantify air-sea exchange of momentum, heat, gases, biological processes and aerosol distributions using remote sensing measurements should be integrated with field programmes. While most of the satellite sensor requirements of SOLAS have been enunciated through the Ocean and Atmospheric Chemistry Themes of the Integrated Global Observing System (IGOS), there is a requirement to review these plans

as implementation planning for Focus 2 become more detailed. Additionally, it is crucial that communication between the remote sensing and *in situ* communities be explicit to maximise progress. This should include development of potential communication with satellite downlink facilities for collecting high resolution data sets during event-driven air-sea flux processes, such as storms.

Modelling for Focus 2

Modelling specifically for Focus 2 has the dual objectives of scaling up from small-scale process studies, as well as improving the boundary parameterisations used in regional and global-scale coupled climate models. Contemporary coupled 3D climate models transfer information between the oceanic and atmospheric components to determine the air-sea fluxes, but process models concentrate either on the upper ocean with upper boundary fluxes given, or on the lower atmospheric boundary layer with SST and sea state given, in order to calculate air-sea fluxes. Because SOLAS will focus primarily on small-scale processes, there is a need for process-level models that will integrate across the MABL and upper ocean layer. Such models will be used to formulate and evaluate parameterisations, especially for gas and other material fluxes, prior to their incorporation into regional and global 3D models.

The two modelling activities planned specifically for Focus 2 are:

I. Models for Assimilation of Sparse Observations

Process studies and time series stations are limited in space and/or time coverage. As in weather forecasting, assimilative models using satellite and ground observations can be used for optimal estimation of properties over space and/or time. These techniques are already well developed in the WCRP community, but the SOLAS studies will be required to develop the appropriate correlation length and time scales for each biogeochemical variable to be used in the optimal estimation schemes.

II. Coupled Boundary Layer Models (CBLMs)

There is a need for intermediate-scale models to bridge between the process scales of SOLAS observational projects and the regional and global 3D models. In SOLAS, we plan to develop 'test bed' 1D CBLMs, where various parameterisations of air-sea exchange processes can be

developed and evaluated prior to implementation into 3D regional and global-scale coupled models. These CBLM models should consist of generalised oceanic mixed layer models, coupled to atmospheric 'single column' models, extending from the air-sea interface to a height well above the atmospheric boundary layer so that cloud effects and mesoscale convective structures can be included.

A possible oceanic mixed layer module is the General Ocean Turbulence Model (GOTM: <http://www.gotm.net>) developed as a community upper ocean model (Burchard and Bolding, 2001; Burchard, 2002), where different oceanic turbulent mixing schemes (e.g. Mellor-Yamada, PWP, KPP, kappa-epsilon) can be implemented with a simple software switch. A potential atmospheric boundary layer module might be a single column atmospheric model, such as those developed in collaboration with the U.S. National Center for Atmospheric Research (SCCM) and the Canadian Centre for Climate Modelling and Analysis, which have identical (1D) physical processes as in the NCAR CCM and the CCC AGCM (e.g. Lohmann et al., 1999). The Canadian model includes extensive chemistry of sulphur and other climatically important substances.

The two modules need to be coupled by two way transfer of information sufficient to calculate the air-sea fluxes on the time scales required by the exchange processes (of order 10 minutes for the parameterised processes). The GOTM modules do not currently contain gas phase chemistry. So, using CO₂ as an example, dissolved inorganic carbon chemistry, including alkalinity, would have to be built into the model. Similarly, gas flux formulations would have to be incorporated into the air-sea flux transfer module.

Focus 3: Air-Sea Flux of CO₂ and Other Long-lived Radiatively Active Gases

The air-sea CO₂ flux is a key inter-reservoir exchange within the global carbon cycle. The oceans also play an important role in the global budgets of other long-lived radiatively active gases including N₂O and to some extent CH₄. The objective of Focus 3 is to characterise the air-sea flux of these gases and the boundary-layer mechanisms that drive them, in order to assess their sensitivity to variations in environmental forcing.

The ocean acts as a major sink for anthropogenic CO₂, absorbing 25-35% of fossil fuel CO₂ emissions (Prentice et al., 2001). The associated net air to sea flux of CO₂ is controlled by the solubility of CO₂ and the rate at which 'older' deep ocean waters are exposed to an atmosphere with elevated partial pressure of carbon dioxide (pCO₂) relative to preindustrial levels. This 'anthropogenic' flux is superimposed on a geographically and temporally varying pattern of large natural exchanges. These exchanges are determined by a variety of processes, including heating and cooling of surface waters, biological uptake and export of organic carbon from the surface layer, marine biocalcification, and the upwelling of carbon-rich deep waters into the surface layer. In the preindustrial ocean, regions where the net flux of carbon was from the ocean to the atmosphere (source regions) were linked to sink regions by carbon transport carried by sinking particles and ocean circulation. The increasing pCO₂ of the atmosphere since 1750 has tended to increase the air to sea flux in CO₂ sink regions and decrease the sea to air flux in the source regions, leading to increased carbon storage within the ocean.

The local air-sea CO₂ flux can be estimated from measurements of the partial pressure difference across the air-sea interface, assuming that gas exchange is well understood (Activity 2.1). In principle, integration of such local fluxes permits quantitative estimation of atmosphere-ocean fluxes on the global scale, and hence quantification of one of the major inter-reservoir fluxes in the global carbon cycle. This becomes possible with the establishment of a global observing network for sea surface pCO₂, plans for which are developing rapidly. Basic research into the variability of air-sea CO₂ fluxes is urgently required to guide both the design of the global measurement network and the optimal utilization of its

products. Even in the absence of a global network, characterisation of regional-scale variability when combined with atmospheric data and models can be used to reduce uncertainties in both ocean-atmosphere and land-atmosphere CO₂ fluxes (Activity 3.1).

Future changes in ocean temperatures and circulation, nutrient supply and other alterations in biological carbon cycling associated with global change have the potential to alter the anthropogenic and natural components of the air-sea CO₂ flux on regional and global scales. A prerequisite for the prediction, assessment and identification of any such change is the characterisation of the present-day air-sea CO₂ flux and the processes responsible for driving it and its variation. Examination of proxies of surface water pCO₂ in the sediment record can also be used to reveal the sensitivity of air-sea fluxes to climate variations.

In addition, the ocean plays an important role in the global budget of at least two other long-lived, radiatively active gases. Notably, N₂O and CH₄ are both produced within the ocean and released to the atmosphere, where they act as greenhouse gases, as well as participating actively in tropospheric and stratospheric chemical cycling. The air-sea flux of these species may be climate-sensitive, although less field observations exist for these gases than for CO₂, and there have been far fewer process studies that can be used to assess such sensitivity. Studies of trace gases are particularly lacking in coastal ecosystems. These areas are extremely diverse, subject to large exchanges and have extensive zones of very high N₂O and CH₄ production, often enhanced by anthropogenic activities. An understanding of trace gas fluxes in these areas is therefore of high importance.

Activity 3.1 - Geographic and Sub-Decadal Variability of Air-Sea CO₂ Fluxes

The oceans contribute significantly to sub-decadal variability in the growth rate of atmospheric pCO₂.

Introduction

The uptake of anthropogenic CO₂ by the oceans is a global-scale net perturbation of the 'natural' temporal and geographic variability of air-sea CO₂ fluxes. Further, the regional and temporal distribution of CO₂ in the atmosphere is determined by both ocean-atmosphere and land-atmosphere fluxes. Hence, characterisation of ocean-atmosphere CO₂ flux variability is fundamental to the estimation of net CO₂ uptake by the oceans and to the understanding of processes driving atmospheric CO₂ variations.

Increasingly, inverse modelling is being used to infer unknown regional and temporal distributions of carbon sources and sinks at the land and sea surfaces, based on measured atmospheric gradients of the partial pressure of carbon dioxide (pCO₂) and carbon-related properties (e.g. O₂, ¹³C), together with atmospheric transport models. Geographic and temporal distributions of atmospheric pCO₂ (and other carbon-related properties) arising from known fossil fuel emissions are predicted, and the magnitude and regional distribution of ocean and land surface sinks adjusted to match the measured atmospheric distributions. A major goal of such studies, driven partly by international attempts to control carbon emissions, is the characterisation of difficult to measure net carbon fluxes at the land surface. Such approaches suffer inevitable limitations arising from inadequate specification of atmospheric transport and mixing (e.g. Denning et al., 1999), as well as imperfect knowledge of atmospheric distributions. Specification of additional constraints on regional and/or global air-sea fluxes should allow improved definition of the location and magnitude of the land-atmosphere fluxes (Tans et al., 1990; Fan et al., 1998). In order to develop and apply such constraints, detailed information is required not only on the mean air-sea fluxes but also their variability. Specifically, inverse models of atmospheric CO₂ and CO₂-related data will benefit from information concerning regional and temporal (seasonal to decadal) variability of the air-sea flux of CO₂ and carbon-related properties.

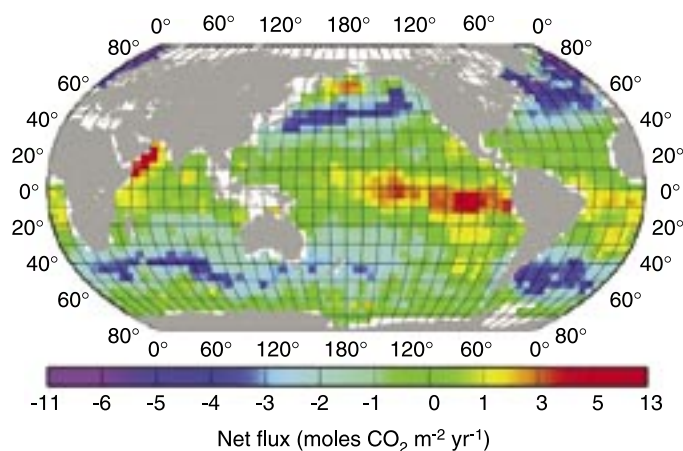
The potential also exists to utilise an increased knowledge of variability in sea surface pCO₂ and CO₂ fluxes to diagnose the sensitivity of coastal and open ocean carbon fluxes to perturbations such as climate change. The variability can be either observed directly (e.g. sub-decadal variability based on time series measurement) or reconstructed on the basis of palaeo records (e.g. ice core data or proxy data recorded in ocean sediments). Presently, there is controversy concerning the relative magnitude of the interannual variability of land-atmosphere and ocean-atmosphere surface fluxes (Rayner and Law, 1999). If the relative oceanic and terrestrial contributions to atmospheric CO₂, ¹³C and O₂ variability can be resolved, the observed sensitivity of land-atmosphere and air-sea carbon fluxes to climate perturbations will become a critical test of the ability of global carbon cycle models to predict future uptake under an altered climate.

State of Present Understanding

Surface water pCO₂ measurements collected over three decades have been extrapolated and interpolated in space and time (Takahashi et al., 2002) to estimate the global distribution of the net flux of CO₂ between the ocean and the atmosphere (Figure 16). Climatologies of seasonal surface water oxygen partial pressures have also been compiled (Najjar and Keeling, 2000). This type of information can contribute directly to quantitative understanding of the contemporary global carbon cycle, including terrestrial biosphere processes, through the provision of constraints for use in atmospheric inversion modelling. However, despite considerable effort, the available surface water pCO₂ data remain sparse with respect to geographical and temporal coverage, and are compromised by variable measurement accuracy among the archived data sets employed. At present, it is necessary to collapse or normalise all extant surface ocean data into one 'virtual year' in order to produce a global map. Even assuming invariant physical and biological controls on surface pCO₂, such a normalisation is non trivial because atmospheric pCO₂ is increasing. The corresponding surface ocean pCO₂ increase may either

parallel, lag behind or even conceivably slightly exceed (Wallace, 2001) the rate of atmospheric $p\text{CO}_2$ increase, depending on the circulation and mixing dynamics of the specific ocean region in question. If surface ocean $p\text{CO}_2$ varies significantly from year to year, the production of such flux climatologies from sparse data becomes even more problematic.

Figure 16. Global climatology of the annual net air-sea CO_2 flux based on interpolation of air-sea $p\text{CO}_2$ differences referenced to the year 1995 (Takahashi et al., 2002). Reprinted with permission from Elsevier Science.



Significant interannual variability as large as 2 PgC yr^{-1} has been observed in the overall rate of increase of atmospheric $p\text{CO}_2$ over the past 40 years. These interannual fluctuations in net CO_2 sinks and sources are comparable in magnitude to the mean accumulation rate of fossil fuel- CO_2 in the atmosphere. There is major ongoing controversy concerning the degree to which such interannual variability is caused by changes in ocean-atmosphere carbon flux, variations in the land-atmosphere flux, or both. Time series studies in the equatorial Pacific Ocean have shown strong interannual variability of the air-sea flux of the order of 0.6 PgC yr^{-1} (Feely et al., 1999). Studies in the Greenland Sea have also shown large year-to-year variations in air-sea CO_2 flux, associated with variable climate forcing and ice cover changes (Skjelvan et al., 1999). However, there are few other extant data sets from regions subject to large net annual air-sea fluxes, including coastal regions, with which to evaluate such flux variability directly.

Time series measurements of atmospheric CO_2 , ^{13}C and O_2/N_2 can, in principle, be used to separate terrestrial and oceanic sources of variability of atmospheric $p\text{CO}_2$. Analyses of such data (Francey et al., 1995; Keeling

et al., 1996; Battle et al., 2000) have apportioned this variability in different ways, but all such studies imply that variability of the ocean-atmosphere flux contributes significantly. On the other hand, ocean modelling studies (Le Quéré et al., 2001) and attempts to extrapolate air-sea flux variability globally (Lee et al., 1998) and regionally (Boutin et al., 1999) imply low ocean-atmosphere flux variability. Terrestrial carbon cycle models appear able to explain all observed atmospheric variability by invoking changes to terrestrial productivity only (Prentice et al., 2001). Resolving such inconsistencies and imposing stricter constraints on carbon cycle models will require continued atmospheric time series measurements of such properties, as well as better understanding of the magnitude and causes of variability in the air-sea flux of CO_2 and carbon-related properties, including O_2 and ^{13}C .

Despite the impressive global picture shown in Figure 16, the relative scarcity of oceanic $p\text{CO}_2$ data, which it hides, together with uncertainty in the gas transfer velocity (Activity 2.1), mean that net flux estimates are currently subject to uncertainties of as much as 50-75% (Takahashi et al., 1997; 1999; 2002). The situation for other important carbon-related tracers (^{13}C , O_2) is no better. A major goal of SOLAS is to reduce this level of uncertainty through better parameterisation of gas exchange (Focus 2) and the collection of quality high resolution surface ocean and atmospheric data. Improvements in both global and regional flux estimates should be pursued; even in the absence of global coverage, regional flux estimates from key ocean regions can be of considerable value as constraints on inverse models.

Major Issues that Require Resolution

- ▶ **What is the magnitude and temporal variability (seasonal, interannual and longer) of the air-sea flux of CO_2 , O_2 and ^{13}C on regional to global scales?** Such information can provide a powerful constraint for carbon cycle models aimed at identifying the global distribution of sources and sinks for atmospheric CO_2 .
- ▶ **Is this observed variability accurately represented in carbon cycle models and what scales of flux variability (space, time) can be detected from the inversion of fixed point atmospheric time series?** Numerical models provide an alternative way to estimate regional

and global-scale air-sea fluxes and their variability. Atmospheric time series of carbon-related properties integrate air-sea flux variability over large temporal and spatial scales. These scales must be defined in order to guide interpretation of time series and optimise the design of future measurement networks.

Specific Goals

- I. Support the establishment of surface ocean and atmosphere carbon observing systems (including associated data assimilation schemes) suited to constraining net annual ocean-atmosphere CO₂ flux at the scale of an ocean basin to less than 0.2 PgC yr⁻¹.
- II. Critically evaluate the performance of prognostic carbon cycle models against field observations of seasonal and interannual variability, in order to guide model development and gain insight into the impact of changed forcing.
- III. Use observation-based estimates of air-sea fluxes and atmospheric inversion models to improve determinations of the magnitude and location of terrestrial carbon sinks.

