

### Eddy Covariance as a Means of Improving Gas Exchange Parameterizations

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What an exciting time to be studying air-sea exchange! To start with, we have really important questions to work on. What could be more significant than understanding how changes in wind, bubbles, surfactants, and turbulence (i.e., climate change) are likely to change the rate at which CO<sub>2</sub> is taken up by the ocean? Climate models need to diagnose CO<sub>2</sub> exchange accurately, over a very wide range of conditions. Similarly, marine clouds are largely dependent on gas-to-particle conversion to control their droplet number and thus their ability to scatter sunlight back to space. The feedstock gases certainly include DMS, but might also include isoprene and organohalogens. Those two problems (CO<sub>2</sub> and aerosol precursors) make flux-controlling-factor studies about as societally-relevant as geophysical studies can get.

Fortunately, recent technological innovations enable a new generation of considerably-more insightful field experiments, in which gas fluxes will be measured on the same time scales as their controlling factors and their effects. The ability to constrain the interfacial flux of a gas to within tens of percent also gives us vastly more confidence in budget studies. How much sulfur are we disposing of per day in the SE Pacific? An hourly-measured DMS source flux can constrain that problem very nicely.

There are still challenges: can we measure how the CO<sub>2</sub> flux is likely to behave at high wind speeds? Not yet. Graduate students and ship crews are reluctant to sacrifice their bodies doing controlling factor experiments from ships when the roaring forties are roaring and we lack a suitably stable platform from which to make observations somewhere along the tracks of storms, so we must fall back on modelling. Yet how confident can we be that we know how to model high-wind fluxes, when there is a continuum of drop- and bubble-concentrations between the uniform liquid and air phases? One of the original goals of IGAC's Marine Aerosol and Gas Exchange activity was to quantify exchange in high winds, during which the "interface" is ill-defined. Thus, we must ensure that our flux models rely much more on physics than on parameterizations. To get the physics right the flux-controlling factors will need to be carefully quantified in field experiments at the highest wind speeds in which we can make defensible flux measurements. Then we can be more confident of necessary extrapolations to higher winds.

Some of these controlling-factor experiments will be costly. Funders in many countries naturally want a strong justification for combining their resources on big problems like this. Fortunately, IGBP created SOLAS and WCRP created the WGSF, whose charges are to organize multinational, multidisciplinary programs. The organizational infrastructure is in place.

What kinds of experiments should we do to quantify controlling factors? First they need to include a series of chemical and physical flux measurements on a time scale of an hour or

less. Second, a suite of possible controlling factors needs to be measured on the same time scales: this should include winds and currents, turbulence on both sides of the interface, bubble- and sea salt-spectra, mean-square wave slope, rainfall, surfactants, sea state, and probably several others. Third, as many as possible of the measurements should be redundant, made at least by different groups and hopefully by different physical principles. Finally, similar experiments need to be done in locations and at times where the controlling factors vary over the widest possible range. For example, in and out of blooms might be good for isolating surfactant effects, while Southern Ocean winds and currents could be better for studies of turbulence.

Two exciting programs are on the horizon: GASEX-3 and VOCALS. The former is a flux method comparison experiment in the SW Atlantic, in moderate to high winds. The latter is an ocean/flux/aerosol/cloud experiment in the SE Pacific, which will examine the role of surface fluxes and other factors on cloud radiative properties and feedbacks. These are examples of the kinds of experiments we should be designing here, to ensure that gas flux models properly account for all the factors that might change with a changing climate.

### Air-sea exchange of CO<sub>2</sub> in the Polar Regions

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Changes in temperature in the polar region will cause major changes in the environment, especially in the boundary areas where ice will become sparse. These changes will cause feedback effects e.g. increasing emission of methane, change in albedo and change in fluxes of CO<sub>2</sub>. Thus the Polar regions are especially sensitive to climate changes.

A world wide Danish research cruise was started in August 2006 going from Greenland down through the Atlantic Ocean, around Australia and down to the Antarctic Peninsula; back along the west coast of South America and across the North Atlantic to Denmark.

During the cruise, fluxes of CO<sub>2</sub> have been measured using micrometeorological techniques in order to validate the CO<sub>2</sub> transfer velocity for different oceans and to evaluate the potential uptake and potential feedback mechanisms in the Arctic and Antarctic waters. We present here data from direct measurements of CO<sub>2</sub> fluxes and water pCO<sub>2</sub> measurements from the Antarctic circumpolar current in the Southern Ocean and the Antarctic Peninsula and from the Greenland Sea and the Greenlandic fjords.

Measurements of pCO<sub>2</sub> in the Greenlandic fjords show a large potential for CO<sub>2</sub> uptake. The low pCO<sub>2</sub> in the fjords are well correlated to water temperature and only poorly correlated to chlorophyll. From preliminary data it is hypothesized that temperature is the main driver for CO<sub>2</sub> fluxes in the Greenlandic fjord systems in summer months. Contradictory it was found in the Antarctica that colder water correlating with high pCO<sub>2</sub> was more common. Often the "cold water-high pCO<sub>2</sub>" occurrence affected CO<sub>2</sub> emissions, which implies, that

the events could be caused by local up welling. Preliminary results show that at present the Arctic is a much larger sink for CO<sub>2</sub>.

Do we understand the sea to air flux of volatile iodine species?

