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Ocean-Atmosphere-Sea Ice-Snowpack Interactions in the Arctic, and Global Change

PAGES 349, 355

The discovery of the nature of Arctic haze in the late 1970s and early 1980s [*Barrie*, 1986] showed that the Arctic is not a pristine environment isolated from human activity, but rather, a region well connected to natural and anthropogenic sources of chemicals by winds, ice movement, and marine currents. Copious pollution is carried on the winds to the Arctic during winter and spring from Europe and northern Asia. The study of this phenomenon led serendipitously to the discovery of ozone depletion chemistry in the Arctic marine boundary layer (MBL) at polar sunrise [*Oltmans*, 1981; *Bottenheim et al*., 1986]. In turn, research to understand surface ozone depletion chemistry led to the discovery that it is perturbing the biogeochemical cycle of many elements such as mercury; and that ozone depletion chemistry is likely to have a significant impact on radiative transfer in the atmospheric layer near the surface, with important consequences on the air-sea exchange of biologically-mediated compounds.

Surface layer ozone depletion has now been observed all around the Arctic. It frequently extends from the surface up to 1–1.5 km altitude, with ozone concentrations depleting from background concentrations of ~40 ppb to as low as ~0.050 ppb [*Bottenheim et al*., 2002] (Figure 1). The discovery of the phenomenon of surface ozone depletion in the Arctic has opened a window on a significant deficiency in our understanding of chemistry involving gas-surface interactions. In particular, the global sinks for ozone, an important "greenhouse" gas, a respiratory irritant, and a phytotoxic species—yet an essential atmospheric oxidant at the same time—generally do not include halogen atom chemistry or halogen biogeochemistry.

BY PAUL SHEPSON, PATY MATRAI, LEN BARRIE, AND JAN BOTTENHEIM

Role of Snowpacks and the Sea Ice Surface

Field measurements of particle phase bromine and gas phase BrO radicals have led to the conclusion that ozone is depleted by an efficient chain reaction involving bromine and chlorine atoms in the sunlit Arctic MBL [*Barrie and Platt*, 1997], at least at the time of polar sunrise. It is now known that Br_2 and BrCl are produced in and emitted from sea salt-laden ice and snowpack to the atmosphere in the Arctic Ocean region, where they can photolyze yielding Br and Cl atoms [*Foster et al*., 2001]. In fact, over the past decade, there has been a wide array of observations documenting significant chemical species exchange among snowpacks, sea ice, and the atmosphere. A number of highly photochemically active

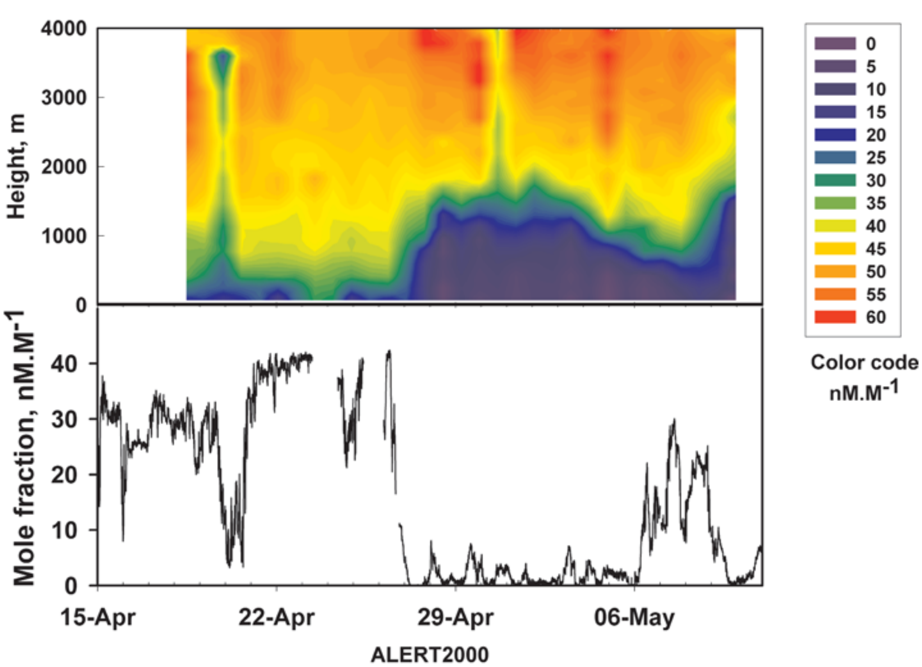

Fig. 1. O_3 vertical profile for a 3-week period at Alert, Nunavut, Canada during the ALERT2000 study. Top: vertical profile of ozone, from ozone sonde; Bottom: surface ozone data from GAW station.

