

Section I: Introduction and Background

Introduction

Over the past couple decades it has become apparent, as a result of several major field studies, that air-snow, air-ice, biosphere-snow-ice-atmosphere, and air-ocean interactions in the Polar regions have a substantial impact on the composition of the overlying atmosphere. Furthermore, it is clear that since the nature and extent of snow and ice cover is changing (Parkinson et al, 2001, Yu et al. 2003), a sound quantitative understanding of these interactions is essential to the development of a predictive capability regarding the future state of the atmosphere in Polar regions, and how that relates to global climate change. However, our understanding of the fundamentals of the associated surface chemical, physical, and biological exchange processes that occur at relevant interfaces is very limited indeed.

To examine the status of our understanding and to discuss and plan appropriate courses of action the community may take in the future, a workshop was held at Purdue University, November 12-14, 2002. The workshop was spawned as a result of discussions occurring among members of the NSF Ocean-Atmosphere-Ice Interactions (OAI) Science Steering Committee. This workshop was funded by the National Science Foundation Office of Polar Programs (ARCSS Program) and was attended by a group of 24 researchers chosen to represent a breadth of subject matters and expertise across the spheres of Polar research, i.e. atmospheric chemistry, meteorology and climatology, toxic substances and transport, ice and snow physics, marine biology, and oceanography. The workshop details and Final Report are available at the following internet site: <http://www.chem.purdue.edu/arctic/ArcticWorkshop.htm>.

Arising from that report is a proposal to develop a new internationally collaborative project, the Ocean-Atmosphere-Sea Ice-Snowpack (OASIS) project. This Science Plan details the main scientific objectives, key questions to be addressed, approaches, logistics solutions, timetable, and key participants to date.

Purpose of the Science Plan

The intent of this Science Plan is to outline and prioritize the science issues and proposed approaches, that will lead to development of an OASIS Implementation Plan, and OASIS Implementation. The Science Plan is organized around a manageable set of research foci. An OASIS mission statement and five overarching research questions have been formulated, based on discussions during the workshop and input from the community during the writing of this Plan. The Action Plan will then derive from the science and logistics needs relevant to these questions.

OASIS Mission Statement

Determine the importance of OASIS chemical, physical and biological exchange processes on tropospheric chemistry, the cryosphere, and the marine environment, and their feedback mechanisms in the context of a changing climate.

Overarching Questions

- I. *What is the nature of feedback loops between OASIS exchange processes and global climate change?*

- II. What are the fundamental physical, chemical, and biologically-mediated chemical exchange processes involving halogens, DMS, NO_x, O₃, VOCs, POPs, Hg, S-constituents, particulate matter, and CO₂ in the Polar regions?*
- III. What is the relationship of OASIS exchange processes with the marine cryosphere (ice/snow) and the underlying Polar ocean?*
- IV. What is the relationship of OASIS exchange processes with the chemistry, physics and biology of airborne gaseous and aerosol particles and cloud/snow formation?*
- V. Environmental pollution: what is the impact on, and by, OASIS exchange and the role of long term changes?*

Answering these questions will require an integrated multidisciplinary effort, which includes both an experimental phase focused on field and laboratory work, and a closely coupled modeling exercise. In what follows we present the background underlying these overarching questions, and a list of research topics that needs to be addressed in order to come to answers. In the second part of this document, we present a discussion on the technical details that need to be considered in order to implement this work.

I. Climate feedbacks, connections to Climate Change

The principal motivating factor in the OASIS research objectives is the fact that climate is changing in Polar regions and is predicted to change at a rate significantly faster than for the planet as a whole in the near future, due to the influence of feedbacks related to the changing surface of Polar Oceans (IPCC, 2001). As discussed in several recent publications, sea ice thickness (e.g., Rothrock et al. xxxx, Yu et al. 2003) and sea ice aerial extent (e.g., Parkinson et al. 200, Barber and Hanesiak, 2004) show sustained reduction over the past 25 years. Snow on the other hand remains a mystery. We expect

increases in snow precipitation as more open water becomes available but there is currently no adequate method to model or measure precipitation, accumulation or redistribution of snow on sea ice. Numerous recent observations indicate that OASIS exchange of atmospherically important chemical species in these regions is driven by physical and photochemical processes occurring on the surface of the snowpack and sea ice, and that this exchange significantly impacts the concentrations of chemical species such as ozone and mercury. Both dynamic (movement) and thermodynamic (temperature) processes in the marine cryosphere affect the exchange process of mass, gas and energy. We know that both dynamic and thermodynamic processes are being affected by global scale climate variability and change. The question then arises how the lower atmosphere in the Polar regions will change as climate and the nature of the snow/sea ice volume change.

In the Arctic, ozone is an important radiatively-active gas while mercury is an important toxic pollutant that impacts the biosphere. Every spring at the time of sunrise, both chemical species are rapidly depleted, due to processes mediated by air-surface exchange of gases, specifically halogen species. Such halogen species may also impact Arctic haze, by accelerating the photochemistry that produces fine aerosol. Fine aerosol may represent an important component of cloud condensation nuclei and, thus, impact cloud cover and subsequent radiation at the surface. Hence, there are important impacts of OASIS chemical exchange on the atmosphere, as well as potentially important feedbacks with respect to the nature of the Arctic surface and radiative balance. These processes should be anticipated to change substantially as sea ice and snow cover change in the Arctic with global climate change.

Predicting the future state of the Polar atmosphere and its implications for a changing climate will require understanding of OASIS exchange and its impacts. It is important to note that the processes under study in the Polar regions, where the signal from OASIS exchange can be large, can also be important at lower latitudes, e.g., in urban winter-time environments. OASIS represents a new and important area of highly interdisciplinary multi-environment research in the Polar regions. Under each of the following headings, the question of climate feedbacks will be addressed in more detail.

II. The fundamental physical, chemical, and biologically-mediated OASIS exchange processes in Polar regions

A. Background and Understanding

Field experiments conducted over the past ~5 years in the Arctic after Polar sunrise have indicated that solar radiation initiates a series of photochemical reactions and biological processes at the interface between the snow and ice covered surface and the atmosphere. As a result, a variety of important gas phase reactive species and particle precursors, such as organohalogen species, dimethyl sulphide (DMS), aldehydes, HONO, NO_x, and molecular halogens (*Heintzenberg and Leck, 1994; Dominé and Shepson, 2002*) are emitted into the atmosphere. There is evidence that these compounds are responsible for processes such as particle production, and ozone and mercury depletions (*Leck and Bigg, 1999; Bottenheim et al., 2002; Lu et al., 2001; Lindberg et al., 2002*). To understand the mechanics of these processes, we need to chart the properties of the surfaces (ocean water, snow, sea-ice) involved. Subsequently, we can determine the impact of the prevailing polar conditions of low temperatures and long absence/presence of solar irradiation on the observed chemical phenomena.

Snow is perhaps the Earth's most dynamically-changing, naturally-deposited porous medium. The nature of the snow grains deposited depends upon the processes of formation of the crystals, saltation and upon post-depositional metamorphism. Dramatic post-depositional physical and chemical changes occur with changing conditions of temperature, humidity, wind, and exposure to sun. Snow metamorphism has been much studied and influence of temperature on the snow morphology on a micro scale is ongoing as new techniques become available (e.g. Barber and LeDrew, 1995, Barber and Nghiem, 1999, *Legagneux et al., 2002*). Snow metamorphism also changes the thermal diffusivity of snow, which in turns affects brine volume changes in the sea ice and the phase proportions of brine, ice and air (Barber et al. 1998).