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The geographical distribution of iodine in rain and soils has long indicated that there must be a major transfer of iodine from the oceans to the land via the atmosphere. The enrichments of iodine in marine rain and aerosols indicate both that the dominant source is not sea salt and that the annual flux of iodine from the oceans is about  $5 \times 10^{11}$  g yr<sup>-1</sup>. This marine supply of iodine is of significant importance to human health as 30% of the world's population is at risk of, and 43 million people are presently affected by iodine deficiency (ID) disorders and related brain damage. The sea to air flux of volatile iodine compounds has become of increasing interest due to recognition of the role that the IO radical may play in atmospheric chemistry. Further, the formation of marine aerosols and cloud condensation nuclei depends on the availability of new nano-scale particles in the marine boundary layer. Laboratory and field studies that shown that ultra-fine particles can be produced from volatile iodine compounds. An improved understanding and quantification of the sea to air flux of volatile iodine compounds is therefore a key goal for SOLAS.

Several mechanisms have been put forward to explain the production of volatile iodine compounds including the formation of molecular iodine via the reaction of ozone with iodate. However, it is the sea to air transfer of volatile iodocarbons (VICs), and in particular iodomethane (CH<sub>3</sub>I) that has received by far the most attention. Extrapolation of a somewhat limited marine CH<sub>3</sub>I dataset suggests that the total annual sea to air flux of CH<sub>3</sub>I is probably  $2 \pm 1 \times 10^{11}$  g I yr<sup>-1</sup>. There is some evidence that other VICs (eg chloriodomethane and diiodomethane), known to be present in seawater, may well contribute to the apparent shortfall in the supply of iodine to the atmosphere. Laboratory and field incubations have shown that a variety of macrolgae and phytoplankton release VICs but crucially not at sufficient a rate to support the observed seawater concentrations. Similarly, a photochemical source of CH<sub>3</sub>I has been shown to operate in tropical waters but production rates are not sufficient to support levels in the tropics let alone temperate oceanic regions.

In this paper, progress that has been made over the last few years on identifying the dominant VICs species in seawater, and on identifying their major production and loss mechanisms, is reviewed. Data will be presented from coastal and open ocean regimes to support the argument that the dominant VIC species in seawater varies in both space and time. Further, it is argued that the mechanisms controlling VICs concentrations in seawater are still poorly understood and that the VIC cycle may yet rival the complexity of DMS in seawater. Finally, the assumption that the dominant supply of atmospheric iodine is gas transfer of VICs is tested. On-going and future SOLAS activities on marine iodine cycling will be highlighted.

The solid air-sea interface: Gas transport in sea ice

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Global carbon cycles studies and models have consistently assumed that ice-covered polar oceans don't directly participate in air-sea gas exchange. This assumption that gas fluxes in sea ice are insignificant is based on a limited understanding of the nature of sea ice and has been challenged by recent data showing large transports of CO<sub>2</sub> above ice surfaces. A variety of methods, including eddy correlation and surface chamber measurements have identified fluxes as high as 1 mol/m<sup>2</sup>day. Most fluxes have been downwards, into the ice, but significant upward fluxes have also been observed. The largest fluxes occur under warming conditions, but at low temperatures small downward fluxes are consistently seen. In addition, the fluxes are sometimes contrary to the air-sea pCO<sub>2</sub> gradient, indicating that the ice is not simply a passive conduit for the gas but is directly involved in the fluxes.

The available CO<sub>2</sub> flux data over ice are still sparse, collected in disparate locations and under disparate conditions. In addition, the structure of sea ice is extremely complex and patchy, with gas and liquid brine pockets and channels scattered throughout the crystalline matrix. Therefore, confident identification of the mechanisms controlling the observed fluxes is still elusive. Nonetheless, the composite nature of sea ice presents some very interesting avenues of inquiry.

Significant amounts of atmospheric gases are trapped within newly-forming sea ice, and as the ice matures, cooling through winter, then warming again in spring, changes in both the biological community and brine chemistry modify the CO<sub>2</sub> content. Without a doubt, algal blooms play some role in the CO<sub>2</sub> drawdowns observed in spring, when the high temperatures (> 5 C), allow the brine pockets to connect and form channels in an open network, allowing almost free vertical movement through the ice. However, even the isolated brine pockets of cold, deep-winter ice still contain viable algal and bacterial cells, often with large quantities of extracellular polymeric matter, which is thought to act as a cryoprotectant. Respiratory activity by these communities is still unconfirmed at low temperatures, but there are certainly large quantities of organic matter (both alive and dead) in the ice. Extremely high pCO<sub>2</sub> values have also been observed in cold sea ice, pCO<sub>2</sub> in sea ice appears to decrease with increasing temperature. This may be partly due to photosynthesis, but it is also related to brine chemistry. Calcium carbonate is one of the first salts to precipitate as the temperature drops and ice brines become more concentrated. This would tend to increase pCO<sub>2</sub> within the ice as it cools during winter, and vice versa during the spring warming period. Finally, mechanical stresses, i.e. cracks, could create opportunities for exchange between sea ice brines (and gas pockets), even in the coldest deep-winter ice, as well as during the break-up period. No single one of these known ice characteristics can adequately explain the observed CO<sub>2</sub> fluxes, and perhaps the only safe conclusion to draw at this time is that a shifting combination of influences most likely controls carbon transport within sea ice.

### Air-sea gas exchange at extreme wind speeds

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Although much is known about air-sea gas transfer rates and transfer mechanisms for moderate to high wind speeds ( $<20 \text{ m s}^{-1}$ ), very little is known about transfer rates and mechanisms at extreme wind speeds ( $>30 \text{ m s}^{-1}$ ). This knowledge gap has implications for important climate-related problems, such as the hypothesis that hurricanes and mid-latitude storms are important in releasing previously stored  $\text{CO}_2$  back to the atmosphere [Bates et al., 1998, 2002]. To begin to address this knowledge gap, air-deployed gas sensing floats were deployed into the path of Hurricane Frances [D'Asaro and McNeil, 2007, papers in press]. A summary of the key results of that study will be presented. The measurements include changes in the oceanic mixed layer T, S,  $\text{O}_2$  and  $\text{N}_2$  associated with the passage of hurricane, budget-derived air-sea fluxes of  $\text{O}_2$  and  $\text{N}_2$ , and the first direct measurements of water-side  $\text{O}_2$  covariance fluxes.