Promising Approaches and Implementation Strategy

The accuracy of air-sea CO₂ flux estimates is critically dependent on parameterisation of the gas transfer velocity. However at the same time as an effort is made to reduce this uncertainty (Activity 2.1 and 2.3), a concerted effort should also be made to obtain data suitable for assessing geographical and temporal variability of the air-sea CO₂ flux. This objective is within reach using currently available technologies and sampling platforms (see Doney et al., 2002), as well as from the analysis of palaeo records.

It is not the intention of SOLAS to establish a global-scale pCO₂ observing system. Rather, SOLAS will contribute to the design and support of the measurement infrastructure needed for estimating pCO₂ fluxes on basin scales. The basis for such estimates should be basin-scale surveys of the air-sea pCO₂ difference (including measurements in coastal regions). Platforms that can be used for this purpose include volunteer observing ships, time series moorings (e.g. tethered surface buoys and/or sub-surface moorings that are

equipped with near-surface sensor packs) and drifting buoys. The implementation issues associated with this effort have been worked out in several planning documents (see links and references to planning documents at the IOC-SCOR CO₂ Panel website <http://ioc.unesco.org/iocweb/co2panelObsProgs.htm#strategydocs>), including the US-led Large-Scale CO₂ Observing Plan (<http://www.ogp.noaa.gov/mpe/gcc/co2/observingplan/>). SOLAS will ensure that its efforts are integrated with other national, regional and global programs through the International Ocean Carbon Coordination Project (<http://ioc.unesco.org/ioccp>).

The logistical demands of such a measurement programme, including the need for several streams of supporting data such as temperature, salinity and meteorological data, implies that this activity should not be conducted by SOLAS in isolation. Rather SOLAS should, whenever possible, make use of, and share responsibility for, basic infrastructure that exists or is planned under other activities (especially ocean observing system programmes such as GOOS and GCOS). Of particular significance would be linkages to climate and meteorological observation programmes, for example that of the WMO and the IOC JCOMM Ship Observations Team. Many of the supporting parameters required for estimating CO₂ fluxes are measured regularly from JCOMM's global network. This Team is presently developing a pilot project to expand the set of measurements to include certain biogeochemical parameters; SOLAS is a logical partner in this effort. In addition, regular meridional transits by Antarctic supply ships provide valuable opportunities to sample the remote Southern Ocean.

SOLAS can, of course, also establish its own independent measurement platforms, in cases where no suitable sharing of platforms is possible. Any such 'SOLAS-only' platforms should be selected carefully in order to:

- Fill gaps in measurement programmes that are critical for estimating CO₂ fluxes.
- Provide possibilities for synergistic interactions with other SOLAS activities (e.g. support atmospheric chemistry sampling on volunteer observing ship lines).
- Provide a regional and temporal context for SOLAS process studies and campaigns.

Measurements from all such platforms should include pCO₂ in both surface water and the atmosphere. It

should be noted that uncertainty in the difference between bulk mixed layer temperatures and the skin temperature can lead to significant uncertainty in estimates of the air-sea CO₂ flux (Activity 2.1). Hence, simultaneous measurements of skin temperature will be of value for refining flux estimates. The GODAE High Resolution Sea Surface Temperature Pilot Project is developing this capability. Whenever possible, the atmospheric observations should be of sufficient quality to enhance the existing atmospheric observation network. The surveys should also collect data required to calculate oxygen fluxes and, when possible, carbon isotope fluxes. The measurements will have to be interpolated between observing locations and between measurement times. Remote sensing will be a particularly powerful tool for the spatial and temporal interpolation of these surface-layer measurements. Hence, the planned measurement programme should include key supporting variables that will prove useful for the extrapolation and interpolation of pCO₂ data using data assimilation modelling and/or remote sensing (e.g. nutrients, chlorophyll and particulate organic carbon).

Understanding of the biological and physical factors underlying air-sea CO₂ flux variability has benefited greatly in recent years from the interpretation of atmospheric and oceanic time series data, as well as the analysis of palaeo records. At present however, there are few ocean time series located in regions subject to major air-sea CO₂ disequilibrium and consequent large fluxes and, potentially, significant flux variability. SOLAS and other ocean research projects urgently require additional oceanic time series in such regions (e.g. high latitude North Atlantic Ocean, Northern Indian Ocean, Southern Ocean, Equatorial Pacific Ocean and coastal environments, including upwelling regions). The response of surface pCO₂ to large biological and physical forcing fluctuations is recorded within time series of proxy variables in ocean sediments. Detailed examination of these and other palaeo archives can be used to examine linkages between climate, biological processes and surface water pCO₂ over longer time scales. Collaboration with PAGES will be critical to success in this area.

Finally, time series of atmospheric CO₂, O₂/N₂ and ¹³C provide valuable alternative, complementary information concerning air-sea fluxes. Rapid atmospheric transport and mixing implies that these time series integrate the effects of spatially variable fluxes and are, of course, also affected strongly by exchanges with the terrestrial biosphere.

In addition to supporting immediate use of observing systems based on existing technologies, SOLAS should pursue technology developments in order to make observational approaches more efficient, and to address logistical limitations on improved data coverage (e.g. use of autonomous instrumentation). Commercial ships could play a major role in the conduct of SOLAS as they are excellent platforms for sampling both the surface ocean and the lower atmosphere. Conducting science from commercial shipping vessels is not trivial, however, and requires that measurement systems can be rapidly installed, easily maintained and not impact ship's operations. SOLAS should give high priority to the development of robust and compact measurement systems suited for use on volunteer observing ships. This development programme could extend beyond pCO₂ measurement systems to include, for example, compact mass spectrometry systems for carbon isotope analysis, biological/bioptical sensors and water sampling devices. In the longer term, priority should be given to working with the shipping industry on the design of standardised installations that can be built into the next generation of commercial vessels.

The development of improved technologies for fixed point moored measurements and profiling sensor platforms should also be supported. Sensors and measurement systems for the autonomous measurement of near-surface pCO₂ are already commercially available but can certainly be improved. Problems exist with the deployment of such sensors for long periods in the ocean surface layer. These problems include biofouling, as well as risks to near-surface sensors and moorings associated with wave action, ship traffic and ice. SOLAS should encourage further development of methodologies for making long-term autonomous measurements in the oceanic surface layer, and work collaboratively with CLIVAR and others on the design and deployment of near-surface moorings.

At least three main classes of models are relevant to this activity:

- I. Data assimilation into models offers the possibility to combine surface ocean observations, as well as remotely sensed data, with information derived from the model, to extrapolate/interpolate sparse pCO₂ observations in space and time. In principle, this should provide a more comprehensive picture of the air-sea carbon flux distribution. Basic experimental,

statistical and theoretical work is required to develop such approaches. Links to operational oceanography and modelling programmes will be encouraged.

- II. Inverse modelling of atmospheric observations will continue to play a major role in improving our estimates of the contribution of the ocean to variability of atmospheric CO₂. Such modelling should explore the sensitivity of inversions of atmospheric CO₂, O₂/N₂ and ¹³C data to constraints imposed by observation-based estimates of the air-sea flux.
- III. Understanding of the processes governing the air-sea carbon flux should be incorporated into advanced, prognostic, coupled atmosphere-ocean carbon cycle models. These models will ultimately permit the analysis of the effects of future forcing variability on air-sea carbon fluxes. They can be tested and refined through direct comparison with observed variability and against the palaeo record, in cooperation with PAGES.

Activity 3.2 - Surface Layer Carbon Transformations in the Oceans: Sensitivity to Global Change

Carbon transformations within the ocean's surface layer are sensitive to global environmental changes predicted for the next 100 years.

Introduction

The ocean is a large sink for anthropogenic CO₂ due to the partial re-equilibration of surface and interior ocean waters with the increased atmospheric pCO₂ of the industrial era. Most studies and models of anthropogenic CO₂ uptake have treated this uptake as a perturbation superimposed on top of a steady state, natural oceanic carbon distribution. With such approaches, the mechanisms and rates of the processes controlling the natural cycle of carbon in the ocean are assumed to remain unaffected (e.g. Sarmiento et al., 1992). Future changes in ocean circulation and stratification, may strongly affect this anthropogenic perturbation of the air-sea carbon flux (e.g. Sarmiento and Le Quéré, 1996). It remains an open question as to what extent the mechanisms and rates of processes involved in the ocean's natural carbon cycle may also alter as a result of future climate change or other environmental forcing, and whether such changes might significantly affect atmosphere-ocean carbon partitioning. As the coastal oceans are generally net heterotrophic bodies, future alterations in rates of biological processes may affect whether these regions will be net sources or sinks of atmospheric CO₂.

That the natural partitioning of carbon between the atmosphere and the ocean and land is sensitive to climate is clear; the ice core record of atmospheric pCO₂ variation over glacial-interglacial periods shows this unequivocally (Petit et al., 1999). At present, there is no single agreed-upon and comprehensive explanation for these changes. An improved understanding of such dramatic natural changes will help reveal the carbon cycle mechanisms that are sensitive to climate variability, and that need to be evaluated in the context of future change.

An understanding of the mechanisms underlying past change is necessary to guide the research required for prediction of carbon cycle behaviour in the future. However, the future may look quite different from the past. For example, the global-scale climate forcing associated with anthropogenic climate change is potentially more rapid than that which occurred over glacial-interglacial transitions. Further, atmospheric CO₂ has already reached

levels that are unprecedented for the past 15 million years (Prentice et al., 2001). Chemically, this implies an atmosphere-ocean system that is in a state of significantly reduced buffer capacity. The effect of this on the climate sensitivity of air-sea carbon partitioning cannot be assessed straightforwardly. In addition, if climate predictions are correct, the Earth will become significantly warmer in the next few centuries than it has been for at least the past 400,000 years. The glacial-interglacial changes of pCO₂ (peak to peak change of less than 100 ppmv) reflect transitions into climates cooler than present. The maximum atmospheric CO₂ level recorded in ice cores (less than 300 ppmv) are also significantly lower than the present-day level of ~370 ppmv. Hence there is no recent palaeo analogue for a rapid (i.e. decade to century) transition into a significantly warmer, high pCO₂ world.

However, in terms of identifying and understanding the processes responsible for ocean pCO₂ changes, these should be similar now and in the future to those that operated in the past. Thus, although unprecedented system changes are in prospect, palaeo studies offer an important means to identify key processes and develop understanding and models of the operative processes.

State of Present Understanding

The potential for future alteration of the large natural component of the air-sea carbon flux is hard to predict with our current level of understanding of processes or from comparisons with the past. Factors that can drive changes in the partitioning of carbon between the ocean and the atmosphere can be subdivided into two categories: physico-chemically mediated and biologically mediated. The physico-chemical factors are relatively well understood and can already be parameterised in ocean models. They include:

Warming

CO₂ is less soluble in warmer water. Any global warming will tend to increase surface water temperatures and progressively reduce the effectiveness of the ocean sink for CO₂. Temperature changes can also drive biologically mediated effects (see below).

Buffering changes

The ability of surface waters to dissolve anthropogenic CO₂ tends to decrease as more CO₂ is taken up. Future decreases in ocean buffering, associated with higher CO₂ concentrations, will inevitably and significantly decrease the effectiveness of the ocean sink (e.g. Sarmiento et al., 1995).

Sea ice extent

Changes in sea ice extent in the Southern Ocean are hypothesised to have caused large changes in atmospheric pCO₂ over glacial-interglacial time scales through controls on the rate of air-sea exchange (Stephens and Keeling, 2000). A rectification of the biologically driven air-sea carbon flux has been proposed for seasonally ice covered regions associated with the timing of biological production, gas exchange and sea ice cover (Yager et al., 1995). Large-scale changes in ice cover are predicted to occur under global warming scenarios (Houghton et al., 2001) and may even already be observable in the Arctic (e.g. Parkinson et al., 1999). Climate-driven changes in sea-ice extent should therefore be evaluated for their direct and indirect roles in altering future air-sea fluxes (Activity 2.1).

Fresh water input

One of the scenarios emerging from global climate models is that the global water cycle will change considerably both in terms of geographical variations and strength. In addition, there is expected to be an increased melt water flux from ice covered areas. These projections will have a significant effect on ocean circulation, ecosystems and surface water chemistry. The effect of such projections needs to be analysed in terms of changes in air-sea gas exchange. This work will benefit from cooperation with GEWEX and the use of its global data sets.

Windiness/storminess/climate variability

Storms are important in the open ocean for driving exchanges across the air-sea interface (e.g. Bates et al., 2002) and for deepening of near-surface mixed layers. The latter is associated with entrainment of nutrients as well as dissolved inorganic carbon into surface waters. Wind patterns also determine the overall distribution and strength of Ekman pumping and suction, as well as coastal upwelling, therefore controlling additional important vertical transfers of CO₂, nutrients, etc., in and out of the surface mixed layer. To date, climate model projections of future changes in storminess show no clear agreement, although there are suggestions that there may be fewer small extra-tropical storms but a

larger number of larger, stronger storms. Such changes in the frequency and intensity of storm events will have consequences for mixed layer ecosystem dynamics, carbon cycling, and fluxes that should be explored using biogeochemical models.

Natural modes of climate variability have been shown to have strong effects on air-sea CO₂ fluxes (e.g. ENSO and more recently, the North Atlantic Oscillation). Future changes in these modes, associated with climate change, are therefore also likely to impact future atmosphere-ocean fluxes.

Biologically mediated processes

To date, these have generally been viewed as having played little or no direct role in the uptake of anthropogenic CO₂. However Falkowski et al. (1998) list three classes of biologically mediated factors that could alter the future air-sea flux and carbon partitioning:

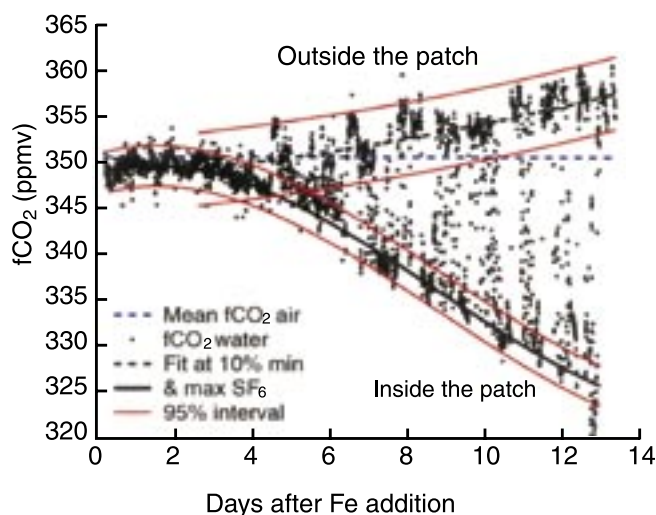
- Changes of nutrient inventories within the ocean;
- Changes in the utilisation efficiency of major nutrients at the ocean surface;
- Changes in the elemental composition of biogenic material sinking from the surface ocean (including the organic carbon to calcium carbonate 'rain ratio' of material exported from the surface layer).

The two main classes of processes operating within the surface ocean that might lead to changes in these factors are:

- I. Changes in the external supply of biologically limiting nutrients (Fe, Si, N and P; see Activities 1.4 and 1.5).

The potential for short-term control on pCO₂ has been dramatically illustrated by iron-enrichment experiments (Figure 17). Alteration of fixed nitrogen supply from internal sources and sinks as a result of *in situ* nitrogen fixation (or denitrification) can also alter nutrient inventories, carbon export and surface water pCO₂. A relationship between nitrogen fixation and external inputs of iron has been hypothesised (Falkowski, 1997) but is contested (Sanudo-Wilhelmy et al., 2001), and has not been experimentally tested (Activity 1.4). Nitrogen fixation in surface waters of the North Pacific Ocean sub-tropical gyre has been suggested to be climate-sensitive (Karl et al., 1997).