The depth and character of the snow cover is closely related to the type of sea ice on which it rests (*Iacozza and Barber, 1999; Warren et al., 1999*). Smooth first-year sea ice produces periodic snow drift features, while uneven multi-year and rubble ice create

irregular patterns of snow depth with directional trends related to the prevailing wind direction. Aeolian transport mechanisms contribute to the statistical periodicity of the drift patterns and they can be backcast to show the influence of predominant wind directions during depositional events (Iacozza and Barber, 2001). Snow thickness and sea ice thickness are correlated but in a rather complex fashion. Due to the fact that snow both affects radiative and conductive exchanges across the ocean-sea ice-atmosphere (OSA) interface, snow tends to decrease ice growth when deposited in the fall (conductive effect) and increase ice growth when the snow falls in the spring (radiative effect).

During sea ice formation brine is rejected both into the ocean and atmosphere. The downward flux has the potential to enhance chemical exchanges between the atmosphere and ocean during the critical early growth phase of sea ice. The upward flux plays a role by the production of frost flowers on the surface of new growing ice. *Wolff et al.* (2003) found that the sea ice surface is the dominant source of sea salt to aerosol in coastal Antarctica. Frost flowers, growing from brine on the top surface of freezing sea ice, are highly saline (often >100ppt). They could be sites for the initiation of the ozone loss reactions and play a significant role in carbon exchanges between the ocean and atmosphere. Frost flowers grown at different temperatures exhibit a variety of crystal structures, and an exponential relationship exists between the lateral growth rates and the temperature gradient (*Martin, Yu, and Drucker, 1996*). When snow deposition occurs in the fall this highly saline frost flower layer is destroyed by sintering snow grains. The new snow mixes with this brine layer and results in the formation of a 'depth hoar'. This depth hoar layer has a high brine volume, large kinetic growth grain structure (highly angular grains) and low (<200kg·m⁻²) density (*Barber et al., 1995*). This layer plays an important role in the overall thermodynamic structure of the snow/sea ice system and likely acts as a physical control/mechanism for chemical fluxes that are associated with brine/temperature gradient processes operating across the OSA interface.

Sea ice is an important component of the Earth's cryosphere and is more appropriately considered as a multiphase alloy rather than a single phase, purer ice form such as snow or lake ice. Once ice has formed, the relationships between ice, liquid brine, and solid salts are governed by the thermodynamic structure within the snow and

sea ice volume. The relative fractions of brine ice and air are controlled by the sea ice phase relationships as originally presented by Weeks and Ackley (1986). These relationships dictate the physical controls on mass, gas and energy fluxes operating within the ocean-sea ice-atmosphere system and undoubtedly play an important role in chemical fluxes associated with the science of the OASIS experiment.

Sea ice consolidation coincides with decreasing solar insolation at the surface. Surface temperatures decrease and there is a significant diurnal variation in the atmospheric forcing on the surface of the growing ice sheet. The winter period occurs when solar insolation is absent from the surface (or at least minimized). Strong temperature gradients in both the snow and sea ice typify this thermodynamic regime. The return of solar insolation, as a significant component of the surface energy balance, leads from the early melt period through melt onset into the advanced melt period. Ablation of the ice surface proceeds rapidly thereafter. Spatial and temporal variability is considerable both within and between each of these thermodynamic regimes. For this reason we consider it more effective to remotely estimate the thermodynamic state of the surface rather than relying on long-term average (climatologies) of the spatial and temporal pattern in this process. For more details on this see Barber, XXXX

Commento: Not sure this last sentence fits here, given the flow- Paty

The snow and ice cover of the Arctic Ocean thus undergoes dramatic seasonal change, with near-shore sections melting entirely in the summer, while leads and melt ponds throughout the basin cause areas of both new ice and multiyear ice. Quantity and composition of snow are influenced by the properties of the particles on which ice crystals form (ice-forming nuclei, IFN), the aerosols they scavenge, and on the properties of clouds in which the ice crystals form. Cloud properties are in turn influenced by the concentration and properties of the particles on which cloud drops form (cloud condensation nuclei, CCN). We note also that these processes are likely to occur for any ice/snow surface, i.e. the processes to be studied here are applicable to air-snow interactions at lower latitudes, for urban environments in winter, etc.

In order to put these processes in larger context, it is critically important to monitor sea ice motion and advection. In the past few years, preferential advection of older (and thicker) multi-year sea ice from the Arctic Basin along the east coast of Greenland has been observed in both radiometer and scatterometer data sets. This

advection has modified the historic thickness distribution of Arctic pack ice and complicates estimates of ice pack thinning due to climate change. Various tools for monitoring ice motion include RADARSAT and other SAR sensors as well as scatterometers and passive microwave radiometers. By virtue of their atmospheric insensitivity they can monitor ice motion irrespective of solar illumination or cloud cover. Scatterometers and radiometers provide rapid global coverage to help place higher resolution SAR data into larger context. Combining scatterometer and radiometer data can further improve monitoring of large scale sea ice motion (Zhao et al. 2002). Recent work has also shown that scatterometers and radiometers operating in the microwave portion of the spectrum can provide information on the geophysical characteristics of snow on sea ice (including snow water equivalent estimates) and the state of melt of the snow cover (Barber et al. 2003, Yackel et al. 2001). The ability to measure both dynamic and thermodynamic processes from space borne microwave platforms will allow us to investigate detailed processes at the local scale and then to 'scale' these relationships to regional and hemispheric scales through numerical modelling and remote sensing.

Chemical processing is intimately linked with the quantity and composition of snow, ice and open water in the Polar Oceans. Physical air-snow processes affect chemical exchange. *Albert et al.* (2002) show that natural ventilation will cause air motion through an entire 40-cm Arctic snow pack even if it is totally composed of wind pack, and that much of the ozone depletion can be expected in the top approx. 5 cm of the pack under natural conditions. Interstitial ventilation is a natural process driven by the wind that can increase transport rates an order of magnitude over diffusion (*Albert and Shultz*, 2002). While it is clear that processes at the snow-air interface must be quantified in order to understand OASIS exchanges, the relationships between the state of the snow, metamorphism, and OASIS exchange is poorly understood. On a much larger scale, it is also not understood what impact large scale changes in sea ice and snowpack extent, and variations in snow physical properties from microscale to large scale, have on OASIS exchange and the state of the atmosphere.

It can be expected that a changing climate will affect the permeability of the snow and the formation of ice layers within and at the top of the snow pack. Equally, changes in climate will affect the crystal structure of the snow and the specific surface area

available for exchange. Specific surface area may well decrease during metamorphism affected by increased temperature. Ventilation, diffusion, and radiation penetration all depend upon the physical character of the snow. Hence, climate change will undoubtedly change the physical character of the snow and thereby affect the processes that control the chemical composition of the snow.

