IGAC*tivities*
Newsletter
of the International Global Atmospheric Chemistry Project

A Note From the IGAC Chair
Guy Brasseur

Urban Pollution and the Global Atmosphere

A recent issue of the World Meteorological Bulletin (published by the World Meteorological Organization in Geneva) highlights the importance of urban sources for *global* atmospheric pollution. "It is clear", states the paper, "that urban activities, taken collectively, have a profound impact on the environment *at all scales*. It is also clear that the environmental problems at the various scales are closely linked."

In 1950, only New York City had a population of more than 10 million. By the turn of the next century, 24 cities will have populations exceeding 10 million, and almost 50 percent of the world's population will reside in urban areas.

The development of mega-cities, especially in Asia and South America, has already produced substantial changes in the chemical composition of those regional atmospheres. Future growth in population and accelerated urbanization will exacerbate this situation. What should be investigated soon is the impact of urban development on larger (hemispheric or even global) scales. This requires a better understanding of intercontinental transport and of the chemical evolution of air masses as they travel around the Earth. Very interesting studies have already been performed within the IGAC framework under the *North Atlantic Regional Experiment* (NARE), *East Asia/North Pacific Regional Experiment* (APARE), and other Activities. Despite their remoteness, the polar regions, and especially the Arctic, are at the receiving end of transported pollutants. In this issue of IGAC*tivities* you will read about some of the exciting results of research conducted under the auspices of IGAC's *Polar Atmospheric and Snow Chemistry* (PASC) Activity over the past several years.

IGAC's role is not to study urban air quality nor to propose abatement policies to reduce urban pollution. However, as the urban factor becomes an increasingly large perturbation to the Earth system, IGAC will work more closely than in the past with other international organizations such as EUROTRAC and NARSTO whose traditional role has been to assess the impact of urban sources on the atmosphere of the industrialized regions of Europe and North America, respectively.

The link between regional and global problems clearly deserves more attention in the future.

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The Polar Atmospheric and Snow Chemistry (PASC) Activity

Contributed by **L. A. Barrie**, *Atmospheric Environment Service, Canada, and* **R.J. Delmas**, *Laboratoire de Glaciologie et Géophysique de l'Environnement du CNRS, St. Martin d'Heres, France*

The polar regions (Figure 1) play a key role in the sustenance of a habitable environment on planet Earth. Since the formation of IGAC in the early 1990s a group of 21 scientists[1] from 14 countries has worked to coordinate polar tropospheric and snow/ice chemistry research via the PASC Activity of IGAC. Environmental issues addressed include Arctic Haze pollution, tropospheric ozone depletion chemistry, the relationship between the chemical composition of the atmosphere and glaciers, and changes in atmospheric composition since industrialization. Ice records play a unique role in current atmospheric chemistry research, particularly in understanding the link between atmospheric chemistry and climate, a major environmental issue.

The scientific goals of PASC are to:

- understand the role of tropospheric chemistry of the polar regions in global change

- detect, by atmospheric measurements or with the aid of ice records, natural or human-induced changes of the polar atmospheric environment

The foci of PASC are:

- the origin, transport and transformations of gaseous and particulate compounds in the high latitude troposphere

- mechanisms of exchange of atmospheric species between atmosphere and snow

- the composition of shallow glacial firn and ice that provide records of atmospheric chemical change over the last several centuries

Individual country and multi-national studies are continuously being undertaken in the polar regions.

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The role of the PASC committee is to:

- identify knowledge gaps in polar atmosphere and snow chemistry

- plan studies of the polar troposphere and of snow chemistry relevant to global change

- encourage coordinated efforts to fill knowledge gaps that cannot be addressed by individual initiatives

- summarize progress in research

In this IGAC newsletter, we wish to highlight some of the exciting new discoveries that have been made. We begin with an account of the discovery of an "ozone hole" near the ground over sea-ice that occurs in the cold, sunlit environment at polar sunrise (article by Barrie, Platt, and Shepson). This has provided a wonderful natural laboratory for photochemistry studies, yielding knowledge that is generally applicable to solving air pollution problems elsewhere. Furthermore, halogen chemistry associated with ozone depletion can enhance the input of mercury—one of the most potentially toxic metals in the environment—to polar ecosystems (article by Schroeder and Barrie). Sea salt halogens drive the ozone and mercury depletion. Previously, it had been thought that the only source of sea salt to ice–covered polar regions was the transport of sea salt aerosol generated by white caps on ice–free ocean waters surrounding the poles. The recent discovery that sea ice within the polar regions is an additional source of sea salt even under very cold conditions (article by Wolff and Martin) sheds new light on the availability of sea salt halogens for atmospheric chemistry.

Because the sun is low to the horizon near the poles, the spectrum of sunlight that influences atmospheric chemistry differs from that at lower latitudes. This is addressed by Jaffe, Herring, and Madronich.

In the wake of deep drilling operations by Americans (GISP 2) and Europeans (GRIP), international field experiments have been conducted around the Summit site in Greenland (ATM Camp and GRIP drilling site). In the Antarctic, long-term coordinated atmospheric studies have been developed at three coastal stations. Combined with deep drilling activities in central Antarctica, studies of post–depositional changes affecting chemical profiles are conducted at sites with very low snow accumulation rates.

One notable product of this research has been the measurement of the atmospheric composition of the middle to upper troposphere for a whole year at
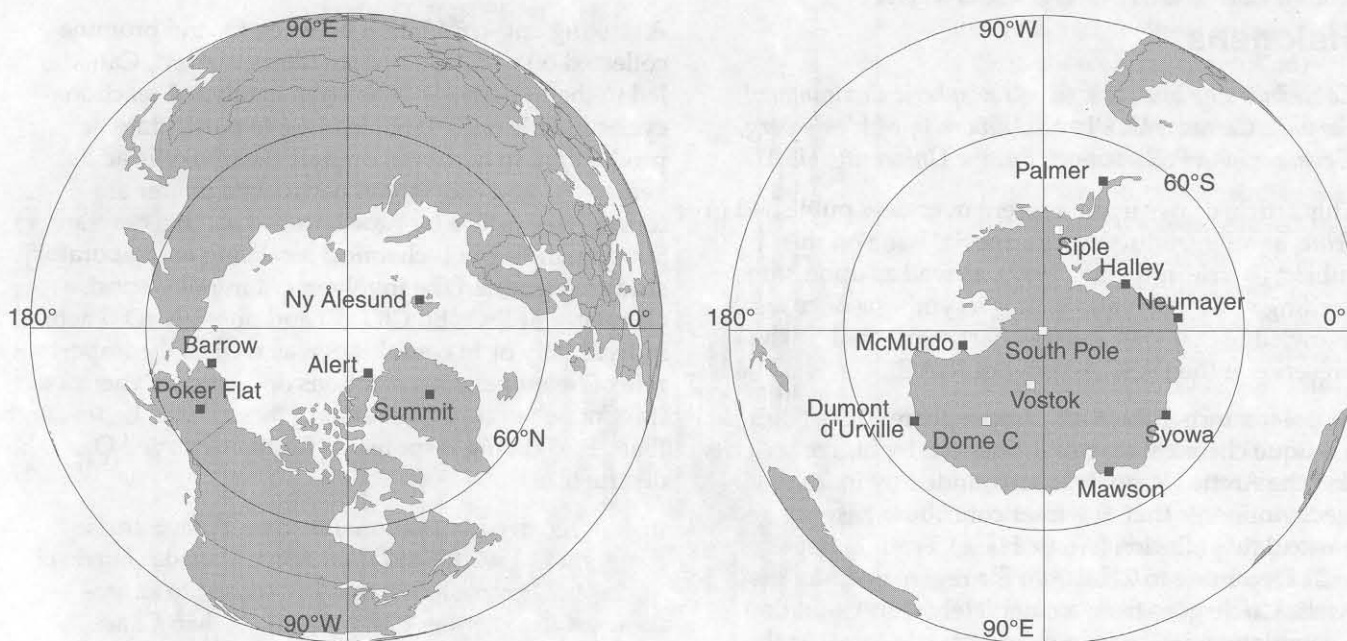
Figure 1. The polar regions and locations of tropospheric chemistry research stations and glaciers.