Figure 17. Surface water carbon dioxide fugacity ($f\text{CO}_2$) during SOIREE (Watson et al., 2000). Reprinted with permission from Nature, Macmillan Magazines Limited.



II. Changes in surface marine ecosystems can directly affect air-sea CO_2 fluxes.

For example, the distribution of calcareous versus siliceous planktonic organisms may have had significant consequences for surface water alkalinity, pCO_2 and air-sea fluxes in the past (Archer and Maier-Reimer, 1994). Marine ecosystem structure, in turn, is affected by climate-related factors including temperature, cloudiness, nutrient availability, mixed layer physics and sea ice extent. Over the next 100 years, at least two direct forcing changes on surface ocean biogeochemical processes should be considered: increased temperature and decreased pH.

Current IPCC scenarios and coupled atmosphere-ocean climate models lead to mean predicted increases in surface air temperatures of 2.2 to 3 °C over the next 100 years. This implies surface water temperature changes of similar magnitude. In contrast to studies of the terrestrial biosphere, where the effects of warming on plant growth and soil respiration have been extensively studied, there has been remarkably little analysis to date of the potential consequences of systematic warming on surface ocean processes. Laws et al. (2000) found

that the ratio of carbon export to total production in the ocean surface layers varies inversely with ambient temperature. This implies that the “export efficiency” will decrease in response to the expected warming of surface waters. This is consistent with the finding that bacterial growth efficiency decreases and bacterial respiration increases with increasing temperature (Rivkin and Legendre, 2001). Since bacterial respiration represents a large fraction of community respiration, warming of surface waters should result in more rapid near-surface respiration of organic material, consistent with a lowering of export efficiency. Additional research into the response of surface-layer processes to warming, including examination of the response to past climate change recorded in palaeo records, is warranted.

The dissolution of anthropogenic CO_2 in surface seawater since preindustrial times implies that the global average surface water pH has decreased by 0.12 units. A further decrease of 0.25 units will occur during the next century if atmospheric CO_2 concentration rises to 750 ppmv (Figure 18). This downward shift is comparable in magnitude to the full present-day range of surface water pH (7.7 to 8.2). The potential effects on marine ecosystems are not well understood, but are likely to include deleterious effects on calcite and, particularly, aragonite-forming organisms, with potential consequences for surface water alkalinity and pCO_2 . Recent studies with corals and coralline macroalgae have shown that calcification rates are significantly reduced by changes of this magnitude (Gattuso et al., 1998; Langdon et al., 2000; Riebesell et al., 2000). Laboratory experiments carried out on planktonic calcifying microalgae demonstrate that biocalcification rates are also very sensitive to pH changes in these organisms. Initial results suggest that planktonic calcification could decrease by 16–83% for an increase of surface water pCO_2 to 700–800 ppmv (Figure 19). Such changes would represent potentially important feedbacks on oceanic uptake of CO_2 , as well as having significant impacts on oceanic life. Decreases in pH could also, conceivably, have more complex effects, such as increased mobilisation of trace nutrients, with possible implications for biological productivity (Activity 1.4).

To these relatively direct global-scale forcings of temperature and pH, the effects of altered dust deposition on iron and nitrogen limitation and surface ocean biological production can be added. The effects of these climate-related forcings on upper ocean carbon cycling are

discussed in Activities 1.4 and 1.5. There are additional classes of carbon transformations that may respond to climate forcing in more subtle ways. One example is the conversion of dissolved organic carbon (DOC) to particulate organic carbon (POC) that is mediated by aggregation on bubbles. On a global scale, this conversion rate has been estimated to be of the order of

2 PgC yr^{-1} (Monahan and Dam, 2001). This physical/chemical process, which may in turn affect the lifetime of DOC in the surface ocean and the overall rate of microbial respiration, is potentially sensitive to the frequency of storms and the process of wave breaking and bubble formation (Focus 2). The overall significance of such a process on large-scale carbon cycling is presently

Figure 18. Equilibrium seawater pH for equilibration with various atmospheric pCO_2 levels, including levels characteristic of glacial periods. The calculations assume no changes in surface alkalinity. Also shown are summer time pH values from the North Atlantic Ocean, calculated from measurements made during the Transient Tracers in the Ocean expeditions in the early 1980s (small circles). Image: D. Wallace.

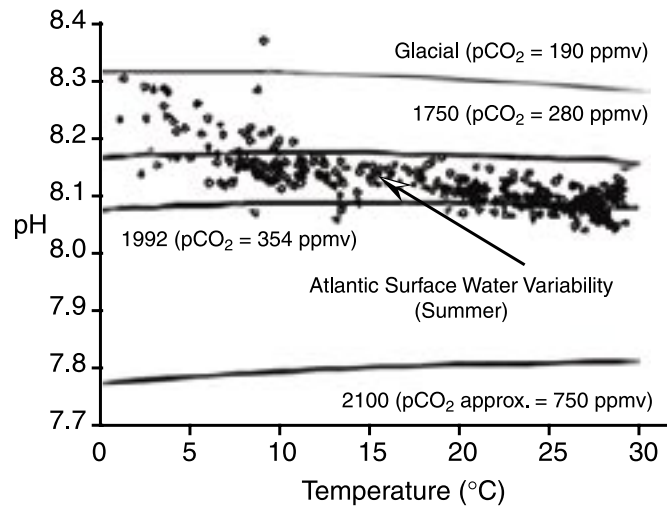
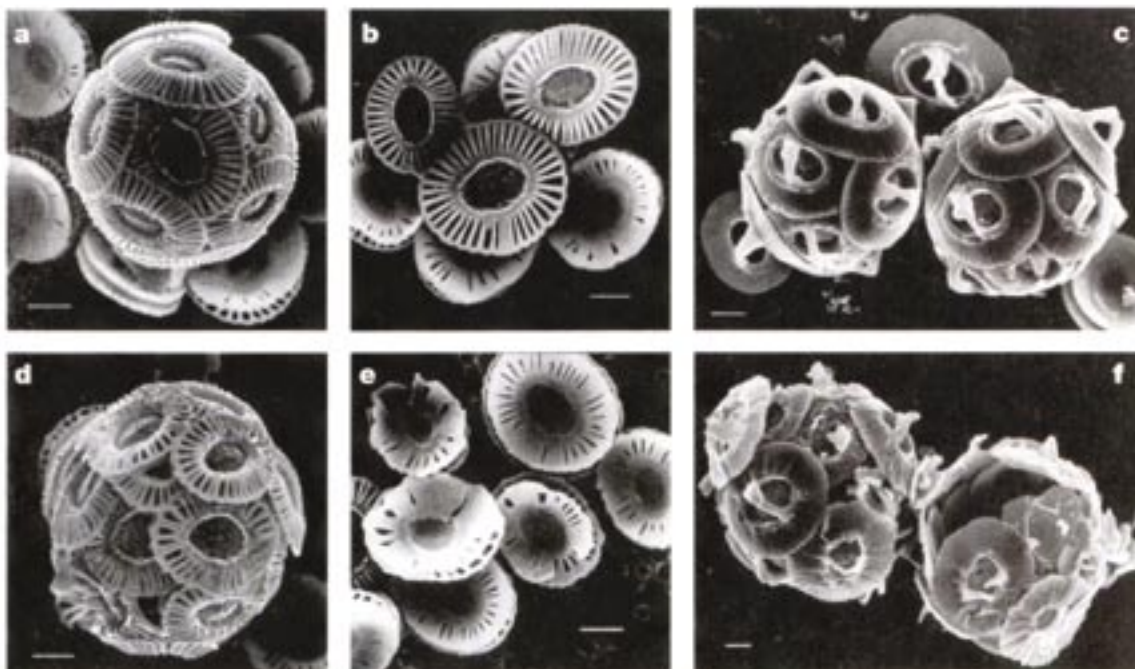


Figure 19. Scanning electron microscope pictures of coccolithophorids grown under low and high CO_2 conditions, corresponding to pCO_2 levels of about 300 ppmv (a-c) and 780-850 ppmv (d-f). Note the difference in the coccolith structure (including malformations) and in the degree of calcification of cells grown at normal and elevated CO_2 levels (Riebesell et al., 2000). Reprinted with permission from Nature, Macmillan Magazines Limited.



unclear, implying a need for basic experimentation, but also a consideration of the role of such small-scale and intermittent processes at larger scales.

The integrated effect of such mechanisms on the net air-sea CO₂ flux and ocean carbon sequestration is a very complex scientific issue involving many research areas (e.g. deep ocean circulation, sub-surface remineralisation, top down controls on ecosystem structure, interactions and biogeochemical dynamics in coastal zones and global ocean carbon cycle modelling). Many of these research areas are beyond the scope of SOLAS alone, as summarised in the statement of its goal and domains in the Introduction. This implies that study of the effects of such processes on global carbon budgets, the associated modelling studies, and other activities will not necessarily be conducted directly or entirely as part of SOLAS, but rather under the auspices of or in association with other projects/programmes. Nevertheless, the special focus of SOLAS on the surface ocean

and processes operating therein can be harnessed to address several key processes (or aspects thereof) that are relevant to the larger carbon cycle questions. Examples of potential SOLAS contributions to process-oriented carbon cycle science are presented in Table 1.

Major Issues that Require Resolution

- ▶▶ **What is the sensitivity of surface ocean carbon cycling and the air-sea carbon flux to the large changes in carbonate system speciation, temperature, and sea ice cover that are projected to occur over the next 100 years?** Significant changes in oceanic and coastal biocalcification rates, and hence surface alkalinity, appear possible based on recent experimental findings and may act as a negative feedback on future atmospheric CO₂ levels. Possible climate-driven changes in surface ocean ecosystem processes are at present poorly understood and quantified. Basic research into these processes can guide the

Table 1. Key carbon transformations that take place in the ocean surface layer, together with their forcing sensitivity and the extent to which study of these transformations is compatible with the overall SOLAS goal.

Surface-Layer Carbon Transformation/Transport	Relevant Forcing	SOLAS Role	Programme Links
Calcification/PIC export	pH, temperature, ecosystem	Major	IMBER, GCP, LOICZ, PAGES
Air-sea CO ₂ flux	Temperature, pCO ₂ , wind/wave, ice	Major	IMBER, CLIVAR, WGSF, WGCM, CLIC, GCP, LOICZ
Food chain C transfer	Ecosystem	Minor	IMBER, GLOBEC, GCP
River-ocean flux	River	Minor	LOICZ, GCP
Carbon fixation, respiration, export	Temperature, ice, dust, ecosystem, river, circulation	Shared	IMBER, GLOBEC, CLIVAR, GCP, LOICZ
POC-DOC conversion	Wind/wave, aggregation, ecosystem	Shared	IMBER, GCP, LOICZ
Continental shelf C cycling	Wind, atmospheric deposition, temperature, [O ₂], ice, ecosystem, riverine input, upwelling	Shared	LOICZ, IMBER, GCP

development of parameterisations of such effects for use in ocean carbon cycle models.

Specific Goals

- I. Design and conduct experiments (in cooperation with Activities 1.4 and 1.5) to address the effect of altered atmospheric dust supply on surface water pCO₂, N₂-fixation and export production.
- II. Conduct experiments to examine the effect of future pH changes on surface ocean carbon cycling, particularly biocalcification.
- III. Determine the sensitivity of upper ocean carbon cycling pathways and net fluxes to projected changes in surface water temperature using experimental, field and modelling studies.
- IV. Examine, using models and time series field observations, the effects of projected changes of fresh water input, wind stress, and ice cover on upper ocean carbon cycling and air-sea CO₂ fluxes.

Promising Approaches and Implementation Strategy

These important issues need to be tackled by a combination of field and laboratory experimental studies and modelling. In many cases, the basic physiological and mechanistic basis for assessing global change effects is incomplete. The studies of temperature effects on export and bacterial respiration cited above illustrate the importance of the synthesis of experimental and field data. Some possible experimental approaches have been discussed in Focus 1. For example, with respect to the role of iron, there is a need for improved basic understanding of the effects of iron supply on the physiology of marine organisms, species succession, etc. This can be attained through a combined programme of laboratory investigation and field iron-fertilisation experiments (pulse or continuous) in key areas (e.g. in oligotrophic or HNLC areas). Alternatively, plumes of iron-rich waters “down-stream” of islands located in the deep ocean could, for example, be exploited as natural laboratories.

With respect to the supply of major nutrients, laboratory and field investigations are required into poorly understood factors such as the magnitude and controls of N fixation, and the role of P, N and Si limitation in determining surface ocean ecosystem structure, species

composition, functional types and their respective C:N:P ratios. A combination of oceanic time series studies, together with controlled perturbation experiments in the laboratory (e.g. mesocosms) and the field, has the potential to advance knowledge in these important areas. It is highly desirable that CO₂ measurements are included in these experiments, particularly in concert with Activities 1.4 and 1.5, and should also include consideration of export of carbon out of the bio-reactive zone (sedimentation). Close links to IMBER and LOICZ will be of value for addressing these questions.

With respect to the effect of decreasing surface ocean pH, there is a need for additional physiological and experimental study of the response of key calcifying species to changes in pH. The possibility that organisms may be able to adapt to such changes in the longer term should be investigated. At larger scales, the relationship between the production and export of organic carbon and the products of biocalcification must be better understood. For example, mesocosm experiments can be used to investigate whether pCO₂ increases trigger systematic changes in community composition, including changes in the ratio of organic carbon production to biocalcification. It may even be possible to conduct such studies at larger scales in the open ocean by, for example, deliberately manipulating the surface ocean pH within an eddy through CO₂ or acid addition. It may be possible to utilise coastal upwelling regions that have a large pCO₂ range (200-700 ppmv) as natural laboratories in this context.

The general approach is to encourage small-scale process studies and experiments in laboratories or/and in mesocosms, and link these studies to larger scales by modelling and field-scale experimentation. The combined approach should allow us to assess potentially important feedbacks on atmospheric CO₂ and provide a basis for modelling such effects in order to assess their global significance. SOLAS can be of particular value by promoting 1) coordination and guidance of small-scale experimental teams; and 2) multi investigator experiments in mesocosms.

Understanding of processes gained in such laboratory and field studies should be translated whenever possible into parameterisations suited to incorporation into numerical models. In this way knowledge gained from SOLAS experimental research can be used to assess the magnitude of effects of surface ocean process changes on overall within-ocean and atmosphere-ocean carbon cycling.

Activity 3.3 - Air-Sea Flux of N₂O and CH₄

The sea to air fluxes of N₂O and CH₄ are sensitive to climate forcing, as well as to human-induced changes in the coastal zone.

Introduction

Nitrous oxide (N₂O) significantly influences, both directly and indirectly, the Earth's climate. In the troposphere it acts as a major greenhouse gas, and in the stratosphere it is also the main source for NO radicals, which are involved in ozone reaction cycles. Present day as well as palaeo records of tropospheric N₂O show significant long and short term variability that is not yet fully explained (e.g. Flückiger et al., 1999).

Atmospheric methane (CH₄) is a major greenhouse gas that also plays an important role in controlling the abundance of the hydroxyl radical. Ocean surface waters are generally supersaturated with CH₄, for reasons that are still not well understood. Presently, the world ocean appears to be a relatively modest natural source of CH₄ to the atmosphere (Lelieveld et al., 1998).

State of Present Understanding

Source estimates indicate that the ocean plays a significant role in the global budget of atmospheric N₂O (Khalil and Rasmussen, 1992; Bouwman et al., 1995; Nevison et al., 1995). Of the global oceanic source, estuaries, coastal upwelling regions and continental shelves cover only a small part of the ocean area yet are assigned 15-60% of oceanic N₂O emissions in various studies (Bange et al., 1996; Seitzinger and Kroeze, 1998; Naqvi et al., 2000). Additionally, N₂O emissions from the Southern Ocean might have been considerably underestimated in previous studies, as suggested by Bouwman et al. (1995). Hence, estimates of even the long-term mean N₂O source from the ocean are still considerably uncertain in spatial and temporal terms (Bouwman et al., 1995).