Laboratory experiments passing ozone over sea salt (*Oum et al.*, 1998) or frost flowers grown from sodium bromide solution demonstrate the production of a photolysable compound that can destroy ozone, suggesting that frost flowers may also be a source of the bromine implicated in polar tropospheric ozone depletion events. While measurements suggest that refrozen sea water is a factor at least in base layers of the snow pack (e.g., *Albert et al.*, 2002), dry deposition of sea salt ions in the upper layers of the pack by wind-induced transport of blowing snow and frost flowers (*Wolff et al.*, 2003) and deposition of Arctic Haze are likely. Climate change will cause temperature changes, which will affect the amount and duration of brine at the snow/sea ice interface. It will also impact the location and frequency of frost flowers, blowing snow, and the ratio of snow/ice/water cover.

Photochemical reactions in the snow impact the troposphere. Interactions between the near-surface snow and the atmosphere cause higher concentrations of hydroxyl radicals over snow-covered areas, resulting in a greater oxidative capacity of the lower atmosphere. The reactions affect the composition of the snow crystals, the interstitial air, and the overlying atmosphere. Since OASIS exchange will depend on snow composition, we need to understand snow composition, the processes that determine it, before we can address the question how climate change will affect those processes. To move forward to a more quantitative understanding of snowpack photochemistry and solar-mediated snowpack and sea ice chemical exchange, it is necessary to answer a series of questions.

Extensive research on biologically-mediated polar processes has concentrated mostly in the open water and under sea ice regions. As shown in the cover figure, extensive plankton and ice algae blooms and related food webs result in the production and cycling of particulate and organic matter, especially in the marginal ice zones (MIZ) of polar regions. The development of such biogeochemical processes in the high Arctic

have also been described; however, the more extensive ice cover and the presence of only seasonal leads providing open water result in lower abundances and, at times, slower rates of biological production and degradation. This marine organic matter is not only recycled within the ocean but also exchanged with the atmosphere (Bigg and Leck 2004) and deposited on snowpack (Grannas et al. 2004) and ice as well as incorporated into sea ice (Krembs 200x, UW). The role of this marine-derived organic matter, as well as any from other sources, in OASIS exchanges is less clear. The direct release of gases from such food web processes is also enhanced in polar MIZ with respect to leads, with significantly more data available for DMS cycling especially in spring and summer. Less or no data are available for either production or degradation of other compounds of interest, especially halogens; we do know that macroalgae, ice algae and some phytoplankton release copious amounts of brominated compounds (e.g., Moore et al xx;) but do not understand the controls.

Recently, primary aerosol nanoparticles of marine origin have shown remarkable similarity to particles in the marine microlayer of Arctic leads (Bigg and Leck 2004 mar chem.). The injection of these submicron organic particles into the overlying atmosphere effectively bypass the traditional gas-to-particle nucleation pathway allowing a faster growth of particles as well as larger surface area onto which sulphur and nitrogen-containing gases can deposit (Bigg and Leck 2001). These primary submicron CCN of marine origin have recently been reported in temperate regions (O'Dowd et al 2004) as well as in subtropical regions (Kuznetsova et al 2004). It is important to note again that processes highly relevant in the Polar regions, where the signal from OASIS exchange can be large, can also be important at lower latitudes.

The role of bacteria in the polar ocean and ice environments is significant and has been quantified (e.g., Sherr et al. xx, Junge et al 2004), showing the importance of heterotrophic processes in seasonally and permanently cold regions (Rivkin, xx). However, their presence and activity in snow and snowpack is less understood although it has been reported for South Pole (Carpenter and Capone 2000); thus, their role in OASIS exchanges in polar regions is an open question. Biologically-mediated processes can also impact the interactions between ocean, ice, and/or snow and the atmosphere.

B. Prioritized Research Topics

The research topics listed below represent several key areas of uncertainty and importance, with regard to chemical exchange processes in the Arctic.

a. Snow, sea-ice, brine, surface microlayer, lead characteristics, and their role in OASIS exchange

1. Role of thermodynamic snow and sea ice processes (e.g. as influenced by temperature) on the chemistry and the rates of gas, mass and energy exchange.
2. Role of dynamic snow and sea ice processes (e.g., as influenced by wind forcing) on the chemistry and rates of gas, mass and energy exchange.
3. Role of brine processes in the snow/sea ice system on the chemistry and rate of gas, mass and energy exchange.
4. The effect of changes in snow crystal structure and metamorphic states on air permeability, heat conductivity, surface area, and rates of snow-atmosphere exchange, and the impact on OASIS exchange
5. The processes that determine snow composition in marine environments. Do chemicals get there from the sea water, through sea ice percolation, or do they get there by dry deposition, including wind blown frost flowers?
6. The nature of the microbial communities (species composition, abundance, biomass and activity) in the open leads, snowpack and surface ice
7. The roles of microlayer composition (particulates and gels), frost flowers (sea salt and halogens) and blowing snow (evaporate-aerosol) as regulators of exchange to the atmosphere. What is the temporal variability of the pools and processes involved, e.g., time scale of gel breakdown in the atmosphere and products of their degradation?
8. The cause of bubble formation in open leads; the bubble size distribution, lifetime on the surface and airborne particle production on bursting; other airborne pathways
9. Role of melt pond physical processes on chemical exchanges within the OASIS system.

Comment: For oceanographers, marine snow refers to the flocs found suspended in the water as “snow” falling from the ocean surface down

10. The exchange of compounds of biological origin present in the snow, ice, microlayer and bulk water with the surrounding or overlying air. What is the nature of the reactive snow phase DOM? What are the fluxes of VOCs and other biogenic particle precursors from ocean, ice and snow surfaces? Is there direct biogenic emission from snow/ice communities?

b. (photo-) chemical processes at the OASIS surfaces

1. The role of surface photochemical and/or biologically mediated processes in activating halogens
2. The sources, photochemical processing, spatial distribution, and fate of organic matter and Hg in ice and snow.
3. The photochemical influences on constituents of the surface microlayer of the open leads and on the particles transferred from it to the atmosphere.
4. The relative importance of OH and halogen radicals as free radical oxidants.
5. The impact of nitric and sulphuric acid deposition on OASIS exchange and surface-mediated halogen chemistry

c. Impact of a changing climate

1. The impact of changes in ice extent, leads, snow cover, blowing snow, and temperature on
 - microstructure and its evolution, including formation of frost flowers and ice layers, and affect OASIS exchange
 - chemical composition of the snow and OASIS exchange
 - DOC, light penetration, and nutrient fluxes
2. The effect of changing sea ice extent on atmospheric and/or oceanic boundary layer stability, and thus the rates of OASIS exchange. Does that affect atmospheric BL/free trop exchange?
3. Will atmospheric transport patterns change with changing ice cover?

4. Will changes in the heat conductivity caused by climate change exert a positive or negative feedback on sea ice extent?

III. What is the relationship of OASIS exchange processes with the cryospheric matrix (ice/snow) and the underlying Polar ocean?

IV. The impact of OASIS exchange processes on the chemistry, physics and biology of airborne aerosol particles and cloud/snow formation

A. Background and Understanding

Airborne aerosol particles over the central Arctic Ocean have potential influences on radiation balance, cloud precipitation processes, snowpack quantity and composition and chemical transformations of gaseous constituents. In winter, Arctic aerosol tropospheric residence times are longer (several weeks to a month) than in any other non-polar region. As a result of an influx of polluted, mid-latitude air during November-April, Arctic aerosol concentrations may reach up to 20 times the pre-industrial levels, a phenomenon referred to as Arctic haze (*Heintzenberg and Leck, 1994*). The annual minimum of air transported from continental sources occurs during June to August as the air tends to be either imported from the North Atlantic Ocean or to circulate for extended periods over the central Arctic basin. This makes it possible to study the evolution of the aerosol from natural in situ (oceanic, ice, snowpack) sources with little interference from continental and anthropogenic sources.