Summit, a high elevation (3.4 km) Northern Hemisphere location. Another product has been a better understanding of the complexity of air–surface exchange of chemicals. Heterogeneous gas–surface reactions at the atmosphere–snow interface are playing a key role not only in influencing lower tropospheric composition but also the transfer of chemicals from the atmosphere to glacial snow and ice.

The various processes that can affect the ice record of aerosols and trace gas compounds are summarized in the paper of Delmas, Jaffrezo, Dibb, and Bales. Two NATO workshops held in 1993 and 1995 reviewed the issue of the air-to-ice transfer function. What is emerging is that, for many substances, chemical reactions at the air–surface interface as well as post–depositional transformation in snow and ice at depth are more complex than has often been assumed.

Trends in glacial ice composition since the industrial revolution are perceptible at both poles. Greenland glaciochemical studies are yielding new insight into the recent changes of the chemical composition of the Northern Hemisphere atmosphere. They are of particular interest for IGAC Activities related to aerosol composition and oxidation capacity of the atmosphere. The paper on trends (Delmas and Legrand) addresses this issue.

Organic constituents in polar air and snow were uncharacterized until recently. Polar researchers have begun to study them in the atmosphere, snow, and ice (article by Kawamura, Legrand and Cachier). Organic aerosols are products of ozone depletion chemistry that can be useful tracers of organic marine, anthropogenic, and biomass burning aerosols. They are prone to post–depositional effects that are poorly understood.

In the next ten years, polar research will be stimulated by a growing community of satellite remote sensing instrumentation, a highly qualified, experienced, young scientist population, and enhanced awareness by governments that polar–region processes cannot be neglected in the global change equation. Furthermore, there will be numerous opportunities for field research. In the Arctic, atmospheric chemistry studies at Alert, Canada, and Ny Ålesund, Spitsbergen, will continue. Furthermore, surface experiments in the polar night on the central Greenland plateau are planned for ATM. In the Antarctic, the ongoing program mentioned above in coastal areas and at central drilling sites will continue, complemented by the shallow coring effort coordinated by the Scientific Committee for Antarctic Research (SCAR) in central Antarctic regions. PASC will work closely with other IGAC activities, other IGBP program elements such as PAGES (Past Global Changes) and WCRP projects such as SPARC (Stratospheric Processes And their Role in Climate).

Surface Ozone Depletion at Polar Sunrise Fueled by Sea-Salt Halogens

Contributed by **L. A. Barrie**, *Atmospheric Environment Service, Canada*, **U. Platt**, *University of Heidelberg, Germany*, and **P. Shepson**, *Purdue University, USA*

This article draws upon a recent overview published in *Tellus* as an introduction to a special issue on this subject (Barrie and Platt, 1997), as well as upon some exciting new observations. It is a synthesis of current knowledge that was, in large part, promoted by the presence of the PASC Activity of IGAC.

At polar sunrise, the Arctic troposphere (0 to ~8 km) is a unique chemical reactor influenced by human activity and the Arctic Ocean. It is surrounded by industrialized continents that in winter contribute gaseous and particulate pollution (Arctic Haze). From 21 September to 21 December to 21 March, the region north of the Arctic Circle goes from a completely sunlit situation to a completely dark one and then back to light. At the same time, the lower troposphere is stably stratified. This hinders vertical mixing and dry deposition of atmospheric chemicals. Since precipitation rates in the high Arctic winter and spring are very low (approaching desert conditions), removal of atmospheric chemicals by snow is relatively slow. Thus, it is not surprising to find a relatively high abundance of photochemically reactive compounds and aerosols in the atmosphere at polar sunrise. However, there are exceptions to the rule of slower reactions in the Arctic troposphere than farther south. Perhaps the most sensational is the destruction of lower tropospheric ozone (O_3) accompanied by the production of bromine and iodine compounds collected on filters.

About fifteen years ago, tropospheric O_3 depletion at polar sunrise was observed by Oltmans and Komhyr (1986) at Point Barrow, Alaska, and by Bottenheim *et al.* (1986) at Alert, Canada. The depletion was subsequently linked to particulate Br formation at polar sunrise by Barrie *et al.* (1988). Since then ground-based, balloon and aircraft observations have confirmed that O_3 depletion in the surface-based inversion layer over the Arctic Ocean is widespread (e.g., Solberg *et al.*, 1996; Hopper *et al.*, 1998). There are strong indications that similar O_3 surface destruction occurs at polar sunrise in Antarctica. Apparently, O_3 depletion only occurs after polar sunrise during the period mid-March to the end of May when sunlight is present and the Arctic Ocean is still frozen. Ground-based O_3 mixing ratios decrease from the mid-winter mean of 30 to 40 ppb to <1 ppb. This process appears to have few or no parallels in other parts of the troposphere except in the Antarctic. Although it is believed to have natural causes, Arctic Haze sulfate aerosols and gaseous pollutants advected from Europe, Russia, and, to a lesser extent, North America may also contribute.

A striking anti-correlation between O_3 and bromine collected on cellulose aerosol filters at Alert, Canada, led to the hypothesis of halogen-catalyzed reaction cycles [Barrie *et al.*, 1988] leading to particulate Br production. In addition, organic dicarboxylic acids, ketoacids, and dicarbonyl particulate matter are formed (see article by Kawamura *et al.*, this newsletter). Subsequently, photochemical modeling and laboratory studies suggested the involvement in polar sunrise chemistry of BrO/Br, ClO/Cl and possibly IO/I acting individually or in combination as well as the important role of heterogeneous reactions on ice or acid aerosols (McConnell *et al.*, 1992; Fan and Jacob, 1992; LeBras and Platt, 1995) being responsible for the observed O_3 destruction.

In an intensive international study—Polar Sunrise Experiment 1992 (PSE92)—at Alert, Canada (Barrie *et al.*, 1994a), it was shown that in contrast to stratospheric O_3 depletion, Br atoms rather than Cl are responsible for most of the O_3 destruction (Jobson *et al.*, 1994) and that BrO was unequivocally present in the lower Arctic troposphere (Hausmann and Platt, 1994). The time for complete removal of O_3 is on the order of days. A schematic of the O_3 destruction process involving sea-salt on the ocean ice surface and atmospheric aerosols is shown in Figure 1.

PSE92 raised questions about the chemical mechanism of tropospheric O_3 loss, the role of halogen oxide radicals and anthropogenic chemicals in this phenomenon, and the environmental consequences of O_3 loss. One unforeseen consequence is the enhancement of mercury inputs to the polar regions (see article by Schroeder and Barrie in this newsletter). A key outstanding issue was the source of reactive halogen species (RHS). The observation that total bromine (i.e., sum of inorganic and organic gas-phase Br compounds and aerosol Br) increases during low O_3 events in the Arctic troposphere rules out the redistribution of Br between different species as a source (Barrie *et al.*, 1994b). Rather volatile, short-lived bromine compounds must be released from a reservoir that is otherwise inactive as a source of gaseous atmospheric bromine.