The pathways of formation and consumption of N₂O in the oxygenated ocean and their sensitivity to changes in environmental forcing also remain poorly understood. Sources of N₂O in the water column include shallow sources (e.g. base of the euphotic zone) associated with bacterial nitrification (Dore and Karl, 1996; Dore et al., 1998), as well as deeper sources associated with nitrifica-

tion and (in proximity to suboxic waters) denitrification (Codispoti et al., 1992). The two formation mechanisms may differ with respect to their sensitivity to climate perturbations. Karl (1999) has recently suggested that the effects of climate variability on the ecosystem of the North Pacific Ocean subtropical gyre might lead to enhanced N₂O emissions, thus suggesting a conceptual framework for an open ocean-atmosphere feedback mediated by N₂O. The air-sea flux of N₂O from coastal waters, estuaries and marginal seas may also be climate sensitive, conceivably via changes in nitrification and denitrification pathways. In this regard, climate change impacts may be particularly strong in coastal systems associated with changes in several compounding variables (sea level rise, changes in riverine inputs, storms and other episodic events). To this should be added the idea that human intervention, through sewage and other discharges to coastal waters has already increased N₂O production (e.g. along the western seaboard of India, Naqvi et al., 2000); an effect that is certain to increase in future with further coastal urbanisation.

A particularly powerful tool in resolving issues concerning the tropospheric budget of N₂O is its stable isotope composition (Kim and Craig, 1990), including, most recently, its "isotopomeric" composition (i.e. the intramolecular position of ¹⁵N in the linear NNO molecule, Yoshida and Toyoda, 2000). Such tools have the potential to resolve ocean, terrestrial and stratospheric contributions to global budgets, as well as, within the ocean, to help identify the specific mechanisms responsible for N₂O production.

With respect to CH₄, less productive open ocean areas presently make a small contribution to overall oceanic emissions, whereas biologically productive regions (e.g. estuaries and coastal areas) appear responsible for approximately 75% of the total oceanic CH₄ emissions (Bange et al., 1994; Bates et al., 1996; Upstill-Goddard et al., 2000). Despite microbial CH₄ production (i.e. methanogenesis) being possible only under anoxic conditions, the results of several studies have indicated that the well oxygenated surface layer of the open ocean can be

enriched considerably with dissolved CH₄ (see overview by Bange et al., 1994). Diffusion and mixing processes could generally be excluded as CH₄ sources, and various *in situ* CH₄ production mechanisms have been proposed, such as CH₄ formation during zooplankton grazing (De Angelis and Lee, 1994), or CH₄ formation in anoxic microenvironments within particles (Karl and Tilbrook, 1994). However, no mechanism is yet able to fully explain the so called “oceanic methane paradox” of CH₄ accumulation in the fully oxygenated ocean surface layer.

In summary, basic information required to resolve the tropospheric budgets of both of these gases is lacking. Further, the controls on N₂O and CH₄ surface water concentrations remain poorly understood. A close interaction is required between Activity 1.5 and this Activity.

Major Issues that Require Resolution

- ▶ **What are the key factors determining the abundance and variability of N₂O and CH₄ in the ocean surface layer and hence their sea to air fluxes?** It will be necessary to resolve the relative roles of physico-chemical processes (e.g. solubility changes, diffusion, mixing, air-sea exchange) and biological processes (e.g. nitrification, denitrification, methanogenesis, methane oxidation, species composition changes). Are there additional, presently unrecognised, processes that may contribute to N₂O and CH₄ formation or consumption in the surface ocean (e.g. assimilatory nitrate reduction, N₂ fixation)? Such considerations will allow the possibility of significant ocean-atmosphere feedback mechanisms operating via N₂O exchanges to be assessed.
- ▶ **What are the effects of eutrophication and other human-induced changes in the coastal zone on the emissions of N₂O and CH₄?** This is an area of growing concern in highly developed coastal regions (Naqvi et al., 2000). Specific attention should focus on whether coastal environments are adequately represented in current global budgets of N₂O, including whether the stable isotopic composition of N₂O in coastal waters matches that of the open ocean surface layer.

Specific Goals

- I. Determine the contribution of oceanic emissions, particularly from coastal regimes, to the global N₂O budget.
- II. Improve understanding of factors regulating surface saturation of N₂O and CH₄, including assessment of sensitivity to climate change and anthropogenic riverine input.

Promising Approaches and Implementation Strategy

SOLAS should utilise a mixture of time series studies, *in situ* rate measurements and experimental investigations in order to examine the key factors controlling the air-sea flux of these compounds. The application of modern biological methods, including molecular techniques, as well as advances in isotope geochemistry has the potential to provide considerable new insight.

Specifically, Activity 3.3 will be focused on studies in coastal regions (in collaboration with LOICZ) where upwelling occurs and well developed O₂ minimum zones are reaching the point of anoxia. Other major regions where N₂O is released are in open ocean upwelling systems. In order to get a complete global budget of fluxes of N₂O and CH₄ and the mechanism that control release of these components into the atmosphere from the ocean, SOLAS should collaborate with the IMBER and GLOBEC projects for studies on deep open ocean denitrification regions down to the required depth, normally 1000 metres.

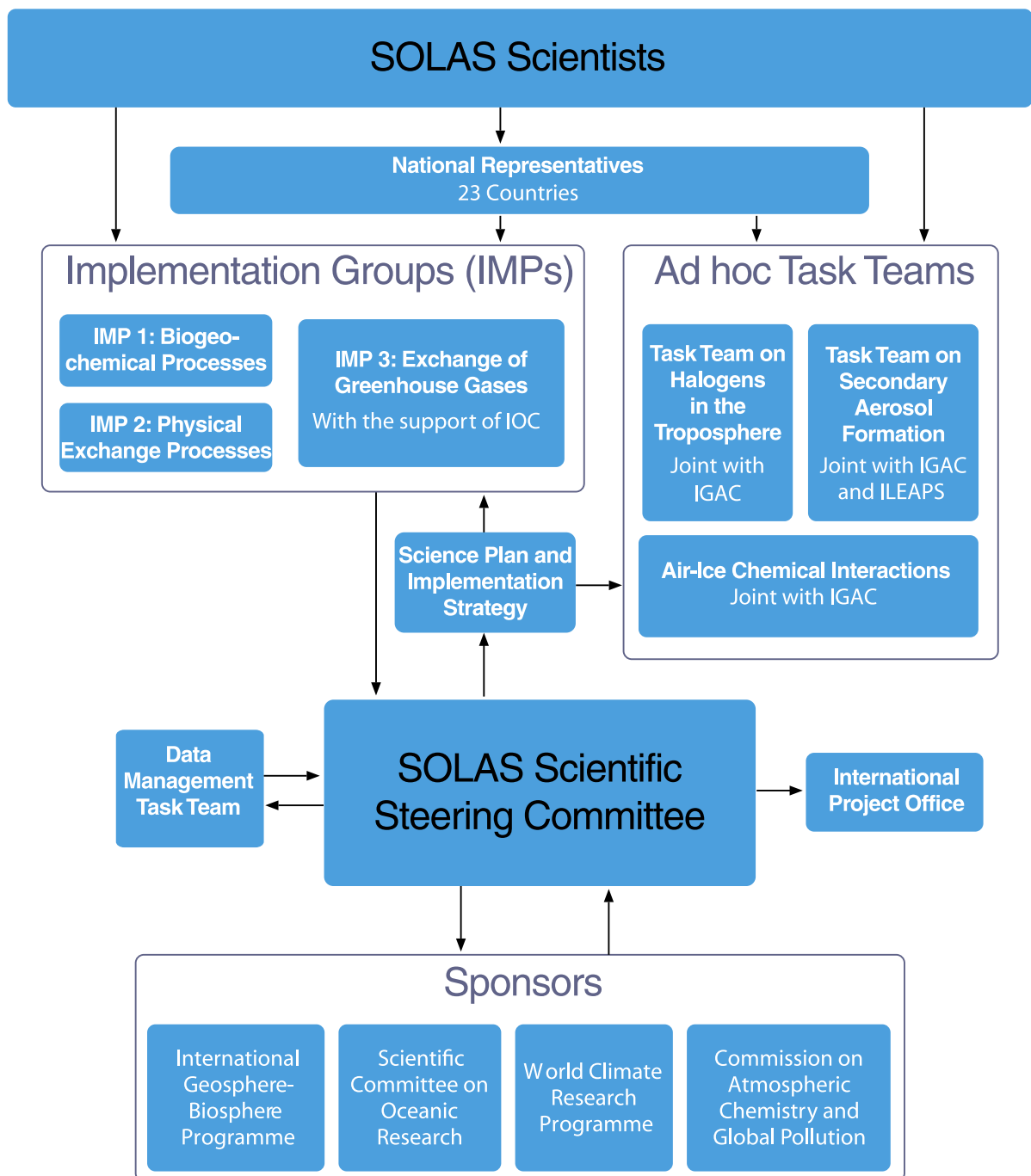
Within the context of these time series studies, research into processes and metabolism should be conducted to identify and quantitatively characterise production and removal processes, including identification of the organisms and metabolisms involved. Use of molecular probes will help in identifying the role of specific microorganisms in the cycling of such gases in the ocean. As described for previous Activities, in addition to field-based process studies, controlled laboratory and mesocosm experiments can be used to evaluate the influence of specific environmental factors on rates of N₂O and CH₄ production and degradation.

Considerable information concerning budgets and production/removal processes can be extracted from the stable isotope composition of N₂O and CH₄. Hence, whenever possible, the *in situ* and experimental studies should include measurements of stable isotope signatures. In the case of N₂O, the isotopomeric composition should be characterised. In support of such isotopic studies there is likely to be a need for additional basic experimental characterisation of fractionation factors as well as reference materials and inter calibration of stable isotope measurements.

Project Organisation and Management

Organisational Structure of SOLAS

Figure 20. The organisational structure of SOLAS.



Scientific Steering Committee

The SOLAS Scientific Steering Committee (SSC) is responsible for providing scientific guidance to, and overseeing the development, planning and implementation of the SOLAS project, including communication of ongoing SOLAS activities and fostering the publication and dissemination of SOLAS results. The SOLAS SSC will encourage national governments, and regional and international funding agencies to support the implementation of core research and the achievement of SOLAS goals through the provision of adequate support at national, regional and international levels. The SSC will also encourage collaboration between SOLAS research and relevant activities of the sponsors and others, including integration with adjacent IGBP, SCOR, CACGP and WCRP projects.

International Project Office

The International Project Office (IPO) serves as the secretariat for SOLAS, and administers the project on a day to day basis. The IPO is responsible for assisting the SSC in all aspects of its work, and collates and communicates information related to national and international SOLAS research. The IPO works with the sponsors to secure resources for SOLAS as an umbrella organisation. It also ensures effective coordination with other activities of the sponsors and supports a data management and archiving system for the project. It is considering the possibility of a shared data management system with other projects.

The IPO will also keep a record of SOLAS products, namely:

- Synthesis and review papers
- Workshop reports
- Books
- Special journal editions
- Data and model output and code

These will be made freely available on the SOLAS website, wherever possible.

The IPO is located in the UK and is funded by the Natural Environment Research Council.

National Contacts and Committees

SOLAS National Contacts and Committees have an important role to play in planning and facilitating the research of the programme. They can coordinate the scientific and communication activities within their countries, as well as acting as the interface between the SOLAS SSC and the scientists and funders in individual nations. For example, a meeting of national representatives was held in Amsterdam 11-12 June 2002 to enable them to participate in the production of this SOLAS Science Plan and Implementation Strategy.

The meeting was attended by representatives of 19 countries, with each nation submitting a written report. Updated national reports are available on the SOLAS website. At the meeting, an informal questionnaire recorded each nation's level of interest in the various SOLAS Activities. The results for 19 country representatives are shown in Table 2. This information should be treated as indicative rather than conclusive, since it reflects the situation at that time and will go out of date rather rapidly, as well as being the assessment of only a small number of people (in some cases only one) from each nation. However, it proved useful at the meeting in identifying areas of SOLAS research where there was good potential coverage globally and, more importantly, activities where resources are currently lacking. It is the intention of the SOLAS SSC to encourage regular two way communication with national committees and contact information is provided on the SOLAS website.

SOLAS national representatives will be appointed in collaboration with the national committees of the sponsors, where appropriate. The IPO should be contacted for further details.

Implementation Groups and Task Teams

Implementation of much of the research described in this Plan will be done through a number of Task Teams and Implementation Groups, for shorter and longer-term activities, respectively.

Task teams will be established on particular topics for which there is a clear need for international coordination. They will often be established jointly with other projects to allow the full scope of the topic to be covered.

SOLAS Implementation Groups will be the key way in which SOLAS will coordinate and plan the implementation of the science described in this document. The Implementation Groups will produce detailed Implementation Plans that will be updated and revised periodically. Each group will work closely with the SOLAS Data Management Task Team (DMTT) to enunciate its needs in terms of data management and quality assurance and control. The membership of these groups will contain modelling and data management expertise, as well as links to partner projects of SOLAS.

SOLAS will also play a full role in the WCRP working group on surface fluxes (WGSF). This is in part a continuation of the previous SCOR/WCRP group on air-sea fluxes of physical quantities (energy, heat, momentum), but with the inclusion of mass fluxes (gases, sea salt, particles, precipitation). Its work will support the research in SOLAS Focus 2 particularly, but also in other parts of the programme, as well as several activities of WCRP.

Table 2. Nations' levels of interest in SOLAS activities in 2002. Higher numbers indicate a greater interest in the Activity.

	1.1 Sea-salt Particle Formation and Transformations	1.2 Trace Gas Emissions	1.3 Dimethylsulphide and Climate	1.4 Iron and Marine Productivity	1.5 Cycling of Nitrogen	2.1 Air-Sea Interface	2.2 Oceanic Boundary Layer	2.3 Atmospheric Boundary Layer	3.1 Air-Sea CO ₂ Fluxes	3.2 Surface Layer Carbon	3.3 Air-Sea Flux of N ₂ O and CH ₄	Modelling	Remote Sensing	Time Series
Australia/NZ	1	1	3	3	1	3	3	1	3	2	2	3	2	3
Belgium	0	0	2	3	0	1	2	0	3	3	0	3	1	0
Brazil	1	1	1	1	1	3	3	3	3	1	1	3	1	3
Canada	3	3	3	3	2	3	3	2	3	1	1	3	3	3
Chile	0	0	0	0	2	0	3	2	3	0	2	0	0	0
China (Beijing)	3	3	3	3	1	3	2	2	3	2	3	3	2	3
China (Taipei)	0	2	0	3	0	3	3	1	3	0	0	3	3	3
France	1	2	3	3	2	1	2	1	3	3	1	3	3	3
Germany	2	3	2	3	3	2	1	2	2	3	2	3	3	2
Japan	2	2	3	3	3	2	1	1	2	2	3	2	2	3
Korea	1	1	2	3	2	1	2	1	2	2	1	2	3	1
Netherlands	3	1	3	3	1	3	1	2	3	1	1	1	3	1
Norway	2	2	3	3	2	3	3	3	3	3	1	3	3	3
Russia	2	0	2	1	0	3	3	3	2	2	1	2	1	3
Spain	1	1	3	3	3	1	1	1	3	2	1	1	2	3
Sweden	0	3	3	3	0	0	0	0	0	3	0	0	0	0
United Kingdom	2	3	3	3	2	2	2	2	3	2	1	3	1	1
United States	2	2	2	3	2	3	2	2	2	3	1	3	3	3
India	1	3	3	0	3	2	3	2	3	3	3	2	2	3
MODE	2	3	3	3	2	3	2.3	2	3	2	1	3	3	3

Data and Model Output Management

Background and Needs

The implementation of SOLAS will involve the collection of large quantities of environmental data by both nationally and internationally organised projects. These data will be collected from process studies and experiments (field and laboratory), time series studies, and large-scale surveys. Similarly, SOLAS will make use of a hierarchy of different modelling approaches. In most cases, the utility of the models and data involved in these projects will extend beyond the projects themselves and be of interest to other investigators. Further, many SOLAS data will be more useful when combined with, or compared against, other data and models, including non-SOLAS data. Scientific findings and conclusions derived from SOLAS projects should be available for assessment by independent scientists: this implies that the underlying data and/or models must be readily accessible.