Over the years, a great deal of effort has been devoted to Arctic aerosol studies focusing on the Arctic haze pollution phenomenon, but much less work has been done on the halogen mediated-photochemistry occurring at sunrise, and the impact of that on Arctic Haze, or on the natural summer aerosol. Possible natural sources of particles or particle-forming material include marginal ice zones, leads and polynyas as open water

sites that exhibit enhanced biological activity, resulting in the release of DMS (and possibly precursors) as well as primary biogenic particles. In addition, the impact of microlayer composition (organic input), frost flowers (sea salt and halogens) and blowing snow as particle sources as well as their role in aerosol composition, size and number abundance are yet to be fully assessed. A major unanswered question is the role of anthropogenic pollution on the natural halogen chemistry. For example – does dry deposited sulfate aerosol impact the activation of halogens in the snowpack or on sea ice? What about deposited nitrate? Nitrate ion photolysis is an important precursor to OH radicals in the condensed phase, and these radicals are hypothesized to activate halogen chemistry. Thus there may be strong connections between the anthropogenic and the natural components of Arctic aerosols.

Recently, iodine-containing compounds have also been proposed as particle precursors (*O'Dowd et al.*, 2002; *Jimenez et al.*, 2003) but the quantitative impact of $\text{CH}_3\text{I}/\text{CH}_2\text{I}_2$ as sources of CCN in the Arctic is not well defined. Entrainment of particles from the free troposphere appears less likely due to the presence of shallow mixed layers with strong humidity gradients below very stable layers. The simultaneous, but spatially size-segregated, presence of small, <5nm and larger particles can only be explained by either new production and old growth occurring in the same region and the particles being suddenly transported to the surface (in spite of the atmospheric stability), or in fact both size ranges being part of a single production process. The composition of these newly formed particles has not yet been established; in summer, they occurred on almost every day with significant sunshine, and were always associated with enhanced concentrations of particles from the microlayer (*Bigg et al.* 2004). It is clearly necessary to establish the relative contributions to the CCN population of sulfate formation processes, and direct production from the sea, snow and ice surfaces in the Arctic, if we are to understand the sensitivity of surfaces-aerosol-cloud interactions to climate change.

The chemical composition of bulk samples of the aerosol over the central Arctic pack ice in summer show sulfate and methanesulfonate derived from DMS to generally dominate the submicron component of the aerosol (*Leck and Persson, 1996; Leck et al. 2002*), following the accepted the homogeneous nucleation of sulfuric acid. However, *Leck and Bigg (1999) and Bigg and Leck (2001)* found that airborne particles smaller

than 50nm diameter were not generally liquid like sulfuric acid, but resembled the “microcolloids” found in seawater in lower latitude oceans (*Wells and Goldberg, 1991*). During AOE-2001, particles from the surface microlayer of the water between ice floes (“open leads”) contained numerous small insoluble virus-like individual and aggregated particles (*Leck et al., 2004; Bigg et al. 2004*). A comparison of airborne and microlayer particles showed that almost all the atmospheric particles <80nm in diameter, and some of those having larger sizes, appeared to have come from the surface microlayer. Both types of particles were usually surrounded by an almost electron-transparent hydrophilic polymer gel that would make them very efficient cloud condensation nuclei (CCN) and also potential sites for the aqueous oxidation of gaseous compounds such as SO₂. Thus, the evolution of Arctic aerosol may depend on biological processes beyond those resulting only in DMS production. Larger particles will likely have an intimate mixture of sulfate, methanesulfonate, sea salts and other halogens, insoluble particulates and the organic components resulting from the destruction of the parent gel.

When free from all particles, small water drops do not freeze until the temperature falls to about -40°C. At temperatures of -30°C most insoluble particles larger than about 50nm can stimulate ice formation. The proportion having this property falls steeply as the temperature rises and at -5°C the only naturally occurring particles known that can act as ice forming nuclei (IFN) are bacteria (*Bigg and Leck, 2001b*). Bacteria can be viable in supercooled cloud water (*Sattler et al., 2001; Bauer et al., 2003*) opening the possibility for biogenic processes. In a narrow temperature range around -5°C, an ice crystal multiplication process can convert a few primary IFN into a shower of ice crystals (*Mossop, 1985*) providing that there are cloud water drops larger than 24µm diameter present. In Arctic boundary layer clouds, the generally low CCN concentration makes the presence of drops of this size highly probable. Thus both IFN and CCN concentrations have an influence on the probability of snow formation, its crystal structure and the impurities it contains.

Some of the remaining issues include the influence of biological, snow and ice sources on particle production or growth, the causes of sudden changes in surface concentrations of gases and particles, the extent to which surface cloud condensation nuclei (CCN) measurements can be used to predict cloud droplet concentrations and the

sensitivity of cloud-aerosol relationships to climate change. The greatest deficiency has been an inability to relate aerosol and cloud properties other than theoretically because of the difficulties of performing *in situ* measurements in super-cooled clouds in a remote and hostile environment. The fact that stratification of aerosols and gases is a common feature shows that application of surface based measurements of aerosol properties to predicting cloud properties is critically dependent on atmospheric mixing between the two levels as well as the vertical extent of the influence of snow, ice and water gas/particle exchange with the atmosphere.

B. Prioritized Research Topics

1. The impact of OASIS exchange on the boundary layer gas to particle conversion, e.g. SO₂
2. Detailed investigation of airborne aerosol particles multi-component and multiphase nature, state of mixture and morphology. Determine the interaction between the organic content including gel material and the inorganic fraction within a particle and how this will influence cloud nucleation.
3. Real-time measurements of CCN concentrations at a supersaturation of <0.3%. What processes lead to newly formed (<5 nm) particles, ultrafine (10-20nm) particles and other particles up to about 50nm in the atmosphere and what are the sources?
4. Real-time measurements of IFN using a continuous-flow counter and filter methods. State of mixture and morphology studies of the contents of individual ice crystals, to see if the IFN can be identified.
5. Vertical profiles of aerosol size distribution, CCN and IFN from surface to above cloud top.
6. The relative importance of boundary layer and higher clouds in determining the formation, crystalline structure and chemical impurities in snow.
7. The fate of CCN and IFN
8. The contribution of surface snow/ice photochemistry to Arctic Haze.

9. Are the natural aerosol and CCN production and transformation processes sensitive to climate change, and if so, will they constitute a positive or negative climate feedback?

