

## 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

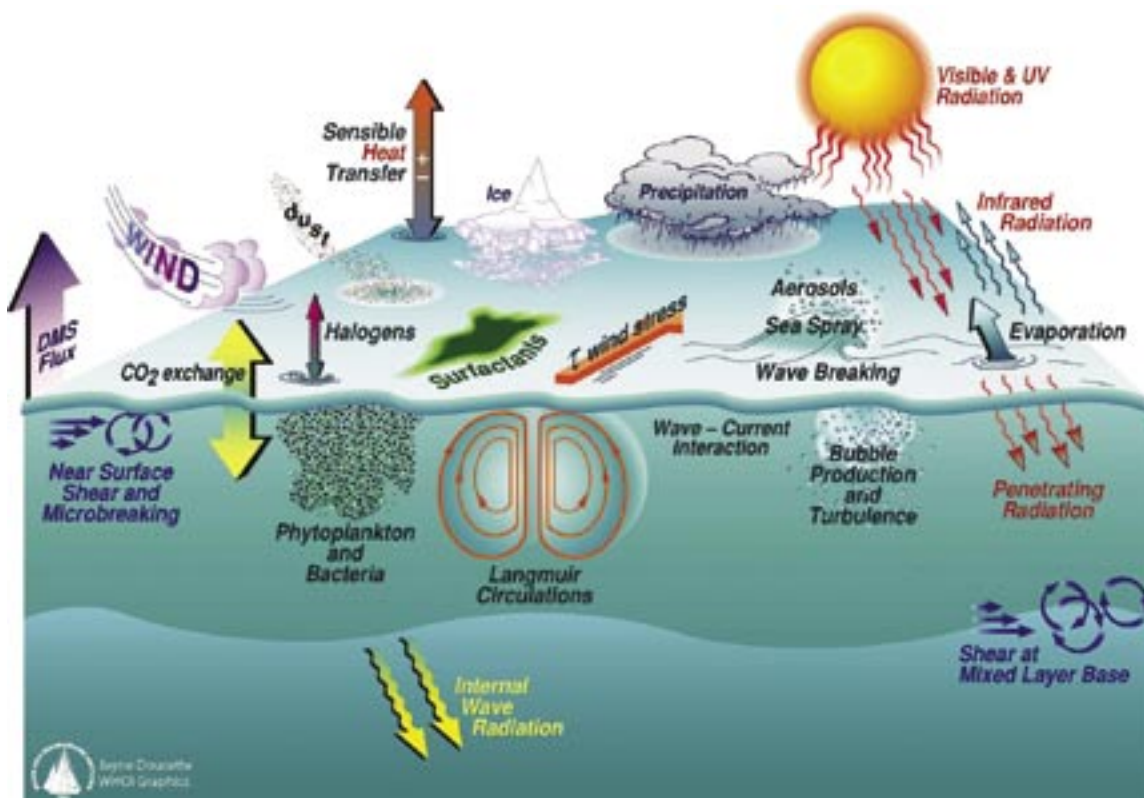
- Bubble plume dynamics
- Factors controlling surface ocean trace gas concentrations
- Upper ocean transport

### 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

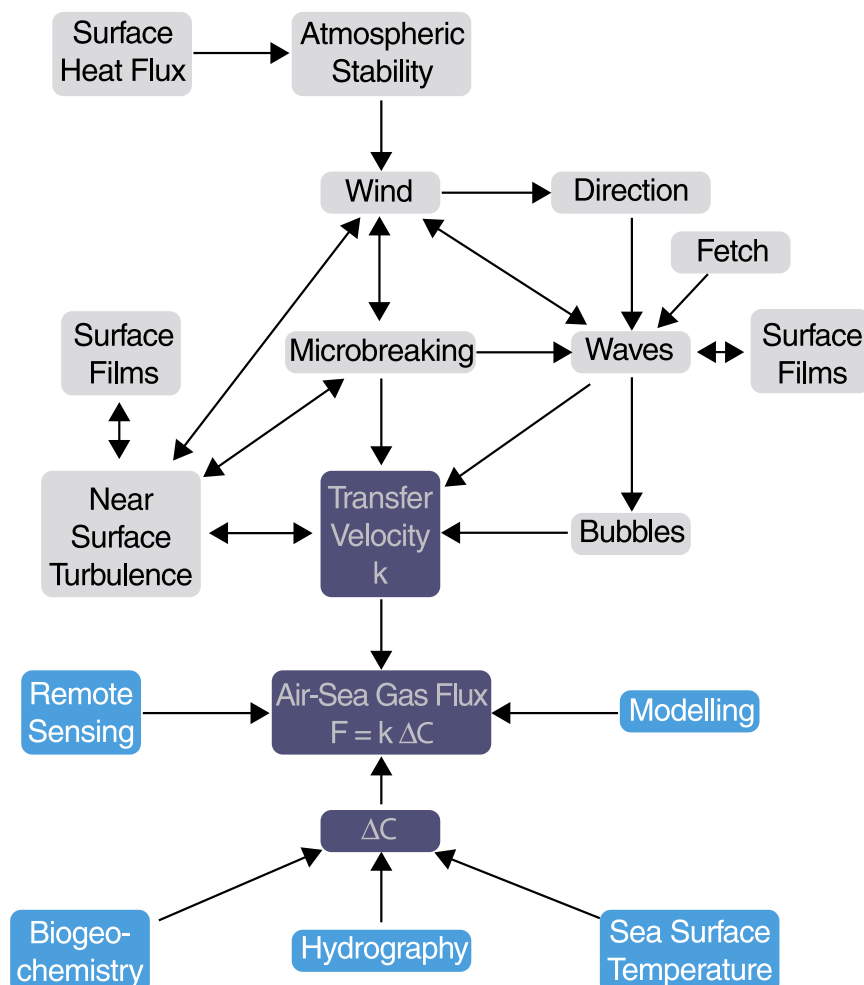
Understanding physical and biogeochemical processes near the air-sea interface is critical for predicting the air-sea exchange of gases and aerosol particles and determining how these processes will affect and be affected by global change.