The analysis revealed first evidence of a 'new regime' of air-sea gas transfer at wind speeds in excess of  $35 \text{ m s}^{-1}$ . In this regime, plumes of bubbles 1mm and smaller in size are transported down from near the surface of the ocean to greater depths by vertical turbulent currents with speeds of up to  $20\text{-}30 \text{ cm s}^{-1}$ . These bubble plumes mostly dissolve before reaching a depth of approximately 20 m as a result of hydrostatic compression. Injection of air into the ocean by this mechanism results in the invasion of gases in proportion to their tropospheric molar gas ratios, and further super-saturation of less soluble gases. A new and simplified formulation of air-sea exchange of weakly soluble gases was devised to interpret the measurements. The formulation has two terms. The first term describes all non-supersaturating near surface equilibration processes. The second term describes all sub-surface gas injection processes that only allow gas to enter the ocean. The fluxes associated with the first term, estimated both from data and from model inversions, were found to increase rapidly at high wind speed but the resulting air-sea gas transfer rates were found to be significantly less than those predicted by the cubic relationship of Wanninkhof & McGillis [1999].

The fluxes due to gas injection terms were found to increase with wind speed even more rapidly, causing bubble injection to dominate at the highest wind speeds. The injection of  $\text{CO}_2$  associated with completely dissolving bubbles was found to be small compared to expected surface evasion fluxes. Results of recent modelling efforts appropriate to the 'stalled' hurricane problem were obtained by applying the new formulation at steady-state to predict spatial variations in the maximum equilibrium super-saturation of dissolved gases over the entire region of the hurricane. Plans for further field studies during the 2007-2008 hurricane season include better characterisation of the air-sea interface by measuring surface waves and ambient noise.

### Carbon dynamics in marginal seas- fluxes and processes

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There remain many uncertainties in the ocean component of the global C cycle. Among others, ocean margins add to the complexity in our understanding of the ocean carbon cycle. Ocean margins are the most heterogeneous areas of the world's oceans, and thus it is extremely difficult to constrain the carbon transport fluxes, including the air-sea  $\text{CO}_2$  fluxes and the interior carbon fluxes within the ocean margin. In addition, due to the diversity of the ecosystems and/or physical regimes (e.g. coral, upwelling, mesoscale eddies) coexisting in marginal seas, processes that modulate the carbon cycle remain poorly understood. This presentation will take the South China Sea, the largest low-latitude marginal sea, and the East China Sea, a highly-productive marginal sea, as examples to examine and contrast the dynamics of carbon fluxes and processes. While our primary foci will be on the air-sea  $\text{CO}_2$  and export fluxes, and their controls at a seasonal base; diurnal and longer term variability will also be examined. In addition, the river-ocean carbon connection will be investigated to see how the riverine input will affect the carbon transport and transformation in the marginal systems.

### Eastern boundary upwelling systems as natural SOLAS laboratories

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Three of the four major upwelling systems (Canary, Benguela, and Humboldt) are on the eastern boundary of the Atlantic and Pacific oceans. Winds from high pressure cells located at mid latitudes over the oceans create an uplift to the surface of cold, deep waters rich in nutrients over the continental shelf. This upwelling is responsible for a significant increase in primary and secondary productions in the coastal zone associated with high organic matter remineralization within the water column. The upwelling intensity is modulated by wind speed and direction, by the topography of the coast line and continental shelf and by the proper physical characteristics of the ocean area. Upwelling areas are spatially heterogeneous, populated with a large variety of mesoscale and sub-mesoscale structures such as fronts, filaments, plumes and eddies. Exchange processes in the transitional area between the shelf and offshore areas are controlled by these sub- and mesoscale structures. They play a major role in modulating the biomass, rates and structure of marine ecosystems. Upwelling areas are also often associated to oxygen minimum zones which act as intense sources of greenhouse gases  $\text{CO}_2$  and  $\text{N}_2\text{O}$ . They may constitute oceanic reserves of both gases. Moreover, they are key areas in the marine N cycle due to the joint venture between denitrification and the anammox process.

The Canary, Benguela and Humboldt upwelling systems represent natural SOLAS laboratories covering issues of the SOLAS Foci, namely Foci 2 and 3. We will first present here results from a lagrangian approach based on Finite Size Lyapunov Exponents (FSLE) using altimetric data to estimate the spatial and temporal variations in the lateral stirring and mixing of tracers in the upper ocean within the two Atlantic upwelling systems. They are not equal in terms of mixing intensity with a northern Canary (Benguela) systems being the most (least) energetic areas, respectively.

Turbulent flows develop chaotic patterns, however their inner organization is strongly hierarchized: they develop the so-called cascades transporting energy from larger to smaller scales and the converse. With an appropriate wavelet representation, missing data in signals submitted to a turbulence regime can be inferred from surrounding areas when the cascade equilibrium is re-established. We will illustrate this approach showing results on merging ocean colour data from multiple satellite missions.

We will finally show that the Humboldt upwelling system in the oxygen minimum zone off Chile produces intense CO<sub>2</sub> and N<sub>2</sub>O ocean-atmosphere fluxes and will discuss the potential effect of the OMZ on coupling/decoupling configurations of both gases fluxes.