Fig. 2. Frost flowers (Courtesy of Don Perovich, CRREL).

gases (e.g., formaldehyde, oxides of nitrogen, and molecular halogens) [*Dominé and Shepson*, 2002] are emitted from sunlit snowpacks into the overlying atmosphere. These species are important free radical precursors that influence the oxidizing capacity of the atmosphere. Although we have learned much in the past 5 to 10 years, this area of inquiry still represents one of substantial unknowns and of environmental importance.

It has long been known that convective mixing above open leads—long breaks in the sea ice—injects heat, water vapor, and sea salt aerosol as much as several kilometers into the atmosphere. This would imply an important source of the halogens involved in springtime ozone depletion, but it is also known from satellite BrO retrievals that ozone depletion seems to occur over completely frozen surfaces. An intriguing possibility is provided by frost flowers, which not only present a high surface area medium for heterogeneous chemical processes, but may also be an important mechanism for sea salt aerosol generation, from wind-driven dispersion. Frost flowers are high surface-area, dendritic, and highly saline (~100 PSU) crystalline structures (Figure 2) that grow in clumps on the surface of re-frozen leads, resulting from vapor deposition and the strong temperature gradients across the first few centimeters of the surface-atmosphere interface.

There is considerable speculation in the literature about the importance of these structures to air-surface exchange. Access to the surface of re-frozen Arctic Ocean leads for sampling and vertical profile measurements across appropriate spatial scales represents a significant logistical challenge for the near future.

Role of Biological Processes

The snowpack, sea ice, and lower atmospheric processes discussed earlier occur above a biologically active and vital Arctic Ocean. Biological processes result in the production of organic matter in sea water and sea ice. Biological, physical, and chemical processes break down the organic matter, releasing it to the surfaces discussed, where it becomes an important reactive component in photo-oxidative processes, followed by substantial exchange of gas and particle phase organic and inorganic material between the ocean and the overlying atmosphere. One early hypothesis regarding ozone depletion at polar sunrise involved photolysis of bromoform, which produces reactive bromine atoms [*Barrie and Platt*, 1997]. Bromoform is emitted by both macro-algae (e.g., kelp) and micro-algae (e.g., ice algae) [*Cota and Sturges*, 1997]. Once the biological emission and photolysis of bromoform initiates the chain reaction that destroys ozone, that process may accelerate via heterogeneous reactions, such as those that occur on snow and ice surfaces involving oxides of chlorine and bromine.

A wide variety of other volatile organic compounds is emitted from the Arctic Ocean surface; however, the biogeochemical cycles and fluxes of these species are poorly characterized. Among them, methyl bromide is an important global source of bromine to the stratosphere, methyl nitrate is a ubiquitous component of atmospheric reactive odd nitrogen, and dimethyl sulfide—emitted as a direct product of marine planktonic and sea ice algae food web processes [*Leck and Persson*, 1996]—is an important source of sulfate aerosols that affect climate through scattering of radiation. Emission of biogenic particle precursors, such as amino acids; pre-formed biogenic particles, such as bacteria, phytodetritus, and viruses [*Leck and Bigg*, 1999]; and organo-iodide compounds, that may be likely particle precursors in the Arctic, has been observed. Bubble-bursting at the ocean surface may cause injection of these and other biogenic organic compounds from the sea surface micro-layer that can be oxidized by atmospheric processes, including those induced by halogen atom chemistry, to produce cloud condensation nuclei.

On the other hand, deposition of toxins (e.g., Hg, pesticides, herbicides, and their oxidation products), micro-nutrients, and organic matter from the atmosphere to the surfaces is equally likely to affect chemical reactions on these surfaces, perhaps changing the bio-availability or toxicity of the material and potentially affecting any biogenic emissions. It seems that although we have identified a variety of mechanisms for coupling between marine biological processes and the atmosphere's chemical and physical properties, our ability to make progress in this area is hampered by the lack of interaction between the Arctic biological and the atmospheric research communities.

A Role for Anthropogenic Inputs?