Two possible sources of RHS during Arctic spring are: (i) degradation of organohalogen compounds of anthropogenic or natural origin, or (ii) liberation from sea-salt either in the aerosol or on the Arctic Ocean ice surface. Due to the relatively long photolysis lifetime of the most abundant gaseous organohalogens (e.g., CH_3Br, $CHBr_3$, $CHBr_2Cl$) under polar springtime conditions, the first source is unlikely. The measurement of total photolyzable bromine by Impey *et al.* (1997) indicated that it is most likely the case that the

OZONE AND MERCURY DEPLETION
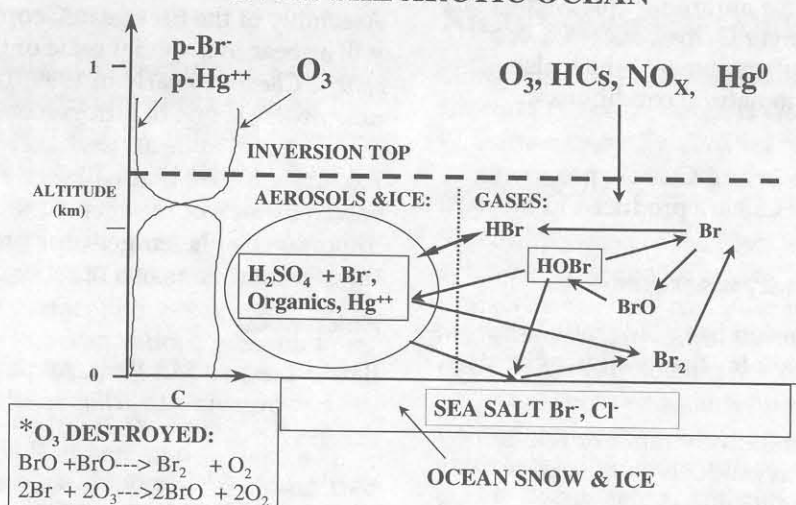## OVER THE ARCTIC OCEAN

Figure 1. A schematic depicting the complex chemical processes that lead to O_3 and mercury destruction over sea-ice covered cold regions after polar sunrise (for the mercury story, see the article by Schroeder and Barrie in this newsletter).

bromine atom precursors are derived from the ocean (or snowpack) surface.

Strong evidence is now emerging to show that atmospheric reactions involving oxidants lead to autocatalytic liberation of reactive bromine from sea-salt (containing by weight 55.7% Cl, 0.19% Br, and 0.00002% I) that can be released to the atmosphere as gaseous reactive halogen species (e.g., Cl_2, Br_2). Proposed reaction sequences involve NO_y species (Finlayson-Pitts et al., 1990; Behnke et al., 1997), HOBr, HOCl, or other oxidants such as H_2O_2. However, recent measurements of NO_x in the Arctic seem to rule out nitrogen species (e.g., N_2O_5) as the oxidant. Once a catalytic reaction cycle has started, there is an exponential growth of the RHS concentration: a 'bromine explosion' (Platt and Lehrer, 1996).

In order to address outstanding questions raised in PSE92, the ARCtic Tropospheric O_3 Chemistry (ARC-TOC) project was organized by European scientists. It consisted of three components: (i) two field studies during spring 1995 and 1996 at Ny Ålesund, Spitsbergen, supplemented by about two years of continuous O_3 measurements at three Greenland sites, (ii) laboratory kinetic investigations of relevant chemical reactions, and (iii) modeling studies of the underlying chemical mechanisms.

As indicated by the research results below (see Platt and Lehrer, 1996), we are now more confident that the observed polar boundary layer O_3 depletion events are caused by catalysis by BrO and ClO under meteoro-

logical conditions of strong inversions which prevent dilution of halogen species and replenishment of O_3 from aloft. Model calculations incorporating the results from laboratory kinetic studies demonstrate that a self-consistent theory of halogen liberation from sea-salt on ice or in aerosols is now available. This theory satisfactorily describes the most important aspects of polar boundary layer O_3 depletion.

Highlights of field observations

- Boundary layer BrO concentrations (several x 10 ppt) are consistent throughout the Arctic and about two orders of magnitude higher than concentrations found in the stratosphere.

- The abundance of ClO is comparable to that of BrO.

- Periods of depleted O_3 in the lower troposphere generally coincide with elevated BrO and ClO mixing ratios but not with that of IO.

- There is very good evidence that halogen catalyzed tropospheric O_3 loss also occurs in Antarctica (Kreher et al., 1997; Wessel et al., 1998).

- Observed halogen oxide levels are sufficient to destroy surface O_3 within 1 to 2 days.

- Reactions involving the nitrogen oxides NO_2, NO_3, or N_2O_5 are unlikely to play a role in halogen release due to low concentrations of these nitrogen compounds in the Arctic and permanent daylight in spring that suppresses NO_3 and thus N_2O_5 formation.

- The chemistry that maintains observed ClO_x remains unknown.

- There may be a role for anthropogenic Arctic Haze in Arctic boundary layer O_3 loss, but it is not a prerequisite for the phenomenon which also occurs under closer to natural conditions in Antarctica.

- Photolytically active Br and Cl atom precursors (presumably Br_2 and Cl_2) are produced in the dark in the Arctic.

Highlights from laboratory measurements

- A considerable extension has been made to the gas phase kinetic data base for the reaction of Br atoms with hydrocarbons.

- After polar sunrise, relatively rapid Br release of brominated oxidation products from solid or liquid surfaces is likely.

- The dissociative or reactive adsorption of small atmospheric molecules on ice and sea-salt surfaces leads primarily to ionic surface products.

- Reaction probabilities of halides on surfaces such as ice or sulfate aerosols are generally found to be greater at higher relative humidities.

Highlights from ARCTOC and other modeling studies

- Observations made during O_3 depletion events could be quantitatively reproduced by existing chemical transport models that were extended to include detailed tropospheric halogen chemistry.

- Autocatalytic release of Br (and to a lesser extent Cl) either from sea-salt aerosol or salt deposits on the snow pack leading to 'bromine explosions' is the most likely source of reactive halogens in the Arctic.

- If heterogeneous reactions of gases on aerosol or ice surfaces are included, models are capable of reproducing the observed release of reactive bromine from sea-salt.

- Higher concentrations of formaldehyde observed during O_3 depletion events cannot be explained by models that assume gas phase production takes place by Cl atom oxidation of hydrocarbons (Shepson *et al.*, 1996).

Recent developments

Since the ARCTOC studies, there have been several noteworthy advances that will shed new light on this subject. Perhaps the most significant is the observation of lower tropospheric BrO in the Arctic and Antarctic from satellite by several groups using remote sensing techniques. Maps of this important product of lower atmospheric ozone depletion on a week-to-week basis from polar night to summer light will enhance our ability to understand this phenomenon and to assess its impact. Second, there are new observations from laboratory kineticists that were reported at the Annual Assembly of the European Geophysical Society and will appear in a special issue of the *Journal of Atmospheric Chemistry* early in 1999. Third, there are exciting new observations of nitrogen oxides, hydrocarbons, and formaldehyde at Alert during Polar Sunrise Experiment 1998 that will shed new light on unresolved aspects of the chemistry, and point to the importance of heterogeneous processes in controlling the concentrations of a number of gas phase species.