Increasingly, key management issues are based on model results as well as data. Model-derived results are also used extensively as input for other models, for scientific planning and for policy decisions. SOLAS must therefore ensure that the models developed and/or used in SOLAS research, as well as the data collected, are documented sufficiently to allow independent evaluation and be readily accessible to the scientific community for assessment and interpretative purposes.

Data and model management are therefore critical logistical tasks for SOLAS and we recognise that there are significant challenges ahead: effective data management is a global problem and SOLAS will make strenuous efforts to adopt best practice and learn from past experiences (e.g. WOCE, JGOFS etc.).

SOLAS science will involve collection of complex and sophisticated data sets. This will include difficult, error-prone measurement of biological, physical and chemical parameters. Because SOLAS is an international, multi investigator programme, such measurements will be made all over the world, at different times, by different groups, often using different equipment and techniques.

Attention to data quality management will be critical for the scientific integrity and success of SOLAS.

Data Management Principles

Certain basic principles should guide the development of data management procedures in SOLAS:

- Do not 'reinvent the wheel'; use existing knowledge and infrastructure, wherever appropriate.
- Use internationally agreed standards and protocols (e.g. those of ISO, W3C, IOC/ICES), wherever possible.
- Work with other projects towards an integrated data management system and policy.
- Plan ahead for rapid data assembly.
- Data managers should support data gatherers.
- SOLAS should reward excellence in data collection and data release.
- Participation in SOLAS research requires submission of data to a SOLAS-approved database or centre.

Specific Steps Towards Data Management

SOLAS will establish an international data management task team with at least one staff member. This team should:

- Evaluate and document the likely data needs of SOLAS (data types, quantities and sources, metadata requirements).
- Conduct a review and have intense discussions with the WCRP (WOCE/CLIVAR) and IGBP/SCOR (JGOFS, IMBER, GLOBEC, LOICZ, GEOHAB) data management communities concerning lessons learned and present data management policies, problems and solutions. Identify the potential for SOLAS data management within existing structures and programmes.

- Host a workshop for the modelling community in order to develop and write a practical model management and documentation plan.
- Evaluate together with other programmes the feasibility and benefits of establishing a peer reviewed 'Journal of Global Change Data' and participate in constructing the IGBP Global Change Atlas.
- Write a detailed SOLAS data management policy. This policy is to include time limits, enforcement procedures, access rights, meta-data requirements, reporting requirements and procedures, data quality and archiving, and linkages to data agencies. Potentially, this document will include guides to model description and data organisation.
- Initiate negotiations with data centres about possibilities for their direct support of individual PIs with respect to data management procedures and tools.

Data Quality Management

In addition to establishing clear guidelines for data management, SOLAS must also establish procedures for assessing and controlling data quality. Once again, lessons learned during WOCE and JGOFS can be used to help address such issues.

Data quality management should be addressed by the Data Management Task Team by:

- establishing clear quality targets for SOLAS data;
- documenting recommended protocols for 'standard' SOLAS measurements;
- providing support for technical workshops, training sessions and calibration and intercalibration activities.

Recognition of Research by SOLAS

The aim of SOLAS is to provide a framework to encourage the fullest participation of multi national, regional, and national efforts in its scientific activities. It does not impose a rigid template on the nature of these efforts. However, some recognition procedure (often called “endorsement”) is necessary so that (1) the SOLAS SSC knows what research is being conducted under the SOLAS label, (2) research carrying the SOLAS label is within the science areas defined in the SOLAS Science Plan and Implementation Strategy, and (3) such research conforms to the scientific principles outlined in this plan.

Principle Investigators and national/regional groups can submit their projects for approval by the SOLAS SSC on the SOLAS website.

Flowing from recognition as a SOLAS project are the following benefits and responsibilities; they are only intended as a guide and are not a set of regulations. They have been adapted from the practice of the GLOBEC SSC.

Benefits

- Provides the opportunity for participation in the development, planning and implementation of a collaborative international science programme.
- Adds to the scientific value of planned work by providing complementary information; for example, by widening the range of studies and extending their spatial and temporal coverage.
- Promotes rapid communication of ideas and results through meetings and publications.
- Develops and tests standard methods and protocols for measuring variables, thereby facilitating quality control and meaningful data sharing.
- Makes available data sets collected in component studies and develops a common data policy.
- Enables close working links with other relevant international programmes and studies.
- Gives the opportunity for participation in model intercomparisons.

Responsibilities

- Acceptance of general principles and goals outlined in the SOLAS Science Plan and Implementation Strategy.
- Carry out a programme in general accordance with relevant aspects of the SOLAS Science Plan and Implementation Strategy.
- Participation in the activities of the programme through its management bodies, and by assisting in its planning and development as a whole.
- Make data collected within the programme available to the wider community, in accordance with the SOLAS data policy.
- Acknowledge links with SOLAS in the products of the project (e.g. acknowledgment in scientific papers).

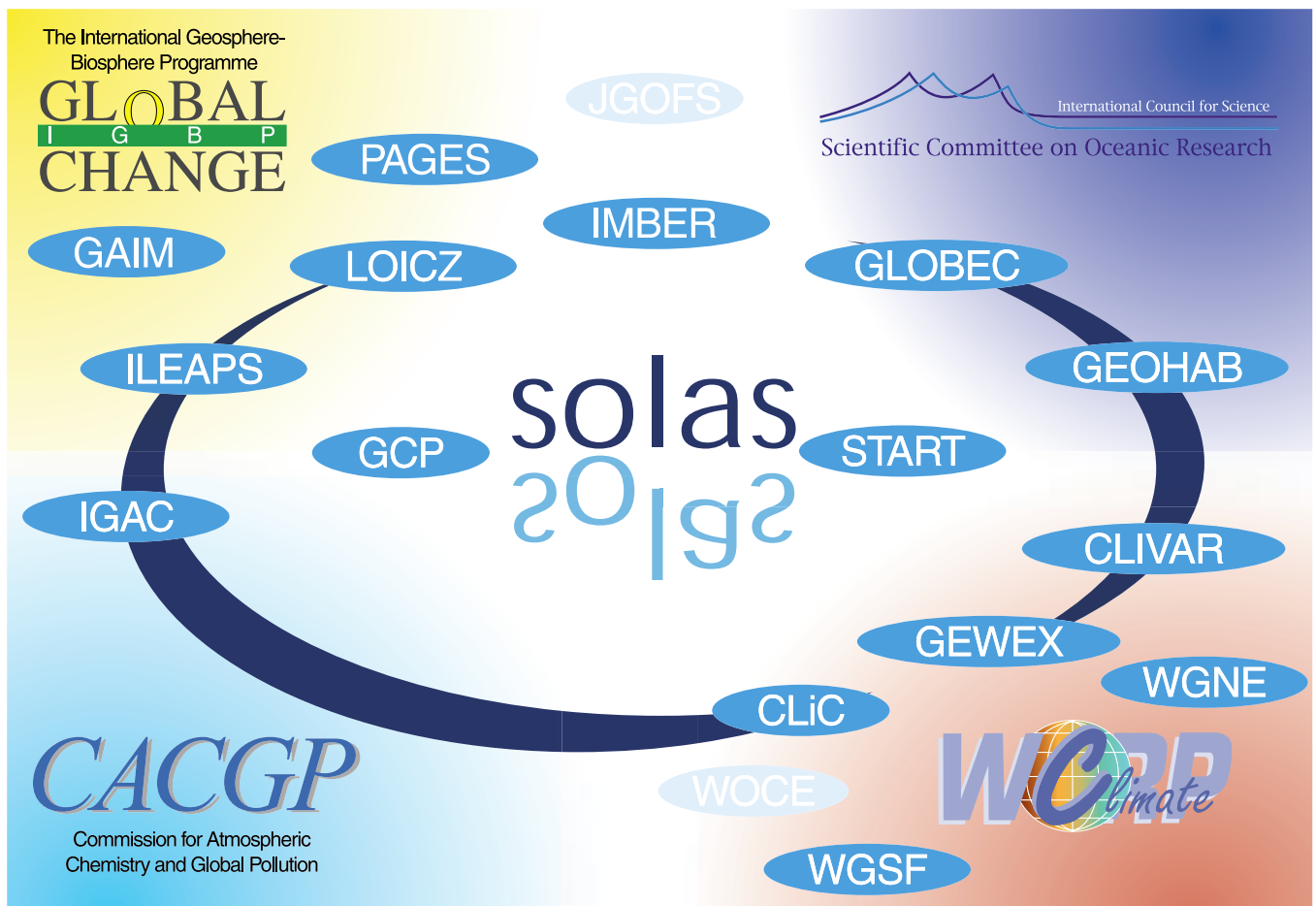
Linkages to Related Programmes and Activities

SOLAS is presently sponsored by IGBP, SCOR, CACGP and WCRP. It is being conducted in the context of ongoing and new projects sponsored by these organisations, within which SOLAS will develop cooperative activities to take advantage of the unique expertise of the different groups and to avoid unnecessary duplication. SOLAS will collaborate with other projects focussing on ocean, atmosphere, and land subsystems and their interfaces, as well as the whole Earth System.

In the area of biogeochemistry, the activities of SOLAS will be coordinated, and wherever appropriate, integrated with the activities of IGAC-II, ILEAPS, the new

IGBP LAND project, GLOBEC, IMBER and LOICZ. It will also participate in the IGBP Fast Track projects (e.g. on Iron and Nitrogen). In the physical aspects of its work, SOLAS will collaborate and integrate with CliC, CLIVAR, GEWEX and WGSE. SOLAS will also collaborate with PAGES (especially IMAGES) in the use of palaeoceanographic records. SOLAS will contribute to Earth System modelling in collaboration with GAIM. The Global Carbon Project will promote the coordination and synthesis of carbon research and results between SOLAS and other relevant projects of IGBP, IHDP and WCRP, to address questions of global sustainability related to carbon. With respect to plan-

Figure 21. Links between SOLAS and other projects of its sponsors. Links to operational programmes are not shown. An explanation of the acronyms can be found in the acronym list.



ning remote sensing and observing systems, SOLAS will work with CEOS, GOOS, GCOS, GAW, WWW and JCOMM. SOLAS will also work with START, IAI and APN to involve broad participation in its activities and develop the capacity of scientists within all regions to carry out research within the scope of SOLAS. In this the National Committees of the sponsors will also have a role to play. Societal impacts of SOLAS will be dealt with in collaboration with IHDP (see “Societal Relevance” section in Introduction).

SCOR currently sponsors several activities that are relevant to SOLAS implementation, including the SCOR-IOC Advisory Panel on Ocean Carbon Dioxide, SCOR Working Group 120 on Marine Phytoplankton and Global Climate Regulation, and the SCOR-IOC Global Ecology and Oceanography of Harmful Algal Blooms (GEOHAB) programme. Relevant collaboration will be established with these groups. IOC also has a declared interest in SOLAS research, in particular the CO₂ studies being conducted in Focus 3.

SOLAS may form joint activities with related projects and activities of the sponsors and others to support implementation of SOLAS research. Specific potential interactions with other projects are detailed under the implementation strategy sections for individual Activities.

Communication

Communication within the SOLAS scientific community and to other groups, both scientific and beyond, will be an important aspect of SOLAS. The international SOLAS website (www.solas-int.org) will be a central source of information, including the Science Plan and Implementation Strategy, science highlights, publications, contacts, internal SOLAS documentation and details of activities. The site will also be a gateway to national SOLAS websites and data centres. Communication within the international SOLAS community and interested scientists will be facilitated through email bulletins and newsletters.

Planning, implementation and synthesis of SOLAS research will be carried out through workshops, field studies and scientific symposia worldwide. The philosophy of SOLAS is to encourage broad national representation in all activities, and to hold its meetings within the regions that contribute to SOLAS, to enable wide participation. National Committees and regional networks will be a vital component of the communication effort.

The results of SOLAS will primarily be published as scientific papers in international journals. In addition to the scientific literature, synthesis documents, including visually rich, easy to understand reports, will be produced periodically and widely distributed. Thus, SOLAS research output will be accessible to a broad audience, in particular the policy and resource management communities, as well as to interested members of the public. Other outreach activities (e.g. press releases, publications in the popular press, contributions to the public understanding of science, educational activities, etc.) will be encouraged.

Education and Capacity Building

As remarked elsewhere in the document, SOLAS has a particular educational role to play in that it not only brings together a range of academic disciplines (e.g. chemistry, biology, physics, etc.), but must also involve scientists working in both atmospheric and oceanic domains in integrated studies. Such multi/interdisciplinarity provides large educational challenges. The communication strategy outlined above will play an important role in this educational process.

Capacity building will be initiated in developing regions through a variety of workshops, both actual and virtual. The SOLAS SSC will strongly encourage intensive courses for graduate students and other younger workers, taught by world experts and held worldwide. Specific initiatives such as the SOLAS Summer School are already in place. The Summer School took place for the first time in summer 2003 in Corsica (further details on the SOLAS website). It is intended for Ph.D. students from any country working on specialised topics of SOLAS science, with the aim of providing a comprehensive overview of air-sea interactive biogeochemistry. This enables them to appreciate how their doctoral work fits into the larger canvas of SOLAS science. We will collaborate with START, IAI, and APN, so that their Fellowship schemes and other mechanisms can be used for capacity development, as well as with similar programmes of the National Committees of the sponsors.

The SSC will encourage workshop and other training approaches, including distance learning (via the World Wide Web), for the introduction of new technologies and techniques valuable for SOLAS research to the widest possible audience of relevant scientists.

Funding will be sought from a wide range of sources to maximise participation from across the globe in these activities.