The phenomenon of surface ozone depletion raises the question as to how global change and anthropogenic inputs may affect this process, or what impacts there are on society. Inputs of SO_2 from fossil fuel burning in North America, Europe, and Eurasia lead to production of highly acidic sulfate aerosol that represents much of the particulate matter associated with Arctic haze. This aerosol, along with HNO_3, deposits to the snowpack surface, and influences the effective pH of the reactions that recycle halogens into molecular bromine. However, the pH dependence of this chemistry is not well understood to date; and our understanding of these processes is limited by our ability to determine the compositional morphology of snow and ice grains, and to make measurements of the composition of sea ice, snow, and particulate matter. This is especially true for the biologically-derived, organic content of all of these phases.

The research community has just begun to think about coupling between the natural chemical system in the Arctic and anthropogenic inputs. The discovery of mercury depletion and deposition of its oxidation products to the surface [*Lu et al.*, 2001], where they may be available for humans and other organisms, is a strong motivator to understand such relationships. To better evaluate connections between anthropogenic inputs and natural air-surface interactions, a series of models needs to be developed, from 0-dimensional photochemical models to hemispheric scale chemical transport models to global climate models. This process is in its infancy.

In a broader perspective, it is well established that the Arctic atmosphere is changing, and that there are significant feedbacks between climate change, and the Arctic system on the macro-scale (e.g., the sea ice albedo feedback and changes in snowpack/sea ice/open water extent) and the micro-scale (e.g., the snow/ice surface water layer) levels. The snow/ice surface is known to have a "quasi-liquid" surface layer, the thickness of which is highly temperature-dependent. A variety of reactive species exists largely in this layer, and their chemistry is thus likely very temperature-dependent, both because of reaction kinetics and snow/ice micro-physics. The now well-documented sea ice extent change [*Comiso*, 2002] and the concomitant change from sea ice to more open water will dramatically alter the surface heat budget in the Arctic Ocean region, affecting boundary layer turbulence and mixing, and thus, the exchange of gases among the ocean, the sea ice/snowpack, and the atmosphere. Changes in sea ice/open water extent will also alter the marine biological productivity, which in turn affects gas exchange rates, affecting the recycling of pollutants through the snowpack and snowpack photochemistry. Our ability to document relationships between climate change and Arctic atmospheric composition and chemistry is substantially dependent on the availability of resources to develop and maintain long-term monitoring in the Arctic.

Recent data have provided more information about halogen- or other chemically-mediated air-snow interactions and chemistry than about similar processes in the sea ice, or the magnitude of any biological mediation, or of the relative roles of open versus frozen water in related fluxes. All of these interconnected processes have led to a complex picture (Figure 3) of the interplay among gas phase photochemistry, ice surface chemistry, marine biological processes, and reactions on/in aerosol particles·

Proposal for an Integrated, International Study of Ocean-Atmosphere-Sea Ice-Snowpack Chemical Exchange

In November of 2002, a workshop (http://www.chem.purdue.edu/arctic/ArcticWorkshop.htm) was convened at Purdue University, aimed at bringing together a cross section of Arctic researchers, covering the ocean, biosphere, sea ice, and atmosphere domains. The objective was to identify the overarching outstanding issues, and to identify viable approaches to pursuing those issues. Arising from that workshop is a proposal to pursue an international, coordinated effort aimed at a better understanding of Arctic Ocean-atmosphere-sea ice-snowpack (OASIS) chemical exchange, its impacts, and its relationships and feedbacks to climate change in the Arctic.

The Arctic OASIS project proposes the following objectives:

1. Understand the solar influence on physical, chemical, and biologically-mediated exchange processes in the OASIS region involving halogens, NO_x, O_3, VOCs, POPs, Hg, S-species. and CO_2 in the Arctic, and links to climate change.
2. Understand the influence of OASIS exchange processes on physical and radiative characteristics of clouds and hence, on climate.
3. Determine the impact of past changes of environmental pollution on OASIS chemical exchange as part of the development of a capability to predict future change.
4. Determine the impact of changes in ice cover characteristics and temperature on OASIS chemical exchange, and associated feedbacks on climate.
5. Determine the impact of OASIS chemical exchange on tropospheric chemistry and climate, as well as on the surface/biosphere and their feedbacks.

OASIS would be pursued through a series of:

• laboratory studies of the fundamental biotic and abiotic processes;
• field studies focusing on measurements of chemical exchanges among the atmosphere, ocean, and various frozen surfaces at various temporal and spatial scales; and
• development of a series of 0–3 dimensional models that provide the conceptual framework for experimental design, and can be used to quantitatively test our understanding of complex interactions on a range of scales.