**New insights on the pre-industrial inter-hemispheric CO<sub>2</sub> gradient in the atmosphere**

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For more than 15 years, the pre-industrial north-south asymmetry in the global carbon cycle has been a matter of debate. In their pioneering work published in 1989, Keeling et al. have shown that the difference in concentrations between Mauna Loa and the South Pole scales linearly with fossil fuel emissions from 1959 to 1988. If this linear relation was to be extrapolated to zero fossil fuel emission, the concentration of CO<sub>2</sub> at the South Pole before the industrial times would be higher than that at Mauna Loa by  $0.8 \pm 0.2$  ppm (Keeling et al. 1989). This had led Keeling and co-workers to hypothesize an atmospheric transport of  $1 \text{ PgC yr}^{-1}$  from the Southern Hemisphere to the Northern Hemisphere before the industrial era, balanced by an oceanic transport from the NH to the SH.

This pre-industrial inter-hemispheric gradient is of interest because it would have large impacts on anthropogenic carbon fluxes estimates obtained from atmospheric inversions techniques. Another important aspect arising from this pre-industrial inter-hemispheric gradient is related to the functioning of the natural oceanic carbon cycle. Understanding the processes responsible for this oceanic transport of carbon may be crucial in estimating the role of the ocean carbon cycle in future climate change scenarios, but also in explaining the large glacial-interglacial difference in ocean carbon storage.

Simulations with 3-D ocean models predict a southward interhemispheric transport of

carbon in the Atlantic of roughly 0.3 to 0.6 PgC/yr, similar to oceanic observations, but this transport is essentially balanced by a northward transport in the Pacific and Indian Oceans. When integrated globally, cross-equatorial transport amounts to only 0 – 0.35 PgC/yr for all models participating in the Ocean Carbon Cycle Model Intercomparison Project.

In this study, we use three different models: (1) the oceanic general circulation model OPA, (2) the ocean carbon cycle model PISCES and (3) the atmospheric transport model LMDZ. We show that improvements in the ocean physics, inclusion of the iron cycle and accounting for the river loop all help to model a southward oceanic transport of carbon more in line with observations.

The river carbon loop includes an uptake of carbon due to organic and inorganic erosion on land, mainly in the Northern Hemisphere, transport of carbon by rivers, subsequent transport of this riverine carbon by the ocean and loss of this riverine carbon back to the atmosphere, which occurs partly in the Southern Hemisphere. We'll show a re-estimate of the river carbon loop effect on the pre-industrial pCO<sub>2</sub> gradient.

The lack of iron limits ocean productivity and the biological carbon pump in all High Nutrient Low Chlorophyll regions (the Equatorial Pacific, the North Pacific and the Southern Ocean). This limitation is asymmetric as it is largely located in the Southern Hemisphere. We'll show how this asymmetry impacts the carbon cycle and the transport of carbon from the North to the South.

Finally, we'll show how the improvements in the physics parameterization of the ocean general circulation models (lateral diffusion, vertical mixing, representation of bathymetry...) also contribute to simulate an oceanic transport of carbon from the Northern to the Southern Hemisphere by improving the representation of large scale circulation.

**Excess carbon export following the spring bloom in extratropical oceans: Implications of N<sub>2</sub> fixer-mediated carbon export**

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New production in the euphotic zone of the ocean occurs when primary production is greater than community respiration. In a steady state, it is quantitatively equivalent to export production, which is the amount of organic carbon exported from the euphotic zone. Nitrate availability is generally considered to be the limiting factor for oceanic new and export production and this concept is central in our observational and modeling efforts. Recent evidence, however, suggests that the metabolic activities of dinitrogen (N<sub>2</sub>) fixing microorganisms, mostly in tropical and subtropical habitats, can directly utilize the non-limiting N<sub>2</sub> and thereby bypass nitrate limitation. If oceanic N<sub>2</sub> fixation supports a significant amount of new and export production in open-ocean ecosystems, then its magnitude and potential change due to future climatic variation need to be known to model the role of

upper ocean in absorbing anthropogenic carbon.

Here we present detailed in situ observations in a Lagrangian mode for three weeks of carbon and nutrients in an anticyclonic eddy (40°N and 20.5°W) in the eastern North Atlantic (McGillis et al., 2001; Zhang et al., 2001), immediately following the spring bloom in 1998. New production in this eddy for three weeks was estimated from changes in salinity-normalized total inorganic carbon ( $N_{Cr} = C_T * 35/S$ ) ( $\Delta N_{Cr}$  in mol C m<sup>-3</sup>) within the surface mixed layer corrected for changes due to net air-sea CO<sub>2</sub> flux and upward flux of N<sub>Cr</sub> via advection and diffusion. During the same observational period, the new production was also estimated using changes in the nitrate inventory within the surface mixed layer. Our calculations indicate that the fraction of new production that was not explained by the mass balance of nitrate accounted for up to 60-80% of the total new production that was estimated from the mass balance of N<sub>Cr</sub>. Such contrasting difference in the estimation of new production is likely to be caused by N<sub>2</sub> fixation. Our estimates of new production in nitrate-depleted waters do not prove that N<sub>2</sub> fixation is the cause. But it is a distinct possibility. Furthermore, our results indicate that the contribution of N<sub>2</sub> fixation-derived new production can be significant in some areas of high latitude ocean following the spring bloom.

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#### Towards near-real-time monitoring of the ocean sink for atmospheric CO<sub>2</sub>

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The air-sea flux of carbon dioxide is determinable from the difference between sea surface and atmospheric partial pressures ( $\Delta PCO_2$ ), and the gas transfer velocity.  $\Delta PCO_2$  varies widely with position and seasonally, but also on inter-annual and inter-decadal periods. Building a climatology of the flux, showing its variation in space and time over an average year, has taken more than 30 years and millions of in-situ measurements. Yet this effort tells little about how the flux is varying on multi-year or decadal time scales.