V. Environmental pollution: the impact on, and by, OASIS exchange and the role of long term changes

A. Background

As noted above, the Arctic provides an exceptionally complex setting for chemical reactions including strong seasonal supply of photons, a variety of surfaces (ice, snow, water, particulates) and a large supply of inorganic and organic chemicals from the ocean and atmosphere. Although it is clear that photochemistry coupled with chemicals at surfaces must lead to a very dynamic chemical cycle within the Arctic, details about this chemistry are only now emerging. The intensification of the entry of a wide suite of contaminants into the Arctic in the 20th century, primarily through atmospheric and ocean transport (*Barrie et al.*, 1992; *Macdonald et al.*, 2000), means that a large number of new compounds (e.g., old 'legacy' POPs, PBDEs, perfluorinated chemicals, current-use pesticides) are entering into what was already a dynamic photo-geochemical cycle. A number of compounds and elements, which have natural global cycles (e.g., Hg, PAHs), now have fluxes in the Arctic augmented by human activities. Contaminant compounds transfer between phases (particle, gas, snow, water) and accumulate at surfaces – in the case of Hg, deposition to surfaces after polar sunrise is primarily a *consequence* of photochemistry (e.g., *Lu et al.* 2001; *Schroeder et al.* 1998; *Lindberg et al.* 2002). If little is known about the details of natural photo-chemical reactions at snow and ice surfaces, even less is known about parallel transformations in contaminants. What is known is that photochemical reactions can destroy contaminants or make them more toxic (*Barron and Ka'aihue*, 2001), and these processes must be understood before ecosystem impacts can properly be assessed.

Recent change in the Arctic that alters cloud cover, snow cover, ice cover and temperature, may have some profound effects on natural geochemical cycles. Contaminants, which enter into biogeochemical cycles, will be no different: climate change will alter their pathways, chemical partitioning, photolysis at surfaces and the way they present risks to biota including humans (*Macdonald et al.*, 2003). Our understanding of what projected and observed changes in the Arctic may mean for biota is at present rudimentary. It is clear, however, that ice as a habitat, and polynyas as important biological oases, will loom large in the equation of change. We are also beginning to recognize that occluded brine pockets in ice harbor life (*Krembs et al.*, 2003a) and do so through some rather remarkable chemistry that supports liquid micro-environments at temperatures below -50 °C. In addition, bacteria can grow in Arctic and Antarctic snow. Brine pockets, sintering of snow, exclusion of solutes by growing ice, and fog formation all represent powerful concentrating processes (*Macdonald et al.*, 2003b; *Leck et al.*, 2004). After polar sunrise, chemicals concentrated through these mechanisms will then be subject to photochemical reactions. Processes like these may, indeed, be crucial for the natural geochemistry that supports biology in and near the polar surfaces. However, the range of new chemical compounds being loaded into the Arctic by human activities to the south, and being deposited by snow, fog and particles (*Macdonald et al.*, 2003; *Chernyak*, 1996; *Welch et al.*, 1991; *Wania*, 2003) is similarly subject to concentration by these processes, with as yet completely unknown effects on the biota living in these extreme environments or, indeed, on the physics of the ice itself.

High levels of sulphate aerosol, heavy metals, gas phase PAN and other combustion exhaust compounds have been measured for several decades. Their concentrations show long term trends that can be related to changes in emission patterns in the densely inhabited midlatitude regions. There is also increasing evidence that naturally occurring oscillations such as NAO and AOs imprint a measurable signature on the long term trends (*Bottenheim et al.*, 2004). For pollutants such as POPs, air monitoring databases are generally shorter compared to basic air pollutants (e.g. data available for the last 10 years), with trend analysis revealing a complicated picture, where levels of certain chemicals are declining while others remain unchanged (*Hung et al.* 2001, 2002). For many organochlorine pesticides, levels in arctic air are marked by a

bimodal seasonality which may reflect air-surface exchange processes within the Arctic rather than varying emissions from source regions (Hung et al., 2002; Halsall 2004).

Recent long term datasets (starting around the late 1970s) on pollution impacts are available from principal Arctic atmospheric observatories (Alert, Barrow, NyÅlesund). In addition, historical data in a climate sense exist from ice core data obtained from snow pits and deep coring at Summit, Greenland. It is imperative that current data gathering activities continue. A 30+ year record of atmospheric measurements may be sufficient to attempt a link with measurements from the snow pit but it is marginal, at best, to do the same for ice core data. Such long term records are required for studies of the aerosol and MSA record, along with investigations of trends in atmospheric Hg concentrations compared to trends of Hg in Arctic biota.

B. Prioritized Research Topics

1. A test of the hypothesis that recent increases in Hg concentrations in the Arctic biosphere have resulted primarily from increases in gaseous oxidant levels, and/or increased production of reactive bromine rather than from increases in atmospheric Hg.
2. The post-depositional behaviour of Hg and POPs in the sea-ice snowpack, a quantification of the re-emission of more volatile fractions following changes in snow structure with ageing, and the identification of those chemicals and by-products which may be retained in snow layers to be subsequently released in meltwater or entrained into ice
3. The processing of O₃, Hg, DMS, POPs, etc. by photochemically produced reactive halogen atoms
6. The photochemical production of HONO and NO_x in the snow pack and sea ice from nitrate deposition, and the impact of its emission to the atmosphere on gas phase halogen chemistry and thus ozone and Hg depletion.
7. The environmental effects of deposition over the pack ice of photochemically transformed chemical compounds originating at lower latitudes and the dependence

of that deposition on cloud precipitation processes. The impact of photochemical and biological post-depositional processing on deposited Hg and other pollutants.

8. The atmosphere-snow partitioning of vapour-phase POPs present in the Arctic Ocean atmosphere. Can the partitioning in the field be accounted for by a chemical's temperature-dependent Henry's Law constant, even at temperatures significantly below 0°C, and what is the effect of wind on the mass transfer and subsequent chemical flux into and out of the snow pack?
9. The gas-particle distribution of semi-volatile organic pollutants (e.g. POPs), including detailed measurements/knowledge of the aerosol composition. Investigate the role of anthropogenic versus biogenic particles on influencing the particle-bound fraction of these contaminants present in oceanic air.
10. The historical changes in key pollutant concentrations and flux, focusing on covariances between compounds and meteorological variability. Classes of compounds of interest include O₃, SO_x, Hg, POPs, NO_y.

Section II. OASIS Action Plan

A) Synthesis of existing data; expansion of data collection

Long term measurements form the backbone for any assessment of environmental change. There are a few locations around the Arctic with well established measurement programs aimed at documenting trends in the chemical composition of the lower atmosphere. The most well-known observatories include Alert, on the northern end of Ellesmere Island at latitude 83°N, Ny-Ålesund on the west coast of Spitsbergen at latitude 79°N, and Barrow, AK at latitude 71°N. These sites include regional heterogeneity, i.e. they are within the pack ice zone in summer or only about 200km south from it, as well as land-based, with a variety of local scale meteorology. Alert has meteorological records going back to 1950, an aerosol chemistry program since 1980 and an extended trace gas program as well as weekly ozone soundings since 1987. Barrow features the Barrow Environmental Observatory (www.sfos.uaf.edu/basc/beo/), 7,466 acres of preserved tundra on the North Slope. This site hosts the DOE atmospheric radiation measurement (ARM) program, and a NOAA CMDL laboratory. Ny-Ålesund has also made aerosol and trace gas measurements since the mid 1980's; ozone soundings started are obtained since 1991. Stations north of the Arctic Circle in Finland, Sevettijärvi, Pallas, Sodankylä and Varriö have included monitoring of aerosols and various gases, many of the records going back to 1991. Data have been collected since 1991 at Station Nord on the northern edge of Greenland. Meteorological sounding data extend back to 1949 at Sodankylä and ozone sounding records from 1986. Since the early 1990s, routine atmospheric data for a range of POPs are now available through continued air-toxics monitoring at both Alert and Ny-Ålesund. Additional routine measurement programs have been initiated since that time following the establishment of the Arctic Monitoring and Assessment Program (AMAP). Furthermore, we note that historical paleoclimate data exist from ice core data obtained from snow pits and deep coring at Summit, Greenland. It is highly desirable to determine the link between these data and the more recent observations. However, while a 30+ year record of atmospheric measurements may be sufficient to attempt a link with measurements from a snow pit, it is marginal, at best, to do the same for ice core data. For instance, such long term records are required for studies of the aerosol and MSA

record, along with investigations of trends in atmospheric Hg concentrations compared to trends of Hg in Arctic biota.