References

Barrie, L.A., and U. Platt, Arctic tropospheric chemistry: overview to *Tellus* special issue, **49B**, 450-454, 1997.

Barrie, L.A., J.W. Bottenheim, and W. Hart, An overview of Polar Sunrise Experiment 1992, *J. Geophys. Res.*, **99**, 25,313-25,314, 1994a.

Barrie, L.A., S.-M. Li, D.M. Toom, S. Landsberger, and W. Sturges, Measurements of aerosol and gaseous halogens, nitrates and sulphur oxides by denuder and filter systems during Polar Sunrise Experiment 1992, *J. Geophys. Res.*, **99**, 25,453-25,468, 1994b.

Barrie, L.A., J.W. Bottenheim, R.C. Schnell, P.J. Crutzen, and R.A. Rasmussen, Ozone destruction and photochemical reactions at polar sunrise in the lower Arctic atmosphere, *Nature*, **334**, 138-141, 1988.

Behnke, W., C. George, V. Scheer, and C. Zetzsch, Production and decay of $ClNO_2$ from the reaction of gaseous N_2O_5 with NaCl solution: bulk and aerosol experiments, *J. Geophys. Res.*, **102**, 3795-3804, 1997.

Bottenheim, J.W., A.C. Gallant, and K.A. Brice, Measurements of NO_Y species and O_3 at 82° N latitude, *Geophys. Res. Lett.*, **13**, 113-116, 1986.

Fan, S.-M., and D.J. Jacob, Surface ozone depletion in the Arctic spring sustained by bromine reactions on aerosols, *Nature*, **359**, 522-524, 1992.

Finlayson-Pitts, B.J., F.E. Livingston, and H.N. Berko, Ozone destruction and bromine photochemistry in the Arctic spring, *Nature*, **343**, 622-625, 1990.

Hausmann, M., and U. Platt, Spectroscopic measurement of bromine oxide and ozone in the high Arctic during Polar Sunrise Experiment 1992, *J. Geophys. Res.*, **99**, 25,399-25,414, 1994.

Hopper, J.F., L.A. Barrie, A. Silis, W. Hart, A.J. Gallant, and H. Dryfhout, Ozone and meteorology during the 1994 Polar Sunrise Experiment, *J. Geophys. Res.*, **103**, 1481-1492, 1998.

Impey, G.A., P.B. Shepson, D.R. Hastie, and L.A. Barrie, Measurement technique for the determination of photolyzable chlorine and bromine in the atmosphere, *J. Geophys. Res.*, **102**, 15999-16004, 1997.

Jobson B.T., H. Niki, Y. Yokouchi, J. Bottenheim, F. Hopper, and R. Leaitch, Measurements of C_2-C_6 hydrocarbons during Polar Sunrise Experiment 1992, *J. Geophys. Res.*, **99**, 25,355-25,368, 1994.

Kreher, K., P.V. Johnston, S.W. Wood, B. Nardi, and U. Platt, Ground-based measurements of tropospheric and stratospheric BrO at Arrival Heights, Antarctica, *Geophys. Res. Lett.*, **24**, 3021-3024, 1997.

Le Bras, G., and U. Platt, A possible mechanism for combined chlorine and bromine catalysed destruction of tropospheric ozone in the Arctic, *Geophys. Res. Lett.*, **22**, 599-602, 1995.

McConnell, J.C., G.S. Henderson, L. Barrie, J. Bottenheim, H. Niki, C.H. Langford, and E.M.J. Templeton, Photochemical bromine production implicated in Arctic boundary-layer ozone depletion, *Nature*, **355**, 150-152, 1992.

Oltmans, S.J., and W.D. Komhyr, Surface ozone distributions and variations from 1973-1984 measurements at the NOAA Geophysical Monitoring for Climate Change baseline observatories, *J. Geophys. Res.*, **91**, 5229, 1986.

Platt, U., and E. Lehrer, Arctic troposphere halogen chemistry (ARCTOC, EVSV-CT93-0318), *Final Report to the European Community*, 1996.

Shepson, P.B., A.-P. Sirju, J.F. Hopper, L.A. Barrie, V. Young, H. Niki, and H. Dryfhout, Sources and sinks of carbonyl compounds in the arctic ocean boundary layer: A polar icefloe experiment, *J. Geophys. Res.*, **101**, 21,081-21,089, 1996.

Solberg, S., N. Schmidbauer, A. Semb, F. Stordal, and Ø. Hov, Boundary layer ozone depletion as seen in the Norwegian Arctic in spring, *J. Atmos. Chem.*, **23**, 301- 332, 1996.

Wessel, S., S. Aoki, P. Winkler, R. Weller, A. Herber, H. Gernand, and O. Schrems, Tropospheric ozone depletion in polar regions: A comparison of observation in the Arctic and Antarctic, *Tellus*, **50B**, 34-50, 1998.

Is Mercury Input to Polar Ecosystems Enhanced by Springtime Ozone Depletion Chemistry?

Contributed by **W.H. Schroeder** *and* **L. A. Barrie**, *Atmospheric Environment Service, Canada*

Unlike other heavy metals that are associated with atmospheric aerosols, mercury exists in ambient air predominantly in the gaseous form (Hg^0) which is estimated to have a mean global tropospheric residence time of ~1 to 2 years, making it subject to long-range atmospheric transport. Because of its environmental persistence, toxicity, and tendency to bioaccumulate in the human food chain, mercury is a pollutant of concern in polar regions.

In January 1995, we began high-temporal-resolution measurements of total gaseous mercury (TGM) in surface air at Alert, NWT, Canada (82.5°N; 62.3°W; see Figure 1). Our observations (Schroeder *et al.*, 1998) reveal an interesting and recurring annual pattern ("fingerprint") characterized by distinct seasonal differences: relatively constant values (between 1-2 ng Hg m^{-3} of air) during the autumn and winter months, consistent with values reported at other Northern Hemisphere background sites. After polar sunrise, springtime TGM levels become highly variable, at times reaching the detection limit of the analyzer (0.2 ng m^{-3}). During the summer, TGM concentrations at Alert are generally higher than at other times of the year, ranging between 1.5-3 ng m^{-3}.

The large variability of TGM concentrations in spring, with frequent episodes of surprisingly low values, is
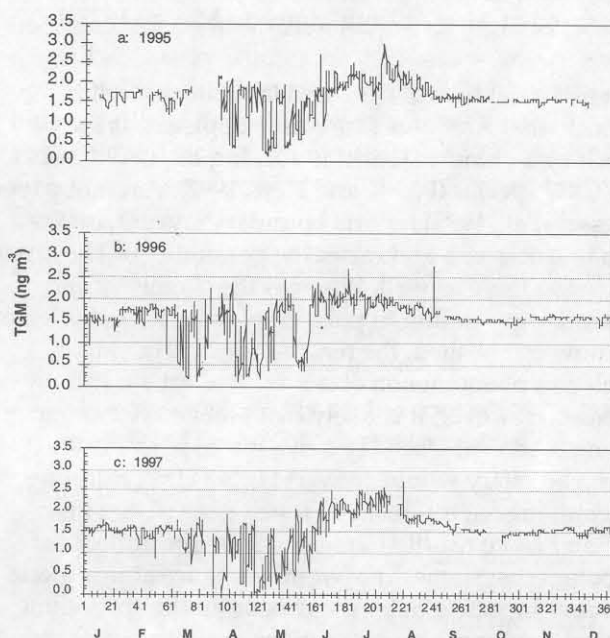