We can do better however, at least in some of the oceans. For the North Atlantic and North Pacific, which are regularly crossed by merchant shipping routes, it is possible to obtain synoptic coverage by instrumenting a relatively few commercial vessels. Useful coverage of these ocean basins has been achieved in this way since the early 90s. In the North Atlantic,

since January 2005 a fully operational multi-ship network has been operating under the EU Carbon-Ocean program. First results reveal a very different picture from the static climatology, and also from numerical models of ocean uptake of atmospheric CO<sub>2</sub>. Basin-wide, there are substantial inter-annual changes in the flux, and also decadal trends: we estimate fluxes have decreased by about 50% from the mid-nineties to the early years of the present decade. The decline is related to changes in the ventilation and circulation of the surface North Atlantic, the strength of the subpolar and subtropical gyre circulations and the formation rates of denser waters in the Labrador Sea.

The success of this network demonstrates that for the oceans it is possible to set up an operational in-situ observing network that constrains air-sea flux over a huge area, for a very modest cost and effort. This contrasts with the situation on land, where it is difficult to up-scale local in-situ measurements of CO<sub>2</sub> flux to large regions, because of the very heterogeneous vegetation cover and the large diurnal and seasonal variations that sum to a small net flux. However, by combining with atmospheric transport models and inversion techniques, the ocean network can be used as a powerful constraint not only on the marine carbon cycle and ocean sink, but also on the sink or source of atmospheric CO<sub>2</sub> on adjacent land masses – Europe and North America in the case of the North Atlantic. The network however requires international collaboration and co-ordination to be successful -- no one country can do the task alone -- as well as co-operation and goodwill from the international shipping industry.

Over the next decade satellite observations of atmospheric CO<sub>2</sub> will become progressively more useful; in conjunction with an effective in-situ network of measurements; a global carbon monitoring system will be established. An ocean observing system based on merchant ships will be a crucial part of that network, and the technology to deliver it is all now reduced to practice.

### Global cycling of methyl bromide and methyl chloride

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Methyl bromide and methyl chloride are major natural sources of stratospheric bromine and chlorine. The global biogeochemical cycles of these gases are not well understood, and the instrumental records of the atmospheric variability of these gases are limited. As a result, there is little basis on which to predict the sign and magnitude of future changes in their atmospheric burdens and impacts on stratospheric ozone and climate. A record of the atmospheric variability of these gases over the past century has been obtained from measurements on air extracted from Antarctic firn, and ice cores have the potential to generate millennial scale atmospheric histories. There is new ice core of climate-driven variations in atmospheric methyl halides. Such variability raises the possibility of changes in atmospheric methyl halides related to global warming, and underscores the need for a full understanding of the global cycling of these gases. The global budgets of methyl halides are strongly influenced by both terrestrial and oceanic processes, and future changes in climate, land use, oceanic ecosystems, and atmospheric photochemistry are likely to govern their variability. Understanding the role of the oceans in both past and future changes in cycling of methyl halides and other halocarbons remains a key challenge to the SOLAS community.

### Solar UV flux, DMS and Climate: Is there a connection?

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There is continuing interest in the connection between solar variability and clouds. Solar UV radiation varies significantly over the solar cycle, and there has been speculation that ocean DMS fluxes may decrease when UV fluxes are at a peak. Surface UV fluxes vary as a result of both variations in the top-of-the-atmosphere solar radiation and variations in atmospheric composition, in particular clouds. Satellite measurements have shown that there is a long term decrease in the outgoing shortwave radiation reflected from the Earth-atmosphere system, which is consistent with a decrease in cloudiness (and an increase in surface UV flux). We review these measurements to examine whether any connection between solar variations and DMS may exist. Here, we use a global aerosol dynamical model to evaluate the possible connection between solar UV variability, DMS flux and cloud properties. We calculate the decrease in DMS fluxes needed to explain the long term decrease in outgoing shortwave flux associated with the decrease in cloud condensation nuclei concentrations from DMS. The calculated changes in cloud properties cause a positive feedback that may further decrease DMS flux.

### Particle formation at Cape Grim, Tasmania

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During February 2006 a 4 week SOLAS campaign focusing on new particle formation in the clean marine boundary occurred at the Cape Grim Baseline Air Pollution Station, Tasmania. Precursor to Particles 2006 involved scientists from Australia, New Zealand and Europe and included boundary layer profiling, MAX-DOAS measurements for IO and OIO, a suite of particle measurements and measurements of gaseous volatile organic precursor compounds including methyl halides, DMS and the concentration of atmospheric oxidants including ozone and NO<sub>x</sub>.

In addition to the atmospheric measurements marine biological activity on a 5km boat transect, along 270° off Cape Grim and from the beach below the station was determined, including flask samples for methyl halides. MAX-DOAS and particle number measurements were also made on the beach.

During the campaign baseline conditions (clean on-shore winds) dominated, interrupted only by the passage of one front and a smoke plume from a local bushfire on two occasions. Particle formation events and their precursors were difficult to detect in baseline air either at the Station, or on the beach. The smoke plume showed a significantly different signature in gaseous species concentration, particle size distributions and composition.

Measurements of IO, OIO and methyl iodide remained at background levels throughout the campaign and DMS concentrations were also typical of background air. In an effort to understand the contribution of the local kelp, *Durvillea potatorum*, and the limiting factors on new particle formation at Cape Grim, flux chamber studies and a marine ecological survey of the waters below the Cape Grim Station were performed.