Figure 1. Research locations in the Arctic

Figure 1 shows the location of many of these stations. The importance of these long term data collection activities cannot be emphasized enough. In the context of OASIS, the data will be essential in modeling activities described in Section II E below. However, without diminishing the importance of these sites it is clear that critical areas are missing. There are virtually no long-term records of measurements on the Central and Eastern Siberian coast. Even more disturbing is the near total lack of long term surface atmospheric chemistry data over the Arctic ocean itself and OASIS will actively endeavor to initiate data collection activities in that centrally important region. Routine measurements over the Arctic Ocean can, and will, be realized from autonomous stations in conjunction with the International Arctic Buoy Program and the newly proposed Arctic Ocean Observing System.

B) Field Studies

Given the variety of scientific objectives associated with OASIS, it is essential that an array of field logistical strategies is pursued. It is clear that much has been and can be learned from land-based coastal sites, such as Alert, Barrow, or the marine Arctic site Ny-Ålesund, which is located on Svalbard Island and is more exposed to the polar oceans, as well as others (e.g. Tuktoyuktuk, Toolik Lake). However, a general problem with field studies at those locations is their geographical representativeness. Several topics raised in Part I of this science plan relate to processes believed to be linked to sea salt liberated from freezing ocean water or from sea spray, but virtually all studies of snowpack and sea ice photochemistry have been conducted in coastal regions. Limited information obtained from sites on the Arctic sea ice surface away from the coast (e.g.

from ice island studies in 1994 and 2004 near Alert, the SHEBA ice breaker in 1997/98, and the CASES project in 2003/4) suggests that coastal studies may not be representative for many processes occurring over the ocean. Given the intent of OASIS, it is very important to study the Ocean surface and exchange processes in the immediate environment in which they are occurring. This view is reinforced by GOME and SCIAMACHY data which suggest that much (but not all) of the active halogens may be concentrated over the ocean proper. Thus, appropriate logistics support will be critically important for the success of OASIS.

Use of remote sensing data is one avenue towards collecting data over a large geographical area that includes the Arctic Ocean. Snow physics and chemistry exhibit much greater spatial variability than atmospheric composition and, as indicated above, the lack of data over the ocean itself is acute. The use of satellite data may partly solve that problem, at least for snow physics. This will require, however, field validation studies before reliable relationships can be established between satellite signals and snow properties such as density, specific surface area, permeability and heat conductivity. The field is clearly at an embryonic stage, but the payoff undoubtedly justifies investing in the detailed interpretation of snow properties from remote sensing data

It is then the intent to undertake multiple intensive field experiments on the frozen ocean, covering multiple seasons. A primary objective of OASIS is to study the impact of sunlight on OASIS exchange processes. Thus many of the questions require measurements spanning the Fall, Winter, and Spring seasons. Snowpack conditions and loading are examined in the Fall, winter measurements are made as part of control measurements, and they are then followed by a focus on the Spring sunrise and full sunlit periods. A likely important approach avenue for such intensive studies is by making use of an ice breaker as a base from which relatively short term (days) ice camp studies are conducted. Fluxes of various species can then be measured from small towers, tethered balloons, blimps, and surface-based sampling of air and snow. Principal candidates in this respect include icebreakers such as the U.S. Polar class icebreakers and the Healy, the Canadian CCGS Amundsen, the Swedish Odin, the Russian nuclear icebreaker Yamal, and the German ice-enforced Polarstern. The Yamal is a preferred platform, as it avoids the difficult issue of contamination by diesel engine exhaust. Another approach

under consideration is the launching of a campaign on a dedicated ice camp. The Russian Arctic and Antarctic Research Institute has commenced planning for an ice island in 2007 (NP-34).

Studies over the frozen ocean are complicated and expensive. Clearly such studies will need to make optimum use of available resources, and be inclusive of all disciplines that have a stake in making observations over the ocean. The upcoming International Polar Year represents an exciting focal point for planning such a study. A well conceived year-long measurement campaign offers the possibility to produce a giant leap in understanding of the Arctic system, and create a lasting data base for future generations. Details of logistics for such a project will require coordination between/among many national organizations such as the US/NSF OPP Arctic Research Support and Logistics Program, the Canadian/NRCAN Polar Continental Shelf project, the Swedish Polar Research Secretariat, the Norwegian Research Council, the French CNRS, and Italian CNR.

C. Technical Considerations, Instrument Development

1. Clean power

The usual procedure of power generation at a remote location involves some form of diesel power generation. Unfortunately, an unwanted byproduct is the concomitant waste production and hence self-pollution, both in terms of chemicals (NO_x, VOCs, SO₂, CO) and heat. It is therefore essential to investigate alternative strategies. Alternative power generation might be considered from solar or wind driven generators but their generating capacity is limited. New, advanced technologies will be pursued but preliminary estimations on the efficiency of such strategies is not promising (see French station Corbell literature). Potentially promising might be the application of fuel cell technology. Progress is being made in Europe and North America, but to date performance under Polar conditions is unknown. Combinations of battery power, with hybrid wind and solar recharging may be a viable option for some measurements. Passive samplers, designed for the collection of semi-volatile organic contaminants (e.g. POPs), have now been used in a variety of field studies in both temperate and polar regions and

would provide a suitable medium to obtain time-integrated measurements (days/weeks) of atmospheric concentrations at remote locations such as Arctic sea-ice, without the need for electrical power.

2. Platform development

Because of the need for good spatial coverage at reasonable costs, there is considerable need for development of new sampling platforms. Among those being used and under development are blimps and tethered balloons, light aircraft, autonomous surface rovers, UAVs, and others. All these platforms can be operated over some distance from a centrally located base (a few kms) and will be considered since they allow measurements away from human interaction. The Arctic research community has explored many of these issues previously. We envision a period of 1-2 years of system shakedown and methods evaluation at appropriate land-based sites

To sample natural sources and interactions as outlined in section 4 of Part I, it will be necessary to operate well into the pack ice area between latitude 86-89°N during ice-melting conditions and high biological activity (i.e., August and early September) and for no less than 6 weeks in duration. Such a study will require combined ship/helicopter/kite/balloon/radio controlled boats and various on ice activities. Vertical mapping of boundary layer structure with respect to meteorology as well as gases, aerosols and cloud drops sampling will be accomplished with helicopter sampling; alternatively, in cloudy conditions, the deployment of a winch-operated, tethered aerodynamic instrumented balloon for semi-continuous vertical measurements may be considered. However, this requires on-ice deployment and large amounts of helium, and hence substantial logistical planning.