A 5- to 10-year effort is envisioned. The proposed OASIS project will be the first Arctic research effort under the international Surface Ocean-Lower Atmosphere (SOLAS) program, and will also be coordinated with the IGAC Air-Ice Chemical Interactions (AICI) project. Interested parties should contact the authors.

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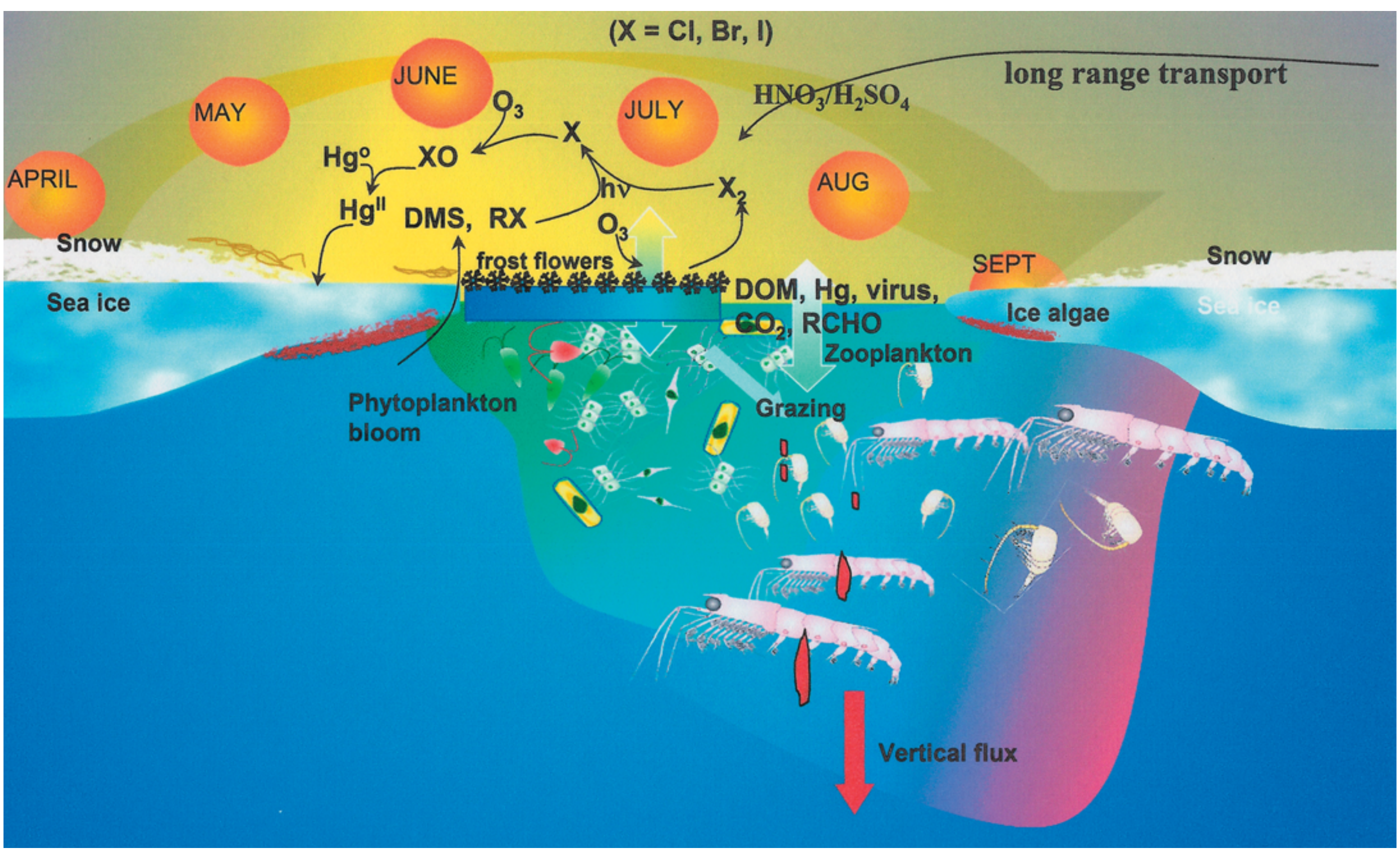

Fig. 3. Arctic OASIS complexities. Redrawn from a figure by M. Fukuchi and P. Wassmann.

beginning stages of this research plan, and this article possible. The list of participants can be found on the Web site listed above. We would also like to acknowledge the Arctic System Science (ARCSS) Ocean-Atmosphere-Ice Interactions (OAII) SSC for their encouragement.