Acronym List

ACE 1,2	Aerosol Characterization Experiments	DYCOMS-II	The Dynamics and Chemistry of Marine Stratocumulus. Phase II: Entrainment Studies
AGCM	Atmospheric General Circulation Model	ENSO	El Niño-Southern Oscillation
APN	The Asia- Pacific Network for Global Change Research	ERS1,2	European Remote Sensing Satellite
ASTEX	Atlantic Stratocumulus Transition Experiment	FRRF	Fast Repetition Rate Fluorometer
CACGP	Commission on Atmospheric Chemistry and Global Pollution	GAIM	Global Analysis, Integration and Modelling Task Force
CBLM	Coupled Boundary Layer Model	GCOS	Global Climate Observing System
CCC	Canadian Climate Centre	GCP	Global Carbon Project
CCN	Cloud Condensation Nuclei	GEOHAB	Global Ecology and Oceanography of Harmful Algal Blooms
CDN	Cloud Droplet Number	GLOBEC	Global Ocean Ecosystem Dynamics Project
CDOM	Chromophoric (Coloured) Dissolved Organic Matter	GEWEX	Global Energy and Water Cycle Experiment
CEOS	Committee on Earth Observing Satellites	GOME	Global Ozone Monitoring Experiment
CFC	Chlorofluorocarbon	GODAE	Global Ocean Data Assimilation Experiment
CLAW	Charlson, Lovelock, Andreae, Warren	GOOS	Global Ocean Observing System
CliC	Climate and Cryosphere	GOTM	General Ocean Turbulence Model
CLIVAR	Climate Variability and Prediction Research Programme	HEXOS	Humidity Exchange Over the Sea
CN	Condensation Nuclei	HNLC	High Nutrient - Low Chlorophyll
DIC	Dissolved Inorganic Carbon	IAI	Inter-American Institute for Global Change Research
DMS	Dimethylsulphide	ICES	International Council for the Exploration of the Sea
DMSP	Dimethylsulphoniopropionate	ICSU	International Council for Science
DMTT	Data Management Task Team	IGAC	International Global Atmospheric Chemistry Project
DNA	Deoxyribonucleic Acid	IGBP	International Geosphere-Biosphere Programme
DOAS	Differential Optical Absorption Spectrometry	IGOS	Integrated Global Observing System
DOC	Dissolved Organic Carbon		

INDOEX	Indian Ocean Experiment	PAGES	Past Global Changes Project
IHDP	International Human Dimensions Programme on Global Environmental Change	PI	Principle Investigator
ILEAPS	Integrated Land Ecosystem - Atmosphere Processes Study	PgC	Petagrams of Carbon
IMAGES	International Marine Global Changes Study	POC	Particulate Organic Carbon
IMBER	Integrated Marine Biogeochemistry and Ecosystem Research Project	PIC	Particulate Inorganic Carbon
IOC	Intergovernmental Oceanographic Commission	POP	Persistent Organic Pollutant
ISO	International Organization for Standardization	ppmv	Parts per million by volume
IPCC	Intergovernmental Panel for Climate Change	SAR	Synthetic Aperture Radar
IPO	International Project Office	SCCM	Single-column Community Climate Model
IR	Infrared	SSC	Scientific Steering Committee
JCOMM	The Joint WMO-IOC Technical Commission for Oceanography and Marine Meteorology	SCOR	Scientific Committee on Oceanic Research
JGOFS	Joint Global Ocean Flux Study	SOIREE	Southern Ocean Iron Enrichment Experiment
LIDAR	Light Detection and Ranging	SOLAS	Surface Ocean - Lower Atmosphere Study
LOICZ	Land-Ocean Interactions in the Coastal Zone Project	SST	Sea Surface Temperature
MABL	Marine Atmospheric Boundary Layer	START	Global Change System for Analysis, Research and Training
MLD	Mixed Layer Depth	TOC	Total Organic Carbon
M-O	Monin-Obukhov	UV	Ultra Violet
MSA	Methane Sulphonic Acid	VOC	Volatile Organic Compound
NASA	National Aeronautics and Space Administration (USA)	WCRP	World Climate Research Programme
NCAR CCM	National Center for Atmospheric Research Community Climate Model	TOPEX	Ocean Surface Topography Satellite
NSS Sulphate	Non-Sea-Salt Sulphate	USGS	US Geological Survey
NERC	Natural Environment Research Council (UK)	W3C	World Wide Web Consortium
NSF	National Science Foundation (USA)	WGCM	JSC/CLIVAR Working Group on Coupled Modelling
NWP	Numerical Weather Prediction	WGNE	Working Group on Numerical Experimentation
OCMIP	Ocean Carbon Model Intercomparison Project	WGSF	Working Group on Surface Fluxes
		WMO	World Meteorological Organization
		WOCE	World Ocean Circulation Experiment
		WWW	World Weather Watch

Appendices

I - The International SOLAS website

The international SOLAS website (www.solas-int.org) contains, *inter alia*, pages on:

- The structure of SOLAS and its various groups and committees
- SOLAS research (provides the ability to submit research for SOLAS endorsement)
- Upcoming meetings and other events that are relevant to SOLAS
- How to get involved with SOLAS (including joining the email list, nominating a member of a group or task team)
- The latest news and progress of SOLAS
- Science highlights
- National contacts and reports
- The SOLAS Science Plan & Implementation Strategy
- Products that can be downloaded (SOLAS poster, graphics, presentation, etc.)
- Links to related projects and organisations

II - National Representatives

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References

- Andreae, M. O. (1990). Ocean-atmosphere interactions in the global biogeochemical sulfur cycle. *Mar. Chem* 30: 1.
- Andreae, M. O. and P. J. Crutzen (1997). Atmospheric aerosols: Biogeochemical sources and role in atmospheric chemistry. *Science* 276: 1052.
- Andreas, E. L. (1998). A new sea spray generation function for wind speeds up to 32m s^{-1} . *J. Phys. Oceanogr.* 28: 2175.
- Andreas, E. L. (2001). A review of the sea spray generation function for the open ocean. *Atmosphere-Ocean Interactions*. Ed. W. A. Perrie, WIT Press.
- Andreas, E. L. and J. DeCosmo (1999). Sea spray production and influence on air-sea heat and moisture fluxes over the open ocean. *Air-Sea Exchange - Physics, Chemistry, and Dynamics*. Ed. G. Geernaert, Kluwer: 327.
- Andreas, E. L. and J. DeCosmo (2001). The signature of sea spray in the HEXOS turbulent heat flux data. *Bound.-Layer Meteor.* 103: 303.
- Andreas, E. L., J. B. Edson, et al. (1995). The spray contribution to net evaporation from the sea: A review of recent progress. *Bound.-Layer Meteor.* 72: 3.
- Archer, D. and E. Maier-Reimer (1994). Effect of deep-sea sedimentary calcite preservation on atmospheric CO_2 concentration. *Nature* 367: 260.
- Archer, D. E. and K. Johnson (2000). A model of the iron cycle in the ocean. *Global Biogeochem. Cycles* 14: 269.
- Asher, W. E., L. M. Karle, et al. (1996). The influence of bubble plumes on air-seawater gas transfer velocities. *J. Geophys. Res.* 101: 12017.
- Ayers, G. P., J. P. Ivey, et al. (1991). Coherence between seasonal cycles of dimethyl sulphide, methanesulphonate and sulphate in marine air. *Nature* 349: 404.
- Bakwin, P. S., S. C. Wofsy, et al. (1990). Measurements of reactive nitrogen oxides (NO_x) within and above a tropical forest canopy in the wet season. *J. Geophys. Res.* 95: 16765.
- Bange, H. W., U. H. Bartell, et al. (1994). Methane in the Baltic and North Seas and a reassessment of the marine emissions of methane. *Global Biogeochem. Cycles* 8: 465.
- Bange, H. W., S. Rapsomanikis, et al. (1996). Nitrous oxide in coastal waters. *Global Biogeochem. Cycles* 10: 197.
- Barrie, L. A. and U. Platt (1997). Arctic tropospheric chemistry: An overview. *Tellus* 49B: 450.
- Bates, N. R., A. C. Pequignat, et al. (2002). A short-term sink for atmospheric CO_2 in subtropical mode water of the North Atlantic Ocean. *Nature* 420: 489.
- Bates, T. S., K. C. Kelly, et al. (1996). A reevaluation of the open ocean source of methane to the atmosphere. *J. Geophys. Res.* 101: 6953.
- Battle, M., M. Bender, et al. (2000). Global carbon sinks and their variability, inferred from atmospheric O_2 and $\delta^{13}\text{C}$. *Science* 287: 2467.
- Berman-Frank, I., J. T. Cullen, et al. (2001). Iron availability, cellular iron quotas and nitrogen fixation in *Trichodesmium*. *Limnol. Oceanogr.* 46: 1249.
- Bishop, J. K. B., R. E. Davis, et al. (2002). Robotic observations of dust storm enhancement of carbon biomass in the North Pacific. *Science* 298: 817.
- Blanchard, D. C. (1963). Electrification of the atmosphere by particles from bubbles in the sea. *Progress in Oceanography*. Ed. M. Sears, Pergamon. 1: 73.
- Blanchard, D. C. (1983). The production, distribution, and bacterial enrichment of the sea-salt aerosol. *Air-Sea Exchange of Gases and Particles*. Eds. P. S. Liss and W. G. N. Slinn, Reidel: 407.
- Blanchard, D. C. and R. J. Cipriano (1987). Biological regulation of climate. *Nature* 330: 526.
- Blanchard, D. C. and L. Syzdek (1972). Concentration of bacteria in jet drops from bursting bubbles. *J. Geophys. Res.* 77: 5087.
- Blough, N. V. and R. G. Zepp (1995). Reactive oxygen species in natural waters. *Active Oxygen in Chemistry*. Eds. C. S. Foote, J. S. Pacentine et al., Chapman and Hall: 280.
- Bock, E. J., T. Hara, et al. (1999). Relationship between air-sea gas transfer and short wind waves. *J. Geophys. Res.* 104: 25821.
- Boers, R., G. P. Ayers, et al. (1994). Coherence between seasonal variation in satellite-derived cloud optical depth and boundary layer CCN concentrations at a mid-latitude Southern Hemisphere station. *Tellus* 46B: 123.
- Boutin, J., J. Etcheto, et al. (1999). Satellite sea surface temperature: a powerful tool for interpreting in situ pCO_2 measurements in the equatorial Pacific Ocean. *Tellus* 51B: 490.
- Bouwman, A. F., K. W. Van Der Hoek, et al. (1995). Uncertainties in the global source distribution of nitrous oxide. *J. Geophys. Res.* 100: 2785.
- Boyd, P. W., A. J. Watson, et al. (2000). A mesoscale phytoplankton bloom in the polar Southern Ocean stimulated by iron fertilization. *Nature* 407: 695.
- Boye, M. and C. M. G. Van Den Berg (2000). Iron availability and the release of iron-complexing ligands by *Emiliania huxleyi*. *Mar. Chem.* 70: 277.
- Brandt, C. and R. Van Eldik. (1995). Transition metal catalyzed oxidation of sulfur(IV)-oxides. *Atmospheric-relevant processes and mechanisms*. *Chem. Rev.* 95: 119.
- Broecker, W. S. and G. M. Henderson (1998). The sequence of events surrounding Termination II and their implications for the cause of glacial-interglacial CO_2 changes. *Paleocean.* 13: 352.
- Broecker, W. S., J. R. Ledwell, et al. (1986). Isotopic versus micrometeorological ocean CO_2 fluxes - a serious conflict. *J. Geophys. Res.* 91: 10517.
- Burchard, H. (2002). *Applied turbulence modelling in marine waters*. Amsterdam, Springer.
- Burchard, H. and K. Bolding (2001). Comparative analysis of four second-moment turbulence closure models for the oceanic mixed layer. *J. Phys. Oceanogr.* 31: 1943.
- Chameides, W. L. and A. W. Stelson (1992). Aqueous-phase chemical processes in deliquescent sea-salt aerosols: A mechanism that couples the atmospheric cycles of S and sea salt. *J. Geophys. Res.* 97: 20565.
- Chuang, P. Y., R. J. Charlson, et al. (1999). Kinetic limitations on droplet formation in clouds. *Nature* 390: 594.
- Coale, K. H., K. S. Johnson, et al. (1996). A massive phytoplankton bloom induced by an ecosystem-scale iron fertilization experiment in the equatorial Pacific Ocean. *Nature* 383: 495.
- Codispoti, L. A., J. W. Elkins, et al. (1992). On the nitrous oxide flux from productive regions that contain low oxygen waters. *Oceanography of the Indian Ocean*. Ed. B. N. Desai, Oxford Publishing: 271.
- Cornell, S., A. Rendell, et al. (1995). Atmospheric inputs of dissolved organic nitrogen to the oceans. *Nature* 376: 243.
- Cornell, S. E., T. D. Jickells, et al. (2003). Organic nitrogen deposition on land and coastal environments: a review of methods and data. *Atmos. Env.* 37(16): 2173.
- Dacey, J. W. H., J. B. Edson, et al. (1999). In situ estimation of air-sea gas transfer using DMS. *Bound.-Layer Meteor.* 425.

- Davis, D., G. Chen, et al. (1999). Dimethyl sulfide oxidation in the equatorial Pacific: Comparison of model simulations with field observations for DMS, SO₂, H₂SO_{4(g)}, MSA_(g), MS, and NSS. *J. Geophys. Res.* 104: 5765.
- Davis, K. J., D. H. Lenschow, et al. (1997). The role of entrainment in surface-atmosphere interactions over the boreal forest. *J. Geophys. Res.* 102: 29219.
- De Angelis, M. A. and C. Lee (1994). Methane production during zooplankton grazing on marine phytoplankton. *Limnol. Oceanogr.* 39: 1298.
- De Baar, H. J. W. and P. M. Boyd (2000). The role of iron in plankton ecology and carbon dioxide transfer of the global oceans. *The Dynamic Ocean Carbon Cycle: A Midterm Synthesis of the Joint Global Ocean Flux Study*. Eds. R. B. Hanson, H. W. Ducklow et al., Cambridge University Press: 61.
- De Leeuw, G. and L. H. Cohen (2001). Bubble size distributions on the North Atlantic and the North Sea. *Gas Transfer at Water Surfaces*. Eds. M. A. Donelan, W. M. Drennan et al., American Geophysical Union: 271.
- De Leeuw, G., G. J. Kunz, et al. (1999). Breaking waves and air-sea gas transfer (LUMINY). TNO Physics and Electronics Laboratory.
- De Leeuw, G., G. J. Kunz, et al. (2001). LUMINY - An overview. *Gas Transfer at Water Surface*. Eds. M. A. Donelan, W. M. Drennan et al., American Geophysical Union: 291.
- De Leeuw, G. and I. Leifer (2001). Bubbles outside the plume during the LUMINY wind wave experiment. *Gas Transfer at Water Surfaces*. Eds. M. A. Donelan, W. M. Drennan et al., American Geophysical Union: 295.
- De Leeuw, G., M. Moerman, et al. (2003). Aerosols, bubbles and sea spray production studies during the RED experiments. AMS conference, Long Beach, CA.
- DeCosmo, J. (1991). Air-sea exchange of momentum, heat and water vapor over whitecap sea states. PhD Thesis, University of Washington
- DeMora, S., S. Demers, et al. (2000). The effects of UV radiation in the marine environment, Cambridge University Press.
- Denning, A. S., T. Takahashi, et al. (1999). Can a strong atmospheric CO₂ rectifier effect be reconciled with a "reasonable" carbon budget? *Tellus* 51B: 249.
- Donelan, M. A. and W. M. Drennan (1995). Direct field measurements of the flux of carbon dioxide. *Air-Water Gas Transfer*. Eds. B. Jahne and E. C. Monahan: 677.
- Doney, S. C., J. A. Kleypas, et al. (2002). The US JGOFS synthesis and modeling project - An introduction. *Deep-Sea Res. Part II-Top. Stud. Oceanogr.* 49: 1.
- Dore, J. E. and D. M. Karl (1996). Nitrification in the euphotic zone as a source for nitrite, nitrate, and nitrous oxide at station ALOHA. *Limnol. Oceanogr.* 41: 1619.
- Dore, J. E., B. N. Popp, et al. (1998). A large source of atmospheric nitrous oxide from subtropical North Pacific surface waters. *Nature* 396: 63.
- Duce, R. A. and E. J. Hoffman (1976). Chemical fractionation at the air/sea interface. *Ann. Rev. Earth and Plan. Sci.* 4: 187.
- Duce, R. A. and N. W. Tindale (1991). Atmospheric transport of iron and its deposition in the ocean. *Limnol. Oceanogr.* 36: 1715.
- Erickson, D. J., C. Seuzaret, et al. (1999). A general circulation model based calculation of HCl and ClNO₂ production from sea salt dechlorination: Reactive Chlorine Emissions Inventory. *J. Geophys. Res.* 104: 8347.
- Ertling, D. and R. A. Brown (1993). Roll vortices in the planetary boundary layer: A review. *boundary-layer meteor.* 65: 215.
- Fairall, C. W., J. E. Hare, et al. (2000). Parameterization and micrometeorological measurements of air-sea gas transfer. *Bound.-Layer Meteor.* 96: 63.
- Falkowski, P. G. (1997). Evolution of the nitrogen cycle and its influence on the biological CO₂ pump in the ocean. *Nature* 387: 272.
- Falkowski, P. G., R. T. Barber, et al. (1998). Biogeochemical controls and feedbacks on ocean primary production. *Science* 281: 200.
- Fan, S., M. Gloor, et al. (1998). A large terrestrial carbon sink in North America implied by atmospheric and oceanic carbon dioxide data and models. *Science* 282: 442.
- Feely, R. A., R. Wanninkhof, et al. (1999). Influence of El Niño on the equatorial Pacific contribution to atmospheric CO₂ accumulation. *Nature* 398: 597.
- Flückiger, J., A. Dällenbach, et al. (1999). Variations in atmospheric N₂O concentration during abrupt climatic changes. *Science* 285: 227.
- Francey, R. J., P. P. Tans, et al. (1995). Changes in oceanic and terrestrial carbon uptake since 1982. *Nature* 373: 326.
- Frew, N. (1997). The role of organic films in air-sea gas exchange. *The Sea Surface and Global Change*. Eds. P. S. Liss and R. A. Duce, Cambridge University Press: 121.
- Fung, I. Y., S. K. Meyn, et al. (2000). Iron supply and demand in the upper ocean. *Global Biogeochem. Cycles* 14: 281.
- Gabric, A. J., P. H. Whetton, et al. (1998). The impact of simulated climate change on the air-sea flux of dimethylsulphide in the subantarctic Southern Ocean. *Tellus* 50B: 388.
- Galbally, I. E., S. T. Bentley, et al. (2000). Mid-latitude marine boundary-layer ozone destruction at visible sunrise observed at Cape Grim, Tasmania, 41 degrees S. *Geophys. Res. Lett.* 27(23): 3841.
- Galloway, J. N., H. Levy, et al. (1994). Year 2020: Consequences on deposition of oxidized nitrogen. *Ambio* 23: 120.
- Galloway, J. N., G. E. Likens, et al. (1982). The composition of precipitation in remote areas of the world. *J. Geophys. Res.* 87: 8771.
- Galloway, J. N., D. L. Savoie, et al. (1993). The temporal and spatial variability of scavenging ratios for NSS sulfate, nitrate, methanesulfonate and sodium in the atmosphere over the North-Atlantic ocean. *Atmos. Env.* 27: 235.
- Gattuso, J. P., M. Frankignoulle, et al. (1998). Effect of calcium carbonate saturation of seawater on coral calcification. *Glob. Planet. Change* 18: 37.
- Geernaert, G. and P. Astrup (1999). Wind profile, drag coefficient, and cross-section over the coastal zone, for quasi-homogeneous conditions. *The Wind Driven Air-Sea Interface, Electromagnetic and Acoustic Sensing, Wave Dynamics, and Turbulent Fluxes*. Ed. M. Banner, University of New South Wales: 305.
- Ghan, S. J., G. Guzman, et al. (1998). Competition between sea salt and sulfate particles as cloud condensation nuclei. *J. Atmos. Sci.* 55: 3340.
- Glover, D. M., N. M. Frew, et al. (2002). A Multi-year Time Series of Global Gas Transfer Velocity from the TOPEX Dual Frequency, Normalized Radar Backscatter Algorithm. *Geophys. Mon.* 127: 325.
- Gong, S. L., L. A. Barrie, et al. (1997). Modeling sea-salt aerosols in the atmosphere, 2, Atmospheric concentrations and fluxes. *J. Geophys. Res.* 102: 3819.
- Gruber, N. and C. D. Keeling (2001). An improved estimate of the isotopic air-sea disequilibrium of CO₂: Implications for the oceanic uptake of anthropogenic CO₂. *Geophys. Res. Lett.* 28: 555.
- Gruber, N. and J. Sarmiento (1997). Global patterns of marine N-fixation and denitrification. *Global Biogeochem. Cycles* 11: 235.
- Haywood, J. M., V. Ramaswamy, et al. (1999). Tropospheric aerosol climate forcing in clear-sky satellite observations over the oceans. *Science* 283: 1299.
- Heimann, M. and E. Maier-Reimer (1996). On the relationships between the oceanic uptake of CO₂ and its carbon isotopes. *Global Biogeochem. Cycles* 10: 89.
- Hessen, D. O. (2002). *UV Radiation and Arctic Ecosystems*, Springer-Verlag.
- Ho, D. T., W. E. Asher, et al. (2000). On mechanisms of rain-induced air-water gas exchange. *J. Geophys. Res.* 105: 24045.
- Ho, D. T., L. F. Bliven, et al. (1997). The effect of rain on air-water gas exchange. *Tellus* 49: 149.
- Hohmann, R., P. Schlosser, et al. (2003). ³He and dissolved oxygen balances in the upper waters of the Weddell Sea: implications for oceanic heat fluxes. *J. Geophys. Res.* 108: art. no. 3087.
- Houghton, J. T., Y. Ding, et al., Eds. (2001). *Climate Change 2001: The Scientific Basis. Contribution of Working Group I to the Third Assessment Report of the Intergovernmental Panel on Climate Change*. Cambridge University Press.
- Huebert, B. J. and D. H. Lenschow (1999). What have Lagrangian experiments accomplished? *IGACactivities Newsletter* 17: 4.