3. Instrument development

Pursuit of the objectives described above will require an array of measurements through time and the three dimensional space through and over the Arctic Ocean surface. Many of the species are present at trace levels in complex matrices, and reliable measurements in these environments are difficult. Obtaining data on the chemical and

biological state of the environment at remote locations poses several challenges.

Prominent among these are requirements for

- extreme sensitivity: many trace components are present at levels that challenge the analytical capability of even the most sophisticated instruments available today
- non-intrusive methods: most measurement techniques require some form of sample preparation before analysis is possible. Procedures may range from bringing a representative sample aliquot to an instrument on-site, to the collection of a sample for later analysis off-site. Unfortunately the mere fact of sampling usually alters and compromises the physical/chemical state of the analyte.
- fast response methods: fluid dynamics theory implies that surface exchange processes are fast and chaotic; as a result any flux measurements from one phase to another require fast response instrumentation
- Fast, reliable, robust, trace-level methods need to be developed, adapted and/or implemented for gas phase, particle phase, and snow phase chemical species, with emphasis on organic and toxic (e.g. Hg) species.
- Experiments in the Arctic add some specific challenges such as operation under extreme adverse weather conditions, in particular at low temperature; most currently available equipment is not designed to operate below 0 °C
- logistically difficult to reach locations, implying a desirability for extensive automation (in addition this will minimize self-pollution) and remote data transmission
- a need for low cost (expendable), low power measurement devices: much of what is known about the large extent of the Arctic ocean surface comes from remote sensing methods (satellites, aircraft studies). Ground truthing of these data is critical but is prohibitive with most currently available measurement methodology

D) Laboratory Studies

As throughout much of the troposphere, the fundamental chemistry of the gas-phase in the Arctic is considerably better understood than the chemistry of the condensed phase and of gas-surface interactions. A common factor in high-latitude, condensed-phase chemistry is ice, whether existing as frozen seawater, as suspended or precipitating ice particles, or as snowpack. However, what distinguishes the ice surfaces pertinent to the OASIS scientific goals from the likely clean ice that exists, for example, in the upper troposphere and lower stratosphere is its chemical complexity and heterogeneity. In the upper troposphere, the ice surfaces are probably relatively clean, with perhaps trace amounts of adsorbed nitric acid but probably low amounts of adsorbed halides and organics. By contrast, in frozen seawater, ice co-exists with solid salts or concentrated brines (*Cho et al.*, 2002) and/or organic flocs (*Krembs et al.*, 2002). Extremely saline constituents are the frost flowers that form routinely on ice. Furthermore, the snowpack and ice clouds have a high degree of deposited chemical species; for example, Arctic Haze consists, to a considerable degree, of sulfate aerosol that deposits on the snow surface, acidifying it, while all polar snow contains organic matter from the biosphere (*Grannas et al.*, 2004). Our understanding of the physico-chemical nature of these surfaces is at best rudimentary. Indeed, in many cases, we do not even know whether these contaminated ice surfaces are best described as liquids or solids. Aside from the sea-ice bottom communities, our understanding of the biological impact on these snow-ice-water surfaces is mostly speculative.

The overarching goal of the laboratory science portion of the OASIS program is to develop a sufficiently accurate fundamental knowledge of the chemistry and physics of these complex ice surfaces so that this information can be incorporated in a chemically-correct manner into a hierarchy of atmospheric models. We emphasize the need for the measurement of condensed-phase diffusion coefficients, the solubility and adsorption of trace species within ice and its surfaces, absorption cross-sections and photochemical quantum yields of dissolved and adsorbed species, and gas-surface and condensed-phase rate constants.

A primary scientific objective is the characterization of ice surface structure under conditions similar to what marine snow is subjected to, especially in terms of ion loading. Is it a liquid, briny surface, or is there just a liquid-like character? A QLL is not water,

but heavy ion loading may turn that surface to a true solution. If we prove that we have a true liquid surface, then modelers can apply liquid phase chemistry to marine snow surfaces, enormously simplifying the problem. It also facilitates lab work, as an acceptable surrogate for natural surfaces may then be just liquids. Thus the physical and resultant chemical nature of the water on the surface of ice is perhaps the most important question to be answered in laboratory studies.

1. The ice surface and gas-to-surface partitioning

Goal #1: It is known that many biologically and anthropogenically produced molecules present in the Arctic environment, including oxygenated, halogenated and sulfur-containing organics and pollutants such as sulfur dioxide and mercury species, adsorb to ice (Abbatt, 2003). *To what degree do these gas-phase species partition to precipitating ice particles and thus affect their gas-phase abundance? Is there sufficient partitioning that a “clean” ice surface does not exist in Arctic conditions?*

It is necessary to conduct ‘cold’ lab experiments for semi-volatile species such as POPs. To understand partitioning, mass transfer and diffusion under controlled snow conditions must be defined.

Goal #2: Considerable emphasis in the past has been given to cold ice studies, close to 200 K, to better characterize ice chemistry in the upper troposphere and lower stratosphere, and because this temperature makes high vacuum methods accessible.. *There is a distinct need for high temperature studies of ice chemistry ($240 < T < 273$ K), typical of Arctic boundary layer conditions, where the quasi-liquid layer on the ice surface is thickest.*

Goal #3: *Increased utilization of advanced instrumentation, such as environmental SEM and surface spectroscopy, is needed to study the physico-chemical nature of Arctic ice surfaces. In particular, the quantitative and fundamental understanding of the air-ice interface, and the physical and chemical reactive nature of the disordered (“quasi-liquid”) water at the surface of ice/snow grains is desperately needed.*

2. Reactive chemistry

Significant advances have been made in the past few years in demonstrating that halides present on ice surfaces or in concentrated brines can be oxidized (photochemically?) to liberate photochemically active halogens (*Abbatt, 1994; Adams et al., 2002; Oum et al., 1998*)

Goal #4: *Conduct similar studies with reaction substrates that more closely simulate those present in the Arctic, e.g. frost flower surrogates, and to systematically examine the impact of temperature, surface pH, and other surface constituents on the kinetics.*

Goal #5: *Laboratory studies should also be conducted on the gas/ice chemistry of the different forms of mercury, e.g. organic mercury and mercury halides.*

3. Condensed-phase photochemistry

There are now clear observations of photochemical activity within the snowpack, activity that gives rise to the release of both NO_x and small oxygenated organics (*Dominé and Shepson, 2002*). Our quantitative ability to model such processes is in its infancy and very much in need of dedicated laboratory studies. For example, the photochemical product yield of NO_x from nitrate photolysis in solution is significantly lower than that of NO_x release from photolysis of gas-phase nitric acid.

Goal #6: *What are the quantum yields of photochemical processes that occur at the quasi-liquid like layer surface of ice? These studies should be conducted with nitrogen oxides, mercury-containing species and small organics.*

A related, but prerequisite, question, is where on/in the crystal are the reactive chemical species? Are they on the surface to begin with? Nitrate may be on the surface on acidic snow, but not in alkaline snow (e.g. *Beine et al., 2003*). Hence the quantum yield may depend on overall snow composition. What is the effect of snow overall composition on the reactivity of species, especially ions?

4. Role of biology

Given that the Arctic ice environments are biologically rich, it needs to be determined whether biota can act as significant sources of both gases and particles to the atmosphere. Preliminary experiments can be done in the lab to investigate these processes.