Figure 1. Annual time series of TGM at Alert (1995-97).

not expected for a pollutant such as mercury with a relatively long atmospheric residence time. However, this variability is strikingly similar to the annual pattern of surface ozone depletion events which occur in the Arctic marine boundary layer after polar sunrise. Low ozone episodes were first observed 25 years ago at Barrow, Alaska (Oltmans, 1981), then at Alert in 1985 (Bottenheim et al., 1986), and most recently at Ny Ålesund, Spitsbergen (Solberg et al., 1996). Figure 2 shows the robust correlation between tropospheric O_3 concentrations at Alert and concurrent measurements of Hg vapor in springtime after polar sunrise.
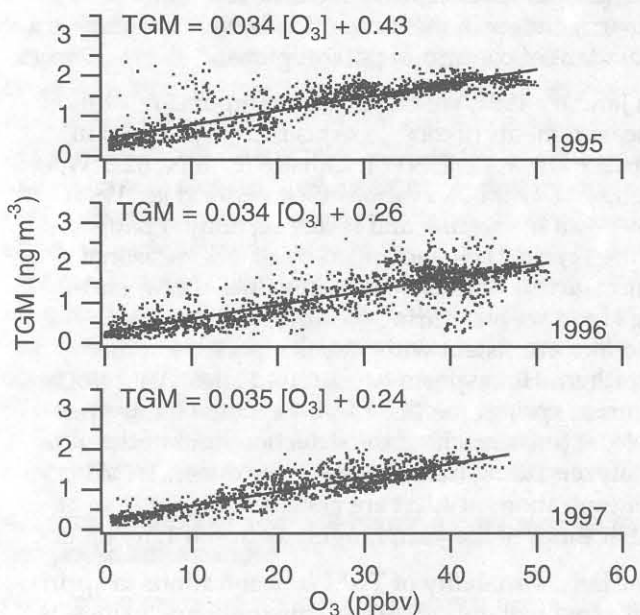

Figure 2. Correlation of ground-level TGM and O_3 measured at Alert, during March to May of 1995-1997.

Extensive field campaigns and laboratory studies indicate that Arctic surface ozone depletion is the result of a chain reaction involving Br/BrO (and Cl/ClO) species (Barrie and Platt, 1997). A recent paper (Wessel et al., 1998) reports boundary layer O_3 depletion in Antarctica and raises the possibility of Hg vapor depletion there as well. Whereas the chemistry and meteorology leading to polar tropospheric O_3 depletion are now established, the reasons for the Hg vapor depletion phenomenon observed at Alert are still unclear. However, it is likely that halogens (or other strong oxidants) also play a major role in this case. Such chemistry would convert Hg^0 to Hg^{2+}, resulting in reaction products which are much less volatile than Hg^0 and more readily deposited from the atmosphere to polar ecosystems. This would enhance atmospheric mercury inputs to polar ecosystems in the springtime. Indeed, preliminary observations indicate considerable aerosol mercury formation during mercury vapor depletion events.

References

Barrie, L., and U. Platt, Arctic tropospheric chemistry: Overview to Tellus special issue, **49B**, 450-454, 1997.

Bottenheim, J.W., A.J. Gallant, and K.A. Brice, Measurements of NO_Y species and O_3 at 82°N latitude, Geophys. Res. Lett., **13**, 113-116, 1986.

Oltmans, S.J., Surface ozone measurements in clean air, J. Geophys. Res., **86**, 1174-1180, 1981.

Schroeder, W.H., K.G. Aulauf, L.A. Barrie, J.Y. Lu, A. Steffen, D.R. Schneeberger, and T. Berg, Arctic springtime depletion of mercury, Nature, in press.

Solberg, S., N. Schmidbauer, A. Semb, F. Stordal and Ø. Hov, Boundary-layer ozone depletion as seen in the Norwegian Arctic in Spring, J. Atmos. Chem., **23**, 301-332, 1996.

Wessel, S., S. Aoki, P. Winkler, R. Weller, A. Herber, H. Gernandt and O. Schrems, Tropospheric ozone depletion in polar regions: A comparison of observations in the Arctic and Antarctic, Tellus, **50B**, 34-50, 1998.

Impact of Large Solar Zenith Angles, Total Column Ozone and New O¹D Quantum Yields on Atmospheric Chemistry at High Latitudes

Contributed by **D. Jaffe**, University of Washington-Bothell, **J. Herring**, Prescott College, and **S. Madronich**, National Center for Atmospheric Research, USA

Introduction

During spring at high latitude the sun makes its annual appearance over the horizon, initiating photochemical processes that are negligible during the long polar night. High latitude photochemistry is not, however, simply turned on and off as the seasons change; large total column ozone and large zenith angles strongly attenuate the actinic fluxes in the UV-B spectral region, and this plays a key role in shaping the atmospheric chemistry in the high latitudes. In this short report we summarize our previously published results and present new calculations of photolysis rates at high latitudes based on newly published O¹D quantum yields [DeMore et al., 1997].

In a previous report [Herring et al., 1997] we calculated in situ ozone production for a surface location in central Alaska during spring, based on measured NO_X, PAN, NMHCs, $J(NO_2)$ (the NO_2 photolysis frequency), surface albedo, and other parameters [Beine et al., 1997]. The basic conclusion from this work was that

measured NO_x during spring appeared to be sufficient to support net photochemical ozone production. The NO_x mixing ratios at this site were most likely elevated due to springtime PAN decomposition. The measured and calculated $J(NO_2)$ during this campaign exhibited the expected pattern, going from near zero in the polar winter, to noontime values of around 8×10^{-3} s^{-1} by April 1 (for clear sky conditions). This value is not very different from noontime values in mid-latitude regions. Although some photons are lost due to the large zenith angles, this is approximately compensated for by the high surface albedo due to snow.

For the photolytic production of O(^{1}D) from O_3, $J(O_3 \rightarrow O^1D)$, which occurs primarily in the 290-320 nm region, the situation is rather different. Here the large springtime total column ozone, combined with the large zenith angles gives rise to substantial attenuation of the actinic flux in this spectral region. This photolysis frequency is significantly reduced (as compared to mid-latitude values) during spring and remains low until the zenith angles and column ozone values are smaller.

For example, Figure 1 shows calculated, noontime clear-sky NO_2 and O_3 photolysis frequencies for two high latitude locations, 65°N and 80°N, respectively, for February to July. Total column ozone values for these calculations are based on local observations at Poker Flat, Alaska (65°N), and TOMS monthly climatological zonal mean observations, for the 80°N location. Climatological temperature data from Poker Flat and Eureka, NWT (80°N), are used for both calculations. For the 65°N calculations we used a surface albedo which is based on measurements at the boreal forest Poker Flat site. The measured albedo went from 0.6 during early spring to 0.2 on May 1. For the 80°N site, we assume a constant albedo of 0.8, consistent with a year round snow or ice covered surface. The fact that the 80°N NO_2 photolysis frequency begins to exceed the value for 65°N in April is a result of maintaining this high albedo.