*Durvillea potatorum* would only produce particles when exposed to radiation and high levels of ozone, greater than 100 ppbv. TEM grids were collected from the chamber and indicated that the derived particles were likely to involve an aromatic compound with a relatively high vapour pressure. It would appear that the particles formed were the result of the breakdown of the kelp by high ozone levels, rather than as a result of the production of a precursor gas.

There was a strong relationship between the number of particles produced and the level of ozone in the chamber and this relationship indicates that at ambient ozone concentrations at Cape Grim only a few tens of particles would ever result from the kelp.

While *Durvillea potatorum* has a high biomass at Cape Grim, it contains only low levels of iodine and due to the limited extent and very steep topography of the reef, combined with a relatively small tidal range this means that only a limited kelp biomass is exposed at low tide, limiting the role stress may have in provoking the release of precursor gases.

The results from Precursors to Particles 2006 suggest that the role of kelp in initiating particle formation at Cape Grim is extremely limited, unlike the processes observed for Northern Hemisphere coastal sites, and that new particles at Cape Grim are derived from the free troposphere or from the ocean surface.

Reactions of SO<sub>2</sub> and NO<sub>2</sub> on mineral dust particles in the atmosphere and their implications for climate and marine ecosystem

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Heterogeneous reactions of atmospheric gases on solid particles play an important role in atmospheric chemistry in aspects of climate change, marine nutrients supply, health impacts, as well as acid deposition. Mineral dust is an important component of air borne particulate matter and can be easily raised to high altitudes and then transported over long distances, during which these particles have opportunities to interact with other trace gases. For example, as an important constituent in mineral dusts, calcite could react with NO<sub>2</sub> to produce nitrate, which would influence the marine ecosystem as a nutrient.

It is hypothesized that the reactions of SO<sub>2</sub> and NO<sub>2</sub> at the surface of mineral dust particles could produce sulfate and nitrate, which in turn would change the surface properties of the mineral particles, such as hygroscopic and optical properties, these changes could further modify the impacts of mineral dusts on climate and marine ecosystems, as well as the lifetimes of mineral dusts in the atmosphere.

Using Diffuse Reflectance Infrared Fourier Transform Spectroscopy (DRIFTS), Raman Micro-spectroscopy, Ion Chromatography (IC), X-ray Photoelectron Spectroscopy (XPS) and Scan Electron Microscopy (SEM), heterogeneous reactions of SO<sub>2</sub> and NO<sub>2</sub> on calcite particles were investigated. The formation of sulfate and nitrate was observed on calcite surface with DRIFTS and was confirmed with IC and XPS, the uptake coefficients were determined and mechanisms were discussed. The impacts of humidity on the heterogeneous reactions were investigated.

Micro-Raman study on the reaction of dry gaseous NO<sub>2</sub> with NaCl particles proves that the product is the amorphous nitrate sodium capping layer, and confirms the results and the gas-solid reaction probability obtained by infrared spectroscopy methods. Micro-Raman study on the reaction of gaseous NO<sub>2</sub> with CaCO<sub>3</sub> particles shows that surface absorbed water is very important for the reaction and the product is proposed to be droplets of nitrate calcium on the surface of CaCO<sub>3</sub> after deliquescence.

Our result shows that Micro-Raman can also be used in in-situ study on heterogeneous reactions of individual particle. The reaction on the surface of individual sample seems to be quicker than the one on the surface of bulk sample. Because atmospheric particles mainly exist with disperse situation, Micro-Raman spectroscopy has a great potential for the study of heterogeneous reaction of atmospheric particles.

Halogens in the marine boundary layer- origin, cycling and relevance for the atmosphere

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This talk aims to give an overview of the current knowledge of halogens (Cl, Br and I) in the marine boundary layer (MBL). Halogens have received increased interest in the last ten years due to their importance for the ozone budget and the sulphur cycle. The major sources for chlorine and bromine in the MBL are sea salt aerosol particles, which are produced at the ocean surface from bubble bursting. Acid displacement and photochemical reactions in and on the surfaces of these aerosol particles lead to the release of inorganic halogen compounds to the atmosphere. The second main sources for halogens in the MBL are organic halogen compounds, which are produced mainly by biological processes in the ocean and include chlorine, bromine and iodine. The lifetimes of these compounds varies between minutes and months so that they are sources for inorganic halogens both for the MBL but also for the free troposphere and even the stratosphere. The latter is especially true for halo-organic emissions in the tropics.

Our main interest in halogen compounds in the MBL stems from their potential to destroy ozone and therefore reduce the oxidation power of the atmosphere but also due to their roles in the atmospheric cycle of sulphur compounds. BrO oxidizes dimethyl sulphide (DMS) very efficiently. The product of this reaction is DMSO, which can be taken up by clouds but also oxidized further, producing not only SO<sub>2</sub>, which is a precursor for new particle formation but also MSA which cannot contribute to new particle nucleation. In addition to these gas phase processes, the hypohalous acids HOBr and HOCl contribute to the production of sulphate in aqueous particles. The implications of these halogen-sulphur links are mainly a reduction in the formation of new cloud condensation particles but a growth in the size of the existing ones with important implications for the climate forcing of, e.g., stratocumulus clouds which are prevalent in the MBL.

In coastal regions macroalgae have been identified as major iodine emitters, mainly in the form of molecular iodine (I<sub>2</sub>). Under these conditions bursts of new particles have been observed and iodine oxides have been implicated in the production of these particles. These new particles can potentially grow to cloud condensation nuclei constituting another chemistry-cloud-climate feedback involving halogens. Recent field campaigns at the coasts of Ireland, New England and Brittany have provided a wealth of new data but also a lot of new scientific questions. Clearly our understanding of iodine chemistry is not sufficient to explain the observations as shown by model studies. I will also briefly discuss the polar boundary layer where in spring drastic ozone depletion events have been observed which are caused by bromine chemistry. A focus of this talk will be on recent field and model studies.