- Huebert, B. J., A. Pszeny, et al. (1996). The ASTEX/MAGE Experiment. *J. Geophys. Res.* 101: 4319.
- Hummelshøj, P., N. O. Jensen, et al. (1992). Particle dry deposition to a sea surface. *Precipitation Scavenging and Atmosphere-Surface Exchange*. Eds. S. E. Schwartz and W. G. N. Slinn, Hemisphere Publ Corp: 829.
- Jacobs, C., P. Nightingale, et al. (2001). Comparison of deliberate tracer techniques and eddy covariance measurements to determine the air/sea transfer velocity of CO₂. *Gas Transfer at Water Surfaces*. Eds. M. A. Donelan, W. M. Drennan et al., American Geophysical Union: 225.
- Jacobson, M. C., H. C. Hansson, et al. (2000). Organic aerosols: Review and state of the science. *Rev. Geophys.* 38: 267.
- Jähne, B., K. O. Münnich, et al. (1987). On the parameters influencing air-water gas exchange. *J. Geophys. Res.* 92: 1937.
- Jickells, T. D. (1995). Atmospheric inputs of metals and nutrients to the oceans: Their magnitude and effects. *Mar. Chem.* 48: 199.
- Jickells, T. D. (2002). Emissions from the Oceans to the Atmosphere, Deposition from the Atmosphere to the Oceans and the interactions between them. *Challenges of a Changing Earth. Proceedings of the Global Change Open Science Conference 10-13 July 2001*. Eds. W. Steffen, J. Jäger et al., Springer-Verlag.
- Jickells, T. D. and L. J. Spokes (2001). Atmospheric iron inputs to the oceans. *The Biogeochemistry of Iron in Seawater*. Eds. D. Turner and K. A. Hunter, Wiley: 85.
- Johannessen, S. (2000). A photochemical sink for dissolved organic carbon in the ocean. PhD Thesis, Dalhousie University
- Johnson, K. S., R. M. Gordon, et al. (1997). What controls dissolved iron in the world ocean? *Mar. Chem.* 57: 137.
- Karl, D. M. (1999). A sea of change: Biogeochemical variability in the North Pacific Subtropical Gyre. *Ecosystems* 2: 181.
- Karl, D. M., R. Letelier, et al. (1997). The role of nitrogen fixation in biogeochemical cycling in the subtropical North Pacific Ocean. *Nature* 388: 533.
- Karl, D. M. and B. D. Tilbrook (1994). Production and transport of methane in oceanic particulate organic matter. *Nature* 368: 732.
- Kawamura, K., R. Sempere, et al. (1996). Water soluble dicarboxylic acids and related compounds in Antarctic aerosols. *J. Geophys. Res.* 101: 18.
- Keeling, C. D., J. F. S. Chin, et al. (1996). Increased activity of northern vegetation inferred from atmospheric CO₂ measurements. *Nature* 382: 146.
- Keene, W. C., R. Sander, et al. (1998). Aerosol pH in the marine boundary layer: A review and model evaluation. *J. Aerosol Sci.* 29: 339.
- Khalil, M. A. K. and R. A. Rasmussen (1992). The global sources of nitrous oxide. *J. Geophys. Res.* 97: 14.
- Kieber, D. J., J. F. Jiao, et al. (1996). Impact of dimethylsulfide photochemistry on methyl sulfur cycling in the equatorial Pacific Ocean. *J. Geophys. Res.* 101: 3715.
- Kim, K. R. and H. Craig (1990). Two isotope characterization of N₂O in the Pacific Ocean and constraints on its origin in deep water. *Nature* 347: 58.
- Kolber, Z. S., R. T. Barber, et al. (1994). Iron limitation of phytoplankton photosynthesis in the equatorial Pacific Ocean. *Nature* 371: 145.
- Kusmierczyk-Michulec, J., G. De Leeuw, et al. (2002). Empirical relationships between aerosol mass concentrations and Angstrom parameter. *Geophys. Res. Lett.* 29: 1145.
- Landing, W. and K. Bruland (1987). The contrasting biogeochemistry of iron and manganese in the Pacific Ocean. *Geochim. Cosmochim. Acta* 51: 29.
- Langdon, C., T. Takahashi, et al. (2000). Effect of calcium carbonate saturation state on the calcification rate of an experimental coral reef. *Global Biogeochem. Cycles* 14: 639.
- Laws, E. A., P. G. Falkowski, et al. (2000). Temperature effects on export production in the open ocean. *Global Biogeochem. Cycles* 14: 1231.
- Le Quéré, C., J. C. Orr, et al. (2001). Interannual variability of the oceanic sink of CO₂ from 1979 through 1997. *Global Biogeochem. Cycles* 14: 1247.
- Leck, C. and E. K. Bigg (1999). Aerosol production over remote marine areas - A new route. *Geophys. Res. Lett.* 23: 3577.
- Lee, K., R. Wanninkhof, et al. (1998). Low interannual variability in recent oceanic uptake of atmospheric carbon dioxide. *Nature* 396: 155.
- Lefèvre, N. and A. J. Watson (1999). Modeling the geochemical cycle of iron in the oceans and its impacts on atmospheric CO₂ concentrations. *Global Biogeochem. Cycles* 13: 727.
- Legrand, M., C. Feniet-Saigne, et al. (1991). Ice-core record of oceanic emissions of dimethylsulphide during the last climate cycle. *Nature* 350: 144.
- Leifer, I. and G. De Leeuw (2001). Gas transfer at water interfaces. *Gas Transfer at Water Surfaces*. Eds. M. A. Donelan, W. M. Drennan et al., American Geophysical Union: 303.
- Lelieveld, J., P. J. Crutzen, et al. (1998). Changing concentration, lifetime and climate forcing of atmospheric methane. *Tellus* 50B: 128.
- Lenschow, D. (1995). Micrometeorological techniques for measuring biosphere-atmosphere trace gas exchange. *Biogenic Trace Gases: Measuring Emissions from Soil and Water*. Eds. P. Matson and R. Harriss, Blackwell Science: 126.
- Lenschow, D. H. and P. L. Stephens (1980). The role of thermals in the convective boundary layer. *Boundary-Layer Meteorol.* 19: 509.
- Liss, P. S., A. D. Hatton, et al. (1997). Marine sulphur emissions. *Phil. Trans. R. Soc. B* 352: 159.
- Liss, P. S. and L. Merlivat (1986). Air-sea gas exchange rates: Introduction and synthesis. *The role of Air-Sea Exchange in Geochemical Cycling*. Ed. P. Buat-Menard, Reidel: 113.
- Lohmann, U., N. McFarlane, et al. (1999). Comparing different cloud schemes of a single column model by using mesoscale forcing and nudging technique. *J. Climate* 12: 438.
- Macintyre, F. (1972). Flow patterns in breaking bubbles. *J. Geophys. Res.* 77: 5211.
- Mahadevan, A. and D. Archer (2000). Modeling the impact of fronts and mesoscale circulation on the nutrient supply and biogeochemistry of the upper ocean. *J. Geophys. Res.* 105: 1209.
- Mahowald, N., K. Kohfeld, et al. (1999). Dust sources and deposition during the last glacial maximum and current climate: A comparison of model results with paleodata from ice cores and marine sediments. *J. Geophys. Res.* 104: 15895.
- Makin, V. K. and V. N. Kudryavtsev (1999). Coupled sea surface-atmosphere model - 1. Wind over waves coupling. *J. Geophys. Res.* 104: 7613.
- Marks, R. (1990). Preliminary investigations on the influence of rain on the production, concentration, and vertical distribution of sea salt aerosol. *J. Geophys. Res.* 95: 22.
- Mårtensson, M., E. D. Nilsson, et al. (2003). Laboratory simulations of the primary marine aerosol generated by bubble bursting. *J. Geophys. Res.* 108: art. no. 4297.
- Martin, J. H., K. H. Coale, et al. (1994). Testing the iron hypothesis in ecosystems of the equatorial Pacific Ocean. *Nature* 371: 123.
- McGillicuddy, D. J. J., R. Johnson, et al. (1999). Mesoscale variations of biogeochemical properties in the Sargasso Sea. *J. Geophys. Res.* 104: 13381.
- McGillis, W. R., J. B. Edson, et al. (2001a). Direct covariance of air-sea CO₂ fluxes. *J. Geophys. Res.* 106: 16729.
- McGillis, W. R., J. B. Edson, et al. (2001b). Carbon dioxide flux techniques performed during GasEx-98. *Mar. Chem.* 75: 267.
- Measures, C. I. and S. Vink (2000). On the use of dissolved aluminium in surface waters to estimate dust deposition to the ocean. *Global Biogeochem. Cycles* 14: 317.
- Melville, W. K., R. Shear, et al. (1998). Laboratory measurements of the generation and evolution of Langmuir circulations. *J. Fluid Mech.* 364: 31.
- Meyers, T. P., P. L. Finkelstein, et al. (1998). A multilayer model for inferring dry deposition using standard meteorological measurements. *J. Geophys. Res.* 22: 22645.
- Miller, W. L. and D. Kester (1994). Photochemical iron reduction and iron bioavailability in seawater. *J. Mar. Res.* 52: 325.