These calculations have been made with an 8-stream discrete-ordinate radiative transfer model and using recently updated temperature-dependent quantum yields presented in the most recent report from the Jet Propulsion Laboratory (DeMore et al., 1997). The new quantum yields indicate a significant long wavelength "tail" which extends to ~330 nm. Compared to previously published quantum yields, the new values will significantly increase the $J(O_3 \rightarrow O^1D)$ photolysis frequency, especially at large solar zenith angles. Even more recent results [e.g., Ravishankara et al., 1998 and references therein] suggest that the tail may extend even further into the long wavelength region. Comparing the noontime, clear-sky $J(O_3 \rightarrow O^1D)$ photolysis frequencies calculated using the updated quantum
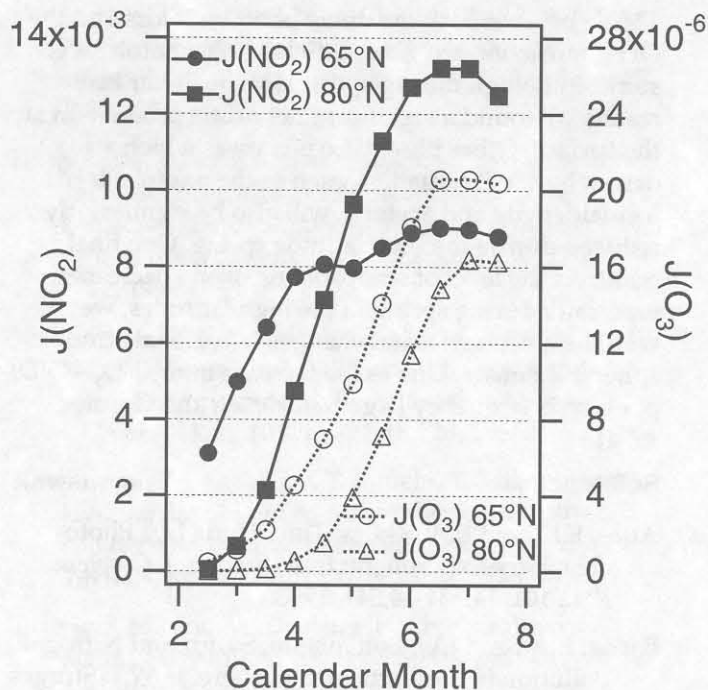

Figure 1. $J(NO_2)$ and $J(O_3)$ for 65°N and 80°N latitude.

yields (DeMore et al., 1997) with our previously published results [Herring et al., 1997], for Poker Flat for March 15th, April 15th, and May 15th, we find that the new results are 1.69, 1.38, and 1.27 times the previous values.

Although the $J(O_3 \rightarrow O^1D)$ photolysis frequencies calculated with the updated quantum yields are significantly higher than the previously calculated results, the values are still much smaller than those for lower latitude locations. Comparing these photolysis frequencies, with values reported for Mauna Loa (Atlas and Ridley, 1996) for mid-April, the Poker Flat values are 65% and 18% of the MLO values for $J(NO_2)$ and $J(O_3 \rightarrow O^1D)$, respectively.

Implications for atmospheric chemistry

Under clear-sky, high-sun conditions, $J(O_3 \rightarrow O^1D)$ photolysis will usually be the most important source of oxygen-containing radicals. At large zenith angles, the $J(O_3 \rightarrow O^1D)$ photolysis is significantly reduced and other radical sources may become more important. Two possible radical sources are decomposition of PAN, which accumulates during the Arctic winter and decomposes during spring into NO_2 and peroxyacetyl radicals [Barrie and Bottenheim, 1991; Beine et al., 1997], and photolysis of HONO (primarily in the UV-A region), although there are other radical sources as well. One additional implication of these results is that the direct (non-halogen) O_3 loss processes are reduced by the diminished $J(O_3 \rightarrow O^1D)$ photolysis frequency.

This is because both the direct photolysis loss and the $OH+O_3$ reaction are slowed. Since NO_2 photolysis is sufficiently high during spring, for the Poker Flat results we found a significant net ozone production at the surface. Other photolytic processes which are driven by UV-B radiation, such as the photolysis of formaldehyde and acetone, will also be significantly reduced during the high latitude spring. One final point: As the level of stratospheric ozone decreases, especially during spring in the high latitudes, we would expect significant changes in regional atmospheric chemistry due to the increase in the $J(O_3 \rightarrow O^1D)$ photolysis frequency [e.g., Madronich and Granier, 1994].

References

Atlas, E.L., and B.A. Ridley, The Mauna Loa Photochemistry Experiment: Introduction, *J. Geophys. Res.*, **101**, 14,531-14,541, 1996.

Barrie, L.A., and J.W. Bottenheim, Sulfur and Nitrogen Pollution in the Arctic Atmosphere, in W.T. Sturges (ed.), *Pollution of the Arctic Atmosphere*, Elsevier Science, NY, 1991.

Beine, H.J., D.A. Jaffe, J.A. Herring, T. Krognes, and F. Stordal, High latitude springtime photochemistry. Part I: NO_X, PAN and ozone relationships at high northern latitudes, *J. Atmos. Chem.*, **27**, 127-153, 1997.

DeMore, W.B., S.B. Sander, D.M. Golden, R.F. Hampson, M.J. Kurylo, C.J. Howard, A.R. Ravishankara, C.E. Kolb, and M.J. Molina, *Chemical Kinetics and Photochemical Data for Use in Stratospheric Modeling*, Eval. No. 12, JPL Publication 97-4, Jet Propulsion Laboratory, Pasadena, 1997.

Herring, J.A., D.A. Jaffe, H.J. Beine, S. Madronich, and D.R. Blake, High latitude springtime photochemistry. Part II: Sensitivity studies of ozone production, *J. Atmos. Chem.*, **27**, 155-178, 1997.

Madronich, S. and C. Granier, Tropospheric Chemistry Changes Due to Increased UV-B Radiation, in: R. Biggs and M. Joyner (eds.), *Stratospheric Ozone Depletion/UV-B Radiation in the Biosphere*, Spinger-Verlag Publishers, 1994.

Ravishankara, A.R., G. Hancock, M. Kawasaki, and Y. Matsumi, Photochemistry of ozone: Surprises and recent lessons, *Science*, **280**, 60-61, 1998.

Sea Ice as a Source of Sea Salt Aerosol in Polar Regions

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Introduction

Sea salt aerosol seems to be one of the simpler components of the atmosphere, with a composition close to that of sea water. In recent years, attention has focused on aspects of sea salt aerosol behavior such as reactions with acid (leading to loss of gaseous HCl), and heterogeneous reactions on sea salt surfaces. Now a new complication has been found in the polar regions, leading to the hypothesis that, for at least the coastal polar areas, sea ice surfaces are a more important source than sea water. This has implications both for present day chemistry, and for paleoatmospheric interpretations made from ice core data.

Generally, sea salt aerosols are produced by the bursting of air bubbles at the ocean surface. The resulting droplets naturally start life with ionic concentrations in the same ratio as bulk sea water. This assumption enables the calculation of how much of components such as sulfate in bulk aerosol originate from sea salt. It is then a matter of simple subtraction to calculate values such as "non-sea-salt sulfate" (nss sulfate), which in remote regions is often equated to the sulfate produced from oceanic DMS emissions.

In the polar regions, a major application of sea salt measurements has been in snow and ice cores. The assumption of a sea water source has enabled authors to infer changes in the position of the sea ice edge and/or wind strengths based on changing ice core concentrations of sea salt ions. However, for many years now, it has been noted that, in coastal Antarctic snow, negative nss sulfate concentrations are often observed.