Using numerical simulations to help understand transport processes at the air-sea interface

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Accurate parameterization of air-sea exchange of mass, momentum, and energy requires a quantitative understanding of the transport processes within the interfacial turbulent boundary layer. Although the processes have been studied extensively, there are still uncertainties in quantifying the physical and physicochemical factors involved due to the strong nonlinear complexities implicit in both the surface waves and the underlying turbulence. Owing to the profound difficulties in conducting in situ measurements, most of the experimental studies on transport processes at the air-water interface have been conducted in laboratory wind-wave fumes. Numerical simulations offer another means for improving understanding the processes, but only recently have computing resources advanced to make sufficiently large-scale simulations possible.

In this talk we will present recent advances in developing a numerical model for process-oriented studies of the three-dimensional turbulent flow bounded by a nonlinearly evolving ocean surface. The developed model has been applied to the studies of micro processes responsible for the immediate transport next to the ocean surface. Three examples of the model applications will be presented:

- Correlation between the submerged “surface renewal eddies” and the characteristic signatures at the air-water interface;
- Hydrodynamic mechanism of transport retardation at the air-water interface by the presence of “surfactants”;
- Generation mechanism of “micro-breaking wind waves” and their impacts on transport at the air-sea interface.

Microbial DMS(P) production in the Subarctic Atlantic and Pacific: does iron matter?

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Ocean production of the climate active gas dimethylsulfide (DMS) contributes to climate regulation via the formation of aerosols that scatter solar radiations and increase the albedo of clouds. DMS emissions thus alter the radiative balance of the Earth and can potentially exert a cooling effect on climate. DMS is produced from the degradation of its algal precursor dimethylsulfoniopropionate (DMSP). Although some microalgae have the capability to directly produce DMS, most of DMSP degradation is believed to occur indirectly through the release of algal DMSP and its subsequent uptake by bacteria. DMS production is thus highly dependent on the floristic composition and development stage of the algal blooms, and on the microbial metabolism of DMSP. Here we use the large set of data collected in the Subarctic Atlantic and Pacific during the Canadian SOLAS program (2001-2007) to highlight the similarities and differences in DMS biological cycling between these two oceanic basins characterized by different bloom species (diatoms versus prymnesiophytes) and limiting nutrients (nitrogen versus iron). DMS standing stocks and DMS biological gross production rates were consistently higher in the NE Pacific than in the NW Atlantic. The prolific nature of the NE Pacific in term of DMS was apparently not related to the iron deficient status of this system. In both oceanic basins, the DMS yield is constrained by the bacterial metabolism of DMSP. These results will be discussed in the general context of the potential impact of iron fertilisation on global DMS production and present and past climate.

Biogeochemical responses of plankton ecosystem to simulated and natural iron additions in the subarctic North Pacific Ocean

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It has been well recognized that iron supply to high nitrate, low chlorophyll (HNLC) regions of the open ocean has a potential to change the primary productivity and the structure of the pelagic food web, both relating to exchange of gases with the atmosphere. Dominant external input of iron to the surface of the open ocean is aeolian dust transport, mainly from the great deserts of the world. Within the three major HNLC regions, the subarctic North Pacific Ocean is unique in that strong zonal gradients in atmospheric iron input exist between the eastern and western gyres, although the pattern and magnitude of dust deposition varies dramatically with season and year. The difference in episodic iron deposition may

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give rise to distinct phytoplankton communities that characterize these biogeochemical provinces.

Three successful meso-scale iron enrichment experiments have been conducted in the western (SEEDS-I & II) and eastern (SERIES) subarctic North Pacific Ocean during 2001–2004. In this talk, I will summarize the key results obtained in these experiments and the major differences observed in the biological and geochemical responses will be highlighted. All three enrichment experiments have confirmed that iron availability impacts primary productivity and food web structure. However, SEEDS-I differed from the other ones by its massive bloom of a chain-forming centric diatom. SERIES on the other hand observed the initial bloom of small phytoplankton followed by the larger bloom of various diatom species. SEEDS-II was conducted in the same area as SEEDS-I but resulted in a much smaller buildup of phytoplankton biomass, in which pico- and nano-phytoplankton such as *Synechococcus* and cryptophytes dominated. Several hypotheses have been proposed to explain the relatively small response of diatoms in SEEDS-II as compared to SEEDS-I, including a higher initial mesozooplankton biomass and grazing pressure, a deeper surface mixed layer depth, short of released iron to fulfill the luxury iron uptake by large diatoms, and iron limitation induced by release of organic iron-complexing ligands by plankton assemblage.

During SEEDS-II, we also observed natural phytoplankton blooms away from the experimental iron-enriched site. Wind trajectory suggests delivery of iron from terrestrial sources to these waters. Significant decrease in silicic acid concentration together with large pCO<sub>2</sub> drawdown in the surface water implies that diatoms dominated in the natural blooms in contrast to the dominance of non-diatom phytoplankton in the SEEDS-II bloom. The unexpected response observed during SEEDS-II and marked differences between simulated and natural phytoplankton blooms emphasize our limited understanding of how iron affects upper ocean biogeochemical processes, as well as the complexity of ecosystem responses to iron deposition in the subarctic North Pacific Ocean.