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New Mexico Votes for Strong Science Education Standards

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On 28 August, the New Mexico State School Board voted unanimously to adopt science education standards which keep biological evolution as a centerpiece of scientific knowledge. The school board voted 13–0 for the standards, which were strongly endorsed by scientific and educational organizations. This defeated efforts by intelligent design creationists to insert alternate language downplaying the treatment of evolution in the curriculum.

Scientists in New Mexico helped develop the standards and stayed active in defending them against the creationists. Numerous scientific organizations, including AGU, signed letters in support of the standards, and urged the school board members to cast a skeptical eye on a recent poll conducted by creationists purporting to show New Mexico scientists' support for intelligent design. When the standards are implemented, they will form the basis for annual performance requirements demanded of students from kindergarten through high school.

—Peter Folger, Public Affairs Manager, AGU Headquarters, Washington, D.C.

Space Infrared Telescope Could Provide New Insights into Some Solar System Objects

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NASA's Space Infrared Telescope Facility, which launched on 25 August, promises to open windows about objects within our own solar system, as well as provide a better understanding about galactic and intergalactic objects and phenomena and the early universe.

The infrared observatory offers new capabilities to explore and characterize aspects of the solar system which cannot be observed from the ground, including some Kuiper Belt objects, distant planets and satellites, asteroids and comets, and interplanetary dust, according to SIRTF solar system observations scientist Victoria Meadows. The observatory could provide new insights into specific targets through the enhanced observational sensitivity and new measurement capabilities it offers at the 3–180 micron wavelengths.

"There is a sense that we are pushing the frontiers out into the universe, but we are also pushing the frontiers of our own solar system, and understanding the extent of this place we live in, which still holds several mysteries for us to unravel," Meadows said.

"We fondly refer to SIRTF as being able to look at 'the old, the cold, and the dirty.' Normally, that is applied to the galactic and extra-galactic, meaning we can see the distant universe, and we can see things shrouded in dust. But that [capability] also applies to our own solar system." Meadows added. In the analogy, she said smaller and primordial fragments of the solar system are 'the old,' far away objects like those in the Kuiper Belt are 'the cold and the old,' and low albedo objects difficult to see at visible wavelengths are 'the dirty.'

After SIRTF completes its in-orbit checkout and science verification period, one of the observatory's initial scientific observations is a 21 January 2004 First Look Survey, which has galactic, extra-galactic, and ecliptical plane components. Meadows, who is lead scientist for the ecliptic plane component of the survey, said the project will provide a better understanding of the main belt asteroid population down to a size of a few hundred meters across. Of the approximately 10,000 known asteroids, just 4% have measured diameters and albedos, she said. The survey also will help to determine whether the asteroids are compositionally different from each other, Meadows added.

SIRTF is not able to observe the Earth and other bodies relatively close to the Sun, because they are too big, too close, or too hot for an observatory designed to study faint objects. However, more distant planets, including Neptune and Uranus, are among the targets Meadows and other planetary scientists are interested in exploring through the observatory.

With no planned space missions to Neptune and Uranus, "SIRTF is basically going to be the only show in town as far as understanding this particular wavelength region [is concerned] and what is happening with these planets right now." She said giant planets have many time-variable phenomena, including atmospheric structures that come and go in time. Uranus, she noted, currently is tilted almost 90° to the ecliptic and may have some very unusual weather.

Kuiper Belt Objects A Major Target

Dale Cruikshank, a SIRTF interdisciplinary scientist for planetary science with the NASA Ames Research Center in Moffett Field, California, said that Kuiper Belt objects could become one of the targets of greatest interest.

Cruikshank, who has been working on SIRTF since the mid-1980s, said the bulk of Kuiper Belt thermal emissions at about the 100 micrometer wavelength cannot be detected from the Earth. He said detection of these objects can provide information about their dimensions and surface albedos, diverse dynamics, and possibly space weathering, and whether any may or have been active by devolitalizing similar to the behavior of ordinary comets. Cruikshank said that while this activity is conjectural, in space exploration, he has learned to be prepared for surprises.

"The Kuiper Belt is the birthplace of about half of the comets that come our way," said Cruikshank, who is devoting about half of his 100 hours of guaranteed observing time to