- Miller, W. L. and R. G. Zepp (1995). Photochemical production of dissolved inorganic carbon from terrestrial input: Significance to the oceanic organic carbon cycle. *Geophys. Res. Lett.* 22: 417.
- Mitchell, G. M. (2001). Determination of vertical fluxes of sulfur dioxide and dimethyl sulfide in the remote marine atmosphere by eddy correlation and an airborne isotopic dilution atmospheric pressure ionization mass spectrometer. PhD Thesis, Drexel University
- Monahan, E. C. and H. G. Dam (2001). Bubbles: An estimate of their role in the global oceanic flux of carbon. *J. Geophys. Res.* 106: 9377.
- Monahan, E. C. and I. G. O'Muircheartaigh (1986). Whitecaps and the passive remote sensing of the ocean surface. *Int. J. Remote Sensing* 7: 627.
- Monahan, E. C., D. E. Spiel, et al. (1986). A model of marine aerosol generation via whitecaps and wave disruption. *Oceanic whitecaps and their role in Air-Sea exchange*. Eds. E. C. Monahan and G. Macniocail, Reidel: 167.
- Moody, J. L., A. A. P. Pszeny, et al. (1991). Precipitation composition and its variability in the Southern Indian Ocean: Amsterdam Island, 1980-1987. *J. Geophys. Res.* 96: 20769.
- Moore, R. M. and O. C. Zafriou (1994). Photochemical production of methyl iodide in seawater. *J. Geophys. Res.* 99: 16415.
- Mopper, K. and D. J. Kieber (2000). Marine photochemistry and its impact on carbon cycling. *The Effects of UV Radiation in the Marine Environment*. Eds. S. Demora, S. Demers et al., Cambridge University Press: 101.
- Moran, M. A. and R. G. Zepp (1997). Role of photochemistry in the formation of biologically labile compounds from dissolved organic matter. *Limnol. Oceanogr.* 42: 1307.
- Murnane, R. J. and J. L. Sarmiento (2000). Roles of biology and gas exchange in determining the $\delta^{13}\text{C}$ distribution in the ocean and the preindustrial gradient in atmospheric $\delta^{13}\text{C}$. *Global Biogeochem. Cycles* 14: 389.
- Murphy, D. M., J. R. Anderson, et al. (1998). Influence of sea-salt on aerosol radiative properties in the Southern Ocean marine boundary layer. *Nature* 392: 62.
- Najjar, R. G., I. Erickson, D. J., et al. (1995). Modeling the air-sea fluxes of gases formed from the decomposition of dissolved organic matter: Carbonyl sulfide and carbon monoxide. Role of nonliving organic matter in the earth's carbon cycle. Eds. R. G. Zepp and C. H. Sonntag, Wiley: 107.
- Najjar, R. G. and R. F. Keeling (2000). Mean annual cycle of the air-sea oxygen flux: A global view. *Global biogeochem. Cycles* 14: 573.
- Naqvi, S. W. A., D. A. Jayakumar, et al. (2000). Increased marine production of N_2O due to intensifying anoxia on the Indian continental shelf. *Nature* 408: 346.
- Nelson, R. K., D. A. Seigel, et al. (1998). Seasonal dynamics of chromophoric dissolved organic matter in the Sargasso Sea. *Deep-Sea Res.* 45: 931.
- Nevison, C. D., R. F. Weiss, et al. (1995). Global oceanic emissions of nitrous oxide. *J. Geophys. Res.* 100: 15809.
- Nightingale, P. D., P. S. Liss, et al. (2000a). Measurements of air-sea gas transfer during an open ocean algal bloom. *Geophys. Res. Lett.* 27: 2117.
- Nightingale, P. D., G. Malin, et al. (2000b). In situ evaluation of air-sea gas exchange parameterizations using novel conservative and volatile tracers. *Global Biogeochem. Cycles* 14: 373.
- Nilsson, E. D., M. Mårtensson, et al. (2003). Eddy correlation measurements of the primary marine aerosol source. AMS conference, Long Beach, CA.
- Nilsson, E. D., Ü. Rannik, et al. (2001). Turbulent aerosol fluxes over the Arctic Ocean 2. Wind-driven sources from the sea. *J. Geophys. Res.* 106: 32139.
- Nurser, A. J. G. and J. W. Zhang (2000). Eddy-induced mixed layer shallowing and mixed layer/thermocline exchange. *J. Geophys. Res.* 105: 21851.
- O'Dowd, C., J. L. Jimenez, et al. (2002). Marine aerosol formation from biogenic iodine emissions. *Nature* 417: 632.
- O'Dowd, C. D., J. A. Lowe, et al. (1997). Biogenic sulphur emissions and inferred non-sea-salt sulphate cloud condensation nuclei in and around Antarctica. *J. Geophys. Res.* 102: 12839.
- Paerl, H. W. (1995). Coastal eutrophication in relation to atmospheric nitrogen deposition: Current perspectives. *Ophelia* 41: 237.
- Parkinson, C. L., D. J. Cavalieri, et al. (1999). Arctic sea ice extents, areas, and trends, 1978-1996. *J. Geophys. Res.-Oceans* 104: 20837.
- Petit, J. R., J. Jouzel, et al. (1999). Climate and atmospheric history of the past 420,000 years from the Vostok ice core, Antarctica. *Nature* 399: 429.
- Plass-Dulmer, C., R. Koppmann, et al. (1995). Light nonmethane hydrocarbons in seawater. *Global Biogeochem. Cycles* 8: 79.
- Platt, U. and C. Janssen (1996). Observation and role of the free radicals NO_3 , ClO , BrO and IO in the Troposphere. *Faraday Discuss.* 100: 175.
- Platt, U. and G. K. Moortgat (1999). Heterogeneous and homogeneous chemistry of reactive halogen compounds in the lower troposphere. *J. Atm. Chem.* 34: 1.
- Prentice, I. C., G. D. Farquhar, et al. (2001). The Carbon Cycle and Atmospheric Carbon Dioxide. *Climate Change 2001: the Scientific Basis. Contributions of Working Group I to the Third Assessment Report of the Intergovernmental Panel on Climate Change*. Eds. J. T. Houghton, Y. Ding et al., Cambridge University Press: 183.
- Raes, F. (1995). Entrainment of free tropospheric aerosols as a regulating mechanism for cloud condensation nuclei in the remote marine boundary layer. *J. Geophys. Res.* 100: 2893.
- Ratte, M., O. Bujok, et al. (1998). Photochemical alkene formation in seawater from dissolved organic carbon: Results from laboratory experiments. *J. Geophys. Res.* 103: 5707.
- Ratte, M., C. Plass-Dulmer, et al. (1993). Production mechanism of $\text{C}_2\text{-C}_4$ hydrocarbons in seawater: Field measurements and experiments. *Global biogeochem. Cycles* 7: 369.
- Ravishankara, A. R. (1997). Heterogeneous and multiphase chemistry in the troposphere. *Science* 276: 1058.
- Rayner, P. J. and R. M. Law (1999). The interannual variability of the global carbon cycle. *Tellus* 51B: 210.
- Rea, D. K. (1994). The paleoclimatic record provided by eolian deposition in the deep sea: The geologic history of wind. *Rev. Geophys.* 32: 159.
- Reid, J. S., H. H. Jonsson, et al. (2001). Evolution of the vertical profile and flux of large sea-salt particles in the coastal zone. *J. Geophys. Res.* 106: 12039.
- Riebesell, U., I. Zondervan, et al. (2000). Reduced calcification of marine plankton in response to increased atmospheric CO_2 . *Nature* 407: 364.
- Rivkin, R. B. and L. Legendre (2001). Biogenic carbon cycling in the upper ocean: Effects of microbial respiration. *Science* 291: 2398.
- Robles-Gonzalez, C. (2003). A new algorithm developed to retrieve the aerosol optical depth over the INDOEX campaign area. submitted for publication.
- Rosenfeld, D., L. Ronen, et al. (2002). The role of sea spray in cleansing air pollution over ocean via cloud processes. *Science* 297: 1667.
- Rue, E. L. and K. W. Bruland (1997). The role of organic complexation on ambient iron chemistry in the equatorial Pacific Ocean and the response of a mesoscale iron addition experiment. *Limnol. Oceanogr.* 42: 901.
- Sadanaga, Y., J. Hirokawa, et al. (2001). Formation of molecular chlorine in dark condition: Heterogeneous reaction of ozone with sea salt in the presence of ferric ion. *Geophys. Res. Lett.* 28: 4433.
- Saltzman, E. S., P. Y. Whung, et al. (1997). Methanesulfonate in the Greenland Ice Sheet Project 2 Ice Core. *J. Geophys. Res.* 102: 26649.
- Sander, R. and P. J. Crutzen (1996). Model study indicating halogen activation and ozone destruction in polluted air masses transported to the sea. *J. Geophys. Res.* 101: 9121.
- Sanudo-Willhelmy, S. A., A. Kustka, et al. (2001). Phosphorous limitation of nitrogen fixation by *Trichodesmium* in the central Atlantic Ocean. *Nature* 411: 66.
- Sarmiento, J., L. and C. Le Quéré (1996). Oceanic carbon dioxide uptake in a model of century-scale global warming. *Science* 274: 1346.
- Sarmiento, J. L., C. Le Quéré, et al. (1995). Limiting future atmospheric carbon-dioxide. *Global Biogeochem. Cycles* 9: 121.
- Sarmiento, J. L., J. C. Orr, et al. (1992). A perturbation simulation of CO_2 uptake in an ocean general circulation model. *J. Geophys. Res.* 97: 3621.

- Schulz, M., G. D. Leeuw, et al. (2003). Sea-salt aerosol source functions and emissions. *Emissions of Atmospheric Trace Compounds*. Eds. C. Granier, P. Artaxo et al., Kluwer (in press).
- Seitzinger, S. P. and C. Kroeze (1998). Global distribution of nitrous oxide production and N inputs in freshwater and coastal marine ecosystems. *Global Biogeochem. Cycles* 12: 93.
- Sievering, H. (1987). Small-particle dry deposition under high wind speed conditions: Eddy flux measurements at the Boulder Atmospheric Observatory. *Atmos. Environ.* 21: 2179.
- Singh, H. B., G. L. Gregory, et al. (1996). Low ozone in the marine boundary layer of the tropical Pacific Ocean: Photochemical loss, chlorine atoms and entrainment. *J. Geophys. Res.* 101: 1907.
- Skjelvan, I., T. Johannessen, et al. (1999). Interannual variability of $f\text{CO}_2$ in the Greenland and Norwegian Seas. *Tellus* 51B: 477.
- Slinn, S. A. and W. G. N. Slinn (1980). Predictions for particle deposition on natural waters. *Atmos. Env.* 15: 123.
- Smith, M. H., P. M. Park, et al. (1993). Marine aerosol concentrations and estimated fluxes over the sea. *Q. J. R. Meteorol. Soc.* 119: 809.
- Solomon, S. (1999). Stratospheric ozone depletion: A review of concepts and history. *Rev. Geophys.* 37: 275.
- Spiel, D. E. (1997). More on the births of jet drops from bubbles bursting on seawater surfaces. *J. Geophys. Res.* 102: 5815.
- Spokes, L. J., S. G. Yeatman, et al. (2000). Nitrogen deposition to the eastern Atlantic Ocean. The importance of south-easterly flow. *Tellus* 52B: 37.
- Stephens, B. B. and R. F. Keeling (2000). The influence of Antarctic sea ice on glacial-interglacial CO_2 variations. *Nature* 404: 171.
- Takahashi, T., R. A. Feely, et al. (1997). Global air-sea flux of CO_2 : An estimate based on measurements of sea-air $p\text{CO}_2$ difference. *NASA Colloquium Volume on Carbon Dioxide and Climate Change*. Ed. C. D. Keeling, *Proc. Natl. Acad. Sci.* 94: 8292.
- Takahashi, T., S. C. Sutherland, et al. (2002). Global sea-air CO_2 flux based on climatological surface ocean $p\text{CO}_2$, and seasonal biological and temperature effects. *Deep Sea Research II* 49: 1601.
- Takahashi, T., R. H. Wanninkhof, et al. (1999). Net sea-air CO_2 flux over the global oceans: An improved estimate based on the sea-air $p\text{CO}_2$ difference. *Proceedings of the 2nd International Symposium CO_2 in the Oceans*, Center for Global Environmental Research, National Institute for Environmental Studies, Tsukuba, Japan.
- Tans, P. P., I. Y. Fung, et al. (1990). Observational constraints on the global atmospheric CO_2 budget. *Science* 247: 1431.
- Toumi, R. (1994). BrO as a sink for dimethylsulphide in the marine atmosphere. *Geophys. Res. Lett.* 21: 117.
- Turekian, V. C., S. A. Macko, et al. (2001). Application of stable sulfur isotopes to differentiate sources of size-resolved particulate sulfate in polluted marine air at Bermuda during spring. *Geophys. Res. Lett.* 28: 1491.
- Turner, S. M., P. D. Nightingale, et al. (1996). Increased dimethyl sulphide concentrations in sea water from in situ iron enrichment. *Nature* 383: 513.
- Tyrrell, T. (1999). The relative influences of nitrogen and phosphorus on oceanic primary production. *Nature* 400: 525.
- Upstill-Goddard, R. C., J. Barnes, et al. (2000). Methane in the southern North Sea: Low-salinity inputs, estuarine removal, and atmospheric flux. *Global biogeochem. Cycles* 14: 1205.
- Uz, M. B., M. A. Donelan, et al. (2001). Laboratory studies of wind stress over surface waves. *Bound.-Layer Meteor.* 102: 301.
- Valentine, R. L. and R. G. Zepp (1993). Formation of carbon monoxide from the photodegradation of terrestrial dissolved organic carbon in natural waters. *Environ. Sci. Technol.* 27: 409.
- Verver, G. H. L., J. S. Henzing, et al. (2002). Aerosol retrieval and assimilation (ARIA). Final report Phase 1. NUSP-2. Royal Netherlands Meteorological Institute.
- Vignati, E., G. De Leeuw, et al. (2001). Modeling coastal aerosol transport and effects of surf-produced aerosols on processes in the marine atmospheric boundary layer. *J. Geophys. Res.* 106: 20225.
- Vodacek, R. L., N. V. Blough, et al. (1997). Seasonal variation of CDOM and DOC in the middle Atlantic Bight: Terrestrial inputs and photooxidation. *Limnol. Oceanogr.* 42: 674.
- Wagner, T., C. Leue, et al. (2001). Spatial and temporal distribution of enhanced boundary layer BrO concentrations measured by the GOME instrument aboard ERS-2. *J. Geophys. Res.* 106(24): 24225.
- Wallace, D. W. R. (2001). Storage and transport of Excess CO_2 in the Oceans: the JGOFS/WOCE Global CO_2 Survey. *Ocean Circulation and Climate - Observing and Modelling the Global Ocean*. Eds. G. Siedler, J. Church et al., Academic Press: 489.
- Wanninkhof, R. (1992). Relationship between wind speed and gas exchange over the ocean. *J. Geophys. Res.* 97: 7373.
- Wanninkhof, R., S. Doney, et al. (2001). The effect of using averaged winds on global air-sea CO_2 fluxes. *Gas Transfer at Water Surfaces*. Eds. M. A. Donelan, W. M. Drennan et al., AGU Press. 127: 351.
- Wanninkhof, R. and W. R. McGillis (1999). A cubic relationship between air-sea CO_2 exchange and wind speed. *Geophys. Res. Lett.* 26: 1889.
- Watson, A. J. (1997). Surface Ocean - Lower Atmosphere Study (SOLAS). *Global Change Newsletter, IGBP* 31: 9.
- Watson, A. J., D. C. E. Bakker, et al. (2000). Effect of iron supply on Southern Ocean CO_2 uptake and implications for glacial atmospheric CO_2 . *Nature* 407: 730.
- Watson, A. J., R. C. Upstill-Goddard, et al. (1991). Air-sea exchange in rough and stormy seas, measured by a dual tracer technique. *Nature* 349: 145.
- Weber, R. J., P. H. McMurry, et al. (1998). A study of new particle formation and growth involving biogenic and trace gas species measured during ACE 1. *J. Geophys. Res.* 103: 16385.
- Weiss, P. S., S. S. Andrews, et al. (1995). Photoproduction of carbonyl sulfide in South Pacific Ocean waters as a function of irradiation wavelength. *Geophys. Res. Lett.* 22: 215.
- Wells, M. L., N. M. Price, et al. (1994). Iron chemistry in seawater and its relationship to phytoplankton. *Mar. Chem.* 48: 147.
- Wennberg, P. O. (1999). Bromine explosion. *Nature* 397: 299.
- Williams, R. M. (1982). A model for the dry deposition of particles to natural water surfaces. *Atmos. Env.* 16: 1933.
- Xie, H., R. Moore, et al. (1998). Photochemical production of carbon disulphide in seawater. *J. Geophys. Res.* 103: 5635.
- Yager, P. L., D. W. R. Wallace, et al. (1995). The Northeast water polynya as an atmospheric CO_2 sink: A seasonal rectification hypothesis. *J. Geophys. Res.* 100: 4389.
- Yoshida, N. and S. Toyoda (2000). Constraining the atmospheric N_2O budget from intramolecular site preference in N_2O isotopomers. *Nature* 405: 330.
- Young, R. M., K. L. Carder, et al. (1991). Atmospheric iron inputs and primary productivity: Phytoplankton responses in the north Pacific. *Global biogeochem. Cycles* 5: 119.
- Zagar, M., G. Svensson, et al. (2003). Method for determining the small-scale variability of the surface turbulent momentum flux seaward of the coast. *Journal of Applied Meteorology* 42: 291.
- Zappa, C. J., W. E. Asher, et al. (2001). Microscale wave breaking and air-water gas transfer. *J. Geophys. Res.* 106: 9385.
- Zepp, R. G. and M. O. Andreae (1994). Factors affecting the photochemical production of carbonyl sulfide in seawater. *Geophys. Res. Lett.* 21: 2813.
- Zepp, R. G., T. V. Callaghan, et al. (1998). Effects of enhanced solar ultraviolet radiation on biogeochemical cycles. *J. Photochem. Photobiol. B: Biology* 46: 69.
- Zhuang, G., Z. Yi, et al. (1992). Link between iron and sulphur cycles suggested by detection of Fe (II) in remote marine aerosols. *Nature* 355: 537.