### 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 CO<sub>2</sub> 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).

### Monolayer 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).

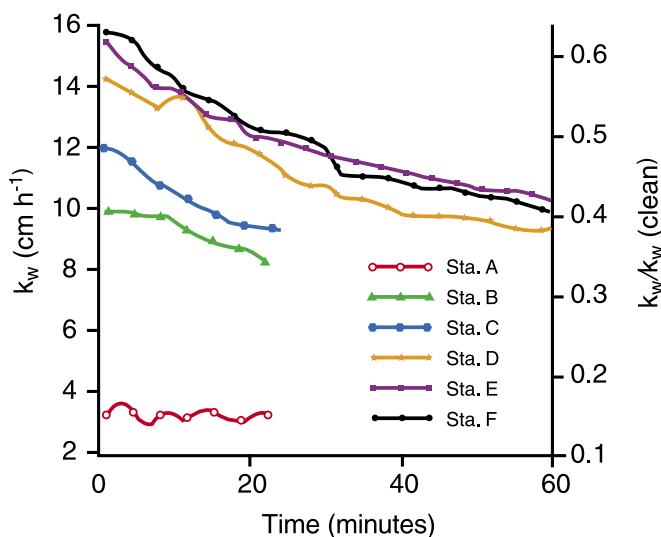
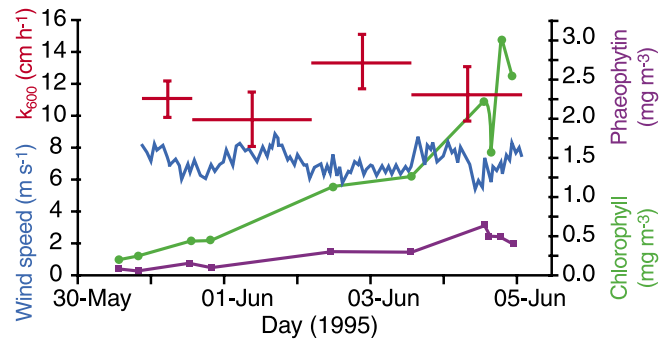


Figure 14. Air-sea gas transfer rates during the development of an open ocean algal bloom in IronEx II. Estimates of the gas transfer velocity normalised to a Schmidt number of 600,  $k_{600}$  (red), plotted against time, together with wind speed from the two nearest TAO buoys (blue), chlorophyll (green), 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 CO<sub>2</sub> 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 <sup>3</sup>He 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<sup>-1</sup>. 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

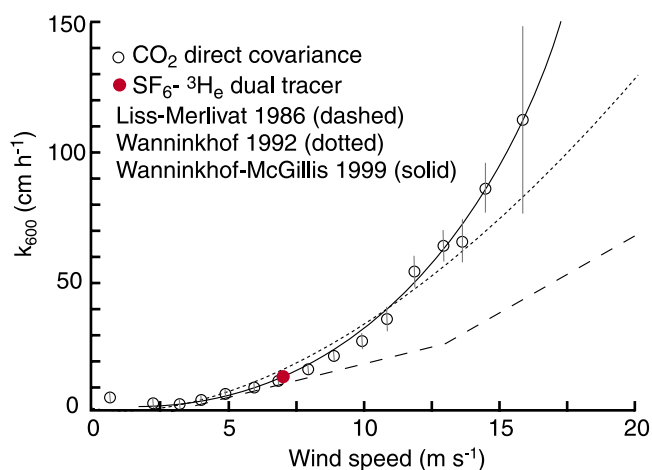
well designed observational programme should span as broad a range of space and time scales as possible, in order to provide robust calibration and validation of air-sea exchange models.

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  $\text{SF}_6$  -  $^3\text{He}$  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  $-5.03 \text{ W m}^{-2}$  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 ( $\sim 1$  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  $\text{CO}_2$

and other gases. However, in the subtropics, the summer time accumulation of photosynthetic oxygen and DMS and the drawdown of  $\text{CO}_2$ , 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, O<sub>2</sub>, CO<sub>2</sub>, 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, O<sub>2</sub>, CO<sub>2</sub>, DMS, NH<sub>3</sub>, 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 CO<sub>2</sub>, 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<sup>-1</sup> s (10 Hz) to perhaps 10<sup>8</sup> 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. <sup>3</sup>He, O<sub>2</sub>/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  $\mu\text{m}$ . 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  $\mu\text{m}$  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  $20 \text{ m s}^{-1}$ , 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  $\mu\text{m}$ . 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  $\text{O}_3$  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  $12 \text{ m s}^{-1}$ .

### 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  $\text{SO}_4^{2-}$ ,  $\text{NO}_3^-$ ,  $\text{NH}_4^+$  and Al provide useful constraints on emission fluxes of precursors ( $\text{SO}_2$ , NO,  $\text{NH}_3$ , 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.  $\text{NO}_3^-$ ,  $\text{SO}_4^{2-}$ , 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  $\mu\text{m}$  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  $\zeta$  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  $20 \text{ m s}^{-1}$ .
- 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 CO<sub>2</sub>, 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 CO<sub>2</sub> (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  $^{13}\text{C}$  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  $\text{CO}_2$ , 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  $\text{CO}_2$  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  $\text{CO}_2$  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 CO<sub>2</sub> 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.