Evidence for fractionation of sea salt

Recently, the data from many years of year-round aerosol and snow analysis at three coastal Antarctic sites (Dumont d'Urville, Halley, and Neumayer) have been brought together and examined. The sea salt data [Wagenbach *et al.*, 1998] show two particularly interesting features. Firstly, the averaged seasonal cycle of sea salt concentrations shows a summer minimum and a broad winter maximum at Neumayer and Halley, as already observed in seasonally resolved firn cores, and in aerosol data from Mawson station, and even at the inland site of South Pole. This finding is surprising, since in summer, the sea ice edge may be very close to the stations, while in winter it is often over 1000 km to the sea ice edge. It is difficult to see how greater storm activity and penetration in winter could compensate such a large difference.

The second finding from the aerosol and snow studies is that of very large negative nss sulfate concentrations during winter. These are found at all three stations in both aerosol and snow, and can only be caused by fractionation of the sea salt itself as compared to sea water. Negative nss sulfate values are also observed in Arctic snow. Plots of nss sulfate against sodium from the coastal Antarctic sites indicate that sulfate is

depleted to less than a third of its sea salt ratio. Of the cations, none of Mg, K, or Ca show a significant depletion [Hall and Wolff, in press], so that Na must be the cation depleted with sulfate. Sea salt concentrations are highly episodic, with concentrations changing by as much as a factor 60 between days, and events lasting usually only 2-3 days.

Causes of fractionation and winter maxima

In fact, fractionation during freezing of sea water is well known, with laboratory experiments suggesting crystallization of mirabilite ($Na_2SO_4 \bullet 10H_2O$) at temperatures below -8°C. The problem is to determine where such fractionation occurs. In a series of laboratory experiments [Wagenbach et al., 1998], no significant fractionation was observed as a result of freezing sea water droplets or bubbles. The mechanism which did produce significant fractionation was one where sea water was frozen onto artificial sea ice, and the remaining liquid was removed for analysis. This strengthens a hypothesis that the source of fractionated sea salt is the sea ice surface. During winter, when temperatures are below -8°C, it is to be expected that fresh sea ice surfaces (i.e., those not covered by overly-

ing snow) will have a surface brine. This brine could be very concentrated in salt (we would calculate 6 times the salinity of sea water or 212 practical salinity units (psu) at -20°C) but almost totally depleted in sulfate.

This source has the advantage that it explains the sulfate depletion, and that sea ice formation is of course strongest in winter. Sea ice formation can also be strong in coastal leads, so that high concentrations at coastal sites are to be expected. However, it is harder to understand how a brine skin becomes airborne. This dilemma could be solved if a significant source is actually the frost flowers that often form on the surface of newly-formed sea ice. These flowers consist of fragile saline ice crystals that grow to heights of 1-3 cm. Beneath the flowers, there is a moist saline surface layer, which forms from upward brine transport within the ice driven by the thermomolecular pressure gradient. Recent laboratory and Arctic field experiments show that the flowers are ubiquitous and grow quickly. Perovich and Richter-Menge (1994), from Beaufort Sea field experiments during March-April, observe that flower formation is "a normal step in the formation of sea ice under springtime conditions", and that the flowers grow to cover a thin ice surface within 24-48 hours of their initial formation. Their observed flower salinities lie in the range 50-115 psu, with the salinity of the surface brine 5-20 psu less. They suggest that the salt in the flowers comes from the upward transport of the surface brine from surface tension effects. These salinities also occur in the laboratory experiments (Martin et al., 1996; Nghiem et al., 1997).

Martin et al. (1996) show that the flowers grow because water evaporates from the brine, giving a near surface region with vapor supersaturated with respect to ice; the form of the flowers depends on the temperature range within the supersaturated region. Dendritic flowers formed in the temperature range -12° to -16°C, and rod or needle-like flowers formed in the range -16° to -25°C. These two flower types, forming only at temperatures below -12°C, are common, and we would expect them to be depleted in sulfate. We hope to verify this depletion from field experiments done at the SHEBA (Surface Heat Budget of the Arctic Ocean project) ship in the Beaufort Sea during this past winter, and from collections being made in the Antarctic.

Because these flowers protrude into the atmospheric boundary layer, they are vulnerable to being broken off and advected by the wind. Although we have no field observations of this process, the highly fractal and non-aerodynamic shape of the flowers suggests it is likely. The flowers can also be observed by remote sensing, because their growth modifies the ice surface to cause a bright transient radar return. Nghiem et al.
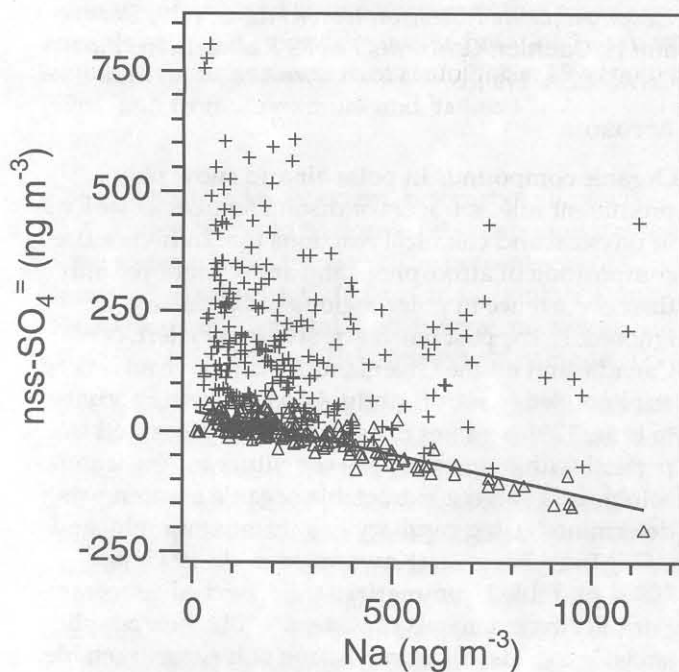

Figure 1. Nss sulfate (calculated using normal sea water ratios) against sodium for 13 years of aerosol data from Neumayer Station, Antarctica. Crosses are summer data, triangles are winter (May-September) data. A few extreme summer values have been excluded. The line is the best fit to the winter data, corresponding to 70% loss of sulfate compared to sea water. (From Wagenbach et al., 1998).

(1997) give a sequence of ERS-1 SAR (Synthetic Aperture Radar) images of this transient return from a newly frozen lead, and show from a combined radar/frost flower laboratory experiment that frost flowers yield a 3-5 dB increase in backscatter over bare ice. They also cite field work showing a 5-10 dB ERS-1 SAR brightness increase associated with flower growth and snow-infiltrated flowers. For the Antarctic stations, this transient radar return associated with the flowers provides a way to observe their presence near the stations by satellite radar. This information, in combination with surface weather charts, should allow estimation of the trajectories of the transported salt.

Implications of a sea ice source

The likelihood that sea ice surfaces are actually the source of sea salt aerosol, at least for coastal Antarctica, has a number of implications. Firstly it calls into question the traditional interpretation of sea salt concentrations in ice cores. Increased concentrations in the past would actually imply more frost flower or brine surfaces, which might be linked to fresh ice formation rather than open water distance. It is urgent that we understand whether sea salt in central Antarctica also derives from a sea ice source or whether it sees a low latitude open water source.