**The Microbiology of the Sea Surface Microlayer- the Bacterioneuston**  
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The sea surface microlayer (SML) is the upper 1mm of the ocean which has been known for some time to be physiochemically and microbiologically distinctive from corresponding subsurface waters [1]. We have developed precise sampling methods using polycarbonate membranes to remove the sea surface microlayer and to study the microbiology of this unique environment using molecular microbial ecology techniques. We have shown that

Nitrogen, oxygen, physics and export production: Links to climate in the late Quaternary ocean

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Intermediate waters in the northeastern Pacific Ocean host the largest body of oxygen-depleted waters in the modern oceans, a consequence of biophysical supply and demand. The rain of organic material from the upper ocean drives biological oxygen demand in the underlying waters, while lateral advection and diffusion supply O<sub>2</sub> at a rate that almost—but not quite—meets that demand. The oxygen-demand deficit in today's northeastern Pacific is met by bacterially-mediated consumption of nitrate, primarily in the uppermost intermediate waters where the rate of supply of labile organic matter is high. The consumption of nitrate in these waters constitutes the major sink for fixed nitrogen in the oceanic water column, rendering NO<sub>3</sub><sup>-</sup> as a limiting nutrient. Consequently, by influencing the whole-ocean nitrate inventory, modulation of the areal scale of the northeastern Pacific oxygen minimum zone (OMZ) through time and/or the intensity of oxygen consumption within it should have an impact on aggregate export production globally in the sea, the biological pump, and the exchange of CO<sub>2</sub> between ocean and atmosphere. Over the last decade, significant progress has been made in support of this hypothesis, the focus being on the late Quaternary. At many sites along the western margins of the Americas, in both hemispheres, there have been sharp and sometimes sudden changes in the intensity of the oxygen minimum on time scales that range from glacial/interglacial to submillennial. Such variability extends from the coast of Peru north to the Gulf of Tehuantepec (southernmost Mexico) and beyond to the Gulf of California, the California, Oregon, and British Columbian margins and into the proximal open ocean in the Gulf of Alaska. Combined isotopic, micropaleontologic and geochemical data from these sites indicate that while changes in physical circulation must play a role, variability in export production has had a major influence on rates of oxygen and nitrogen consumption in upper intermediate waters. Recent and newly-obtained profiles of sedimentary nitrogen isotope and trace metal distributions down core from sites along the margins of Central and North America, for example, imply that during the last deglaciation, the northern margin of the oxygen minimum zone (defined by roughly the 10 μmol L<sup>-1</sup> O<sub>2</sub> isocline) migrated progressively northward over a period of perhaps two thousand years. Circulation dynamics in the Southern Ocean, the northwestern Pacific, and even the North Atlantic, as well as wind-driven teleconnections, appear to have influenced this migration. The expansion of the OMZ in the Gulf of Tehuantepec during the deglacial, for example, occurred at about the same time as changes in sea ice extent and zonal wind shifts around Antarctica, a supposition that is supported by both data and models. Similarly, changes in the rate of production of upper intermediate waters in the Sea of Okhotsk across the deglacial and into the early Holocene probably influenced the rate of oxygen delivery on the opposite side of the Pacific as far south as southern California. An episode of high export production in the Gulf of Alaska and off northern

Japan and Kamchatka caused a short-lived decline in oxygen content in the eastward-flowing intermediate waters during the Bølling-Ållerød interval (~15–13 ka). This is reflected by contemporaneous maxima in sedimentary <sup>15</sup>N and molybdenum concentrations, for example, off southern and northern California and Vancouver Island. The root cause of that production event may have been a sudden increase in the rate of vertical mixing in the deep interior of the North Pacific ocean that dramatically increased the flux of nutrients into the surface waters. Such an event would have released “stored” CO<sub>2</sub> into the atmosphere and, somewhat later, fostered a temporary decrease in the strength of the biological pump by enhancing nitrate depletion in the OMZ. That, in turn, would have reduced the transfer of CO<sub>2</sub> into the deep sea during the last stages of the deglaciation.

In summary, the growing number of high-quality paleoceanographic data sets that has become available through programs like SOLAS is driving increased appreciation—and increased refinement—of the physical and biogeochemical complexity of atmosphere-ocean CO<sub>2</sub> exchange during the last glacial-interglacial cycle. Although the Southern Ocean has rightly received much attention as a region of critical importance in historical CO<sub>2</sub> dynamics, it is now clear that the spotlight must also be aimed at the North Pacific.

Sun, sea and dust: SOLAS in the Tropics

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The tropical oceans are the location for a wide range of key atmosphere-ocean exchanges that are sensitive to climate-dependent forcing. The presentation will focus on key aspects of the forcing in these regions which are: (1) the role of light and temperature; (2) the effect of dust; (3) upwelling. Three key issues and controversies associated with the tropics will be reviewed in the light of recent literature. The issues will be illustrated with data from specific studies conducted in the NW African region during a series of recent expeditions:

1. air-sea fluxes of long-lived gases including CO<sub>2</sub>, oxygen and N<sub>2</sub>O. Large oxygen undersaturations as well as high pCO<sub>2</sub> and pN<sub>2</sub>O values are observed within tropical upwelling systems; however even the overall sign of some of the air-sea fluxes associated with these systems is debated.

2. air-sea fluxes of short-lived trace gases including halogenated species. Organo-halogen fluxes from tropical regions can be large and potentially significant for not only the troposphere but also the lower stratosphere. However both the geographic location of the strong fluxes, as well as the processes controlling them remain unclear.

3. changes in biological productivity associated with variable upwelling and dust inputs. Large apparent changes in the productivity of tropical oceans have been identified from remote sensing data. Controversy also exists between modelling and experimental studies of the role of atmospheric iron inputs to tropical regions for controlling overall nitrogen fixation rates in the ocean.

The various controversies and uncertainties call for a set of concentrated process-oriented studies within contrasting tropical regions. In this context, planned studies of the new German SOPRAN (Surface Ocean Processes in the Anthropocene) programme in the tropical Eastern North Atlantic region will be briefly introduced.