Goal #7: *Is the photochemical production of small oxygenated organics in the snowpack biologically mediated to a significant degree?*

Goal #8: *What are the cloud condensation nuclei and ice nuclei properties of the large number of particles formed by bubble-breaking processes that occur on the surface of leads and open water?*

Goal #9: *Are biologically produced species, e.g. organo-iodine compounds, produced in sufficient amounts that their breakdown products lead to new particle formation events under Arctic conditions?*

Goal #10: *Does deposition of toxins, e.g. Hg, from the atmosphere significantly impact biological processes in the snowpack*

5. Snow physics

In the context of a changing climate, information is required about the evolution of snow physics as a function of changing environmental conditions. These data are essential for the development of a snowpack model (see below).

Goal #11: *How does the air permeability, the specific surface area and the heat conductivity of snow evolve during metamorphism*

E. Model Development

3D models will be developed to simulate the many different environments and address many of the questions that have been outlined above. As is noted below, this development has already begun. Initially, it will be important to extend and improve 1D and box models already in existence and adapt them to Polar environmental conditions. This applies in particular to snow chemistry, but gas phase and aerosol chemistry will also require modifications. These models will then form a core component of the more elaborate 3D models. It is not clear whether there will be a need for simplification of 1D models since it appears that, at present, computer power is further ahead than our knowledge base for input.

E.1 1D models

Boundary layer models.

For both meteorology and chemistry it is important to accurately well define the mixing in the marine or atmospheric boundary layer (MBL, ABL). Typically, 1D models incorporate turbulent vertical diffusion based on the turbulent kinetic energy (TKE) parameterization to diffuse chemical species and aerosols as well as heat and momentum. This formulation appears to work reasonably well for mid-latitudes, and over polynyas (*Mailhot et al.*, 2003) but it is clear that such models will not capture very stable conditions (*Hipkin et al.*, 2003). Hence extensive evaluations and modifications will be required.

Gas and aerosol chemistry modifications.

Comprehensive heterogeneous and gas-phase chemistry such as that for halogen and Hg species and reactions that are now known to drive ozone and mercury depletion (*Sander et al.*, 1997; *Calvert and Lindberg*, 2003) will be included. Aerosol modules should be capable of coping with the influence of Arctic temperatures and humidities and long periods of darkness and light, given recent laboratory experiments demonstrating that the presence of an ice phase can substantially alter the chemistry of many chemical species in the troposphere (*Huff and Abbatt*, 1997; *Oum et al.*, 1998; *Koop et al.*, 2000;

Adams et al., 20002, *Cho et al.*, 2002). The updated chemistry modules (see below) will be merged with the 1D model so that the contribution of chemical processing versus turbulent transport processes to a complete ozone/mercury depletion episode can be numerically resolved.

Snow layer models:

One of the most crucial components of the modeling system will be a snow layer model. The thermodynamic and dynamic attributes of the boundary layer also govern the deposition of aerosols and gaseous materials to the snowpack. The evolution of the physics and chemistry of snow interacting with other OASIS components must be parameterized. In this regard, the evolution of snow permeability, surface area, light attenuation, heat conductivity and snow chemical composition, with metamorphism, currently not in models for snow metamorphism will be considered. Again, in a next step the snow layer model (*Albert et al.*, 200X) will be added to the 1D model in order to define the important and necessary physical and chemical processes for inclusion in 3D models.

Ocean layer models:

Similarly to the atmosphere, mixing in the ocean does not only affect the temperature and salinity distribution, but also the vertical transport of organisms and chemical tracers. To simulate those accurately and evaluate the influence on gas and material exchanges at the ocean surface, coupled ocean-biogeochemical models are indispensable. A variety of these models are already in use, mainly differing in the complexity of the applied ecosystem model (e.g. Denman and Pena 2002; Denman 2003; Monahan and Denman 2004, Lancelot et al ?, Yoshie et al 2004). Another example in the public domain is the General Ocean Turbulence Model GOTM (www.gotm.net), designed to accurately simulate vertical exchange processes in the marine environment. GOTM developers are currently working on the addition of an ecosystem model, to be released by December 2004. GOTM has already been successfully used to study DMS fluxes and ecosystem responses by individual users (e.g. LeClainche et al., 2004; Steiner et al., 2005). Application of coupled ocean-biogeochemical models in polar regions is

very limited (true??? ref?). Further efforts are required towards the adaptation of ecosystem components to polar environments, and improve the ice-snow compartment. Simple ice models are not sufficient. To evaluate gas transport through and within the ice it is necessary to account for

- 1.) the physical evolution of brine channels (aging),
- 2.) the chemical composition and reactions within the brine (e.g. CaCO₃ precipitation), and
- 3.) the biological growth and decay of ice algae (e.g. Lavoie et al 2004).

Synthesis

To be able to simulate gas and material exchanges at the atmosphere-ocean/ice/snow interface, the final step will be to couple the atmospheric boundary layer model to the ocean-ice-snow-ecosystem component. Although partial component combinations have been coupled to the atmosphere (Steiner et al.) a fully coupled 1-D-OASIS model does not exist, and will be emphasized within the OASIS modeling efforts. Such a model will allow for numerical studies on fluxes of DMS, CO₂, halocarbons and other active and inert gases like O₂, N₂ etc. It will also provide a tool to test hypotheses on sea-air fluxes of organic particles, which have been found to contribute significantly to cloud forming aerosols, and surface triggered atmospheric reactions (e.g. frost flowers and their effect on Br₂ formation and consequent ozone destruction).

E.2 3D models and experiments

3-D model building

A logical progression from 1-D to 3-D models will enable us to obtain a more complete ecosystem-wide picture of the Arctic environment and the role of OASIS

processes. Several excellent 3-D chemical transport models exist (3-D CTMs), but these models will require substantial modifications (as outlined above) to make them suitable for Arctic applications. Work of this nature has begun with several groups (e.g. the Danish DEHM model, GEM-AQ in Canada, the GEOS-CHEM- MM5 (polar version)).

There are a variety of coupled ice-ocean models (e.g. AOMIP) as well as atmosphere-ice-ocean models (ARCMIP) available. Based on 1-D-model developments those models can be extended to include ecosystem components that are applicable for polar regions. Although computer resources are still a limiting factor for 3D models in terms of complexity, especially with respect to ecosystem components, the addition of the horizontal component will add important information on transport processes both in the atmosphere and ocean.

3-D model experiments

3D models can be applied to verify the source attribution based on chemical fingerprinting, and delineate the prevailing transport routes of pollutants to and from the Arctic. This will then allow us to place the data obtained at the few Arctic chemical observatories in an Arctic wide context, and determine the seasonal variations in sources and transport routes. The prevailing transport routes from Asia to North America and from North America to Europe are believed to be via the Pacific and Atlantic oceans. However, there is evidence that Eurasian pollution is transported via the Arctic to the North American continent (Bottenheim et al., 2002c; Honrath et al., 1996; Hamlin and Honrath, 2002). This process will be studied in detail, and quantitative estimates of its importance will be made.

3-D dimensional models as planning tools:

3D models will have the feature of being operable in a forecast mode. Once developed and evaluated, they will be particularly suitable as a tools to plan future research endeavors in the Arctic, especially for the planning of the OASIS.