A second point is that nss sulfate concentrations cannot always be calculated using seawater ratios of ions. While such considerations have little effect on the summer concentrations of DMS-derived sulfate calculated for polar regions, they are significant for the calculation of methanesulfonic acid (MSA) to nss sulfate ratios at other times of year [Legrand and Pasteur, 1998]. The choice of the correct ratio for the sea salt source (which may vary with season) will significantly alter the MSA/nss-sulfate ratio, which has been used in ice cores to infer past temperatures. Finally, an important issue in polar tropospheric chemistry has been the discovery of large and short-lived tropospheric ozone depletions, which appear to be catalyzed by halogens. The source of these halogens may well be sea salt, and therefore the behavior of sea ice surfaces is of interest for this work also. Work is already underway to collect winter sea ice surface samples in both the Arctic and the Antarctic as a first step towards confirming the importance of the sea ice source.

References

Hall, J.S., and E.W. Wolff, Causes of seasonal and daily variations in aerosol sea salt concentrations at a coastal Antarctic station, *Atmos. Environ.*, in press.

Legrand, M., and E.C. Pasteur, Methane sulfonic acid to non sea-salt sulfate ratio in coastal Antarctic aerosol and surface snow, *J. Geophys. Res.*, **103**, 10991, 1998.

Martin, S., Y., Yu, and R. Drucker, The effect of frost flower growth at different temperatures on infrared observations of laboratory sea ice, *J. Geophys. Res.*, **101**, 12111-12125, 1996.

Nghiem, S.V., S. Martin, D. K. Perovich, R. Kwok, R. Drucker, and A.J. Gow, A laboratory study of the effect of frost flowers on C-Band radar backscatter from sea ice, *J. Geophys. Res.*, **102**, 3357-3370, 1997.

Perovich, D.K., and J.A. Richter-Menge, Surface characteristics of lead ice, *J. Geophys. Res.*, **99**, 16341-16350, 1994.

Wagenbach, D., F. Ducroz, R. Mulvaney, L. Keck, A. Minikin, M. Legrand, J. S. Hall, and E.W. Wolff, Seasalt aerosol in coastal Antarctic regions, *J. Geophys. Res.*, **103**, 10961, 1998.

Organic Matter in Polar Aerosol, Snow, and Ice

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Aerosols

Organic compounds in polar air and snow play a prominent role as tracers of distant sources as well as in physical and chemical reactions that influence the composition of atmosphere and snow. Until recently their occurrence in polar regions has been largely ignored. In the past ten years, studies at Alert, NWT, Canada, and on the Greenland ice cap have advanced our knowledge significantly. At Alert, from February to June, 1991 organics in aerosols were measured in parallel with inorganic trace constituents. The water-soluble and solvent-extractable organic fraction was determined using capillary gas chromatography and GC/MS techniques (Kawamura *et al.*, 1995a,b; 1996a,b). Table 1 summarizes the observed concentrations in Arctic aerosols of water soluble dicarboxylic acids, ketoacids, dicarbonyls, and solvent-extractable lipids (including hydrocarbons and fatty acids).

Concentrations of total carbon (TC), total nitrogen (TN), and water soluble organic carbon (WSOC) are also given. Aerosol carbon comprises 2.4 to 11% of the total aerosol mass. Considering that a portion of this carbon is associated with oxygen atoms in compounds such as the carboxylic acids, the fraction of aerosol mass that is carbonaceous is even higher than this. Low molecular weight (LMW) dicarboxylic acids

Components	Range	Average
Aerosols	2500–9100 ng m^{-3}	5200 ng m^{-3}
Total Carbon (TC)	88–639 ng m^{-3}	359 ng m^{-3}
Total Nitrognen (TN)	16–154 ng m^{-3}	86 ng m^{-3}
C/N Weight Ratio	2.4–7.1	4.5
TC/Aero.	2.4–11.1 %	6.8 %
TN/Aero.	0.48–2.4 %	1.6 %
Water Soluble Organic Carbon (WSOC)	40.7–300 ng m^{-3}	186 ng m^{-3}
WSOC/TC	30–72 %	53 %
WSOC/Aero.	1.2–5.5 %	3.4 %
Dicarboxylic acids (C$_2$–C$_{11}$)	7.4–84.5 ng m^{-3}	36.6 ng m^{-3}
Ketoacids (C$_2$–C$_6$)	0.76–8.9 ng m^{-3}	3.7 ng m^{-3}
α-Dicarbonyls (C$_2$–C$_3$)	0.05–2.8 ng m^{-3}	0.88 ng m^{-3}
Diacid-C/TC	1.5–9.1 %	3.8 %
Ketoacid-C/TC	0.18–0.78 %	0.34 %
α-Dicarbonyl-C/TC	0.019–0.17 %	0.073 %
Lipid Class Compounds		
n-Alkanes (C$_{18}$–C$_{35}$)	0.15–2.7 ng m^{-3}	0.85 ng m^{-3}
PAHs	0.0002–0.85 ng m^{-3}	0.11 ng m^{-3}
n-Alcohols (C$_{13}$–C$_{30}$)	0.24–0.95 ng m^{-3}	0.50 ng m^{-3}
Fatty acids (C$_7$–C$_{32}$)	1.3–6.5 ng m^{-3}	3.2 ng m^{-3}
Long-chain diacids (C$_{22}$–C$_{26}$)	0.074–0.56 ng m^{-3}	0.27 ng m^{-3}

Table 1. Concentrations of aerosol total carbon (TC), total nitrogen (TN), water soluble organic carbon (WSOC), and dicarboxylic acids, ketoacids, α-dicarbonyls as well as lipid class compounds in Arctic aerosols collected from February to June, 1991 at Alert Station (data from Kawamura *et al.*, 1995a, 1995b, 1996a, and from Kawamura and Yanase).

(C$_2$-C$_{11}$) and, to a lesser extent, ketocarboxylic acids (C$_2$-C$_9$) were found to be dominant compound classes in the water soluble fraction . The percentages of C$_2$ (oxalic), C$_3$ (malonic), C$_4$ (succinic), C$_5$ (glutaric), and other compounds in total diacids were, on average, 44%, 17%, 15%, 5% and 19%, respectively (Figure 1).

During the 1991 polar sunrise at Alert, the abundance of malonic acid relative to total diacids increased from less than 7% in February to more than 20% in April. Selective enrichment of malonic acid in the diacid mixture at polar sunrise is similar to the observed, photochemically induced enrichment in urban aerosols during the high sunlight season (Kawamura and Ikushima, 1993). Total concentrations of LMW diacids (approximately 10-100 ng m^{-3}) show a strong seasonal trend with a maximum in early spring (Figure 2).

Proposed reaction schemes for the production of LMW diacids and related compounds are illustrated in Figure 3. The mechanisms of gas to particle conversion are qualitatively but not quantitatively understood. Research is needed to elucidate homogeneous gas phase chemistry in the atmosphere that produces involatile organic products and, hence, aerosols. In addition, heterogeneous reactions occurring between gas phase organic molecules and solid or liquid organics on surfaces such as aerosols or ice crystals need to be studied.

Small diacids were not only detected in the Arctic but also reported in Antarctic aerosols (Kawamura *et al.*, 1996b). Diacids, ketoacids, and dicarbonyls account for up to 10% of Arctic total aerosol carbon (TC). Together with sulfate production by SO$_2$ oxidation in the Arctic troposphere (Barrie, 1986), photochemical production of LMW dicarboxylic acids and related water soluble compounds should cause changes in the chemical and physical properties of Arctic aerosols. These changes may have a direct and/or indirect effect on the radiation balance in the Arctic. The organic compounds discussed above comprised less than 20% of total WSOC in Alert aerosols. Candidates for part of the missing organic mass are formic and acetic acids that were not measured in this study but have been detected in Greenland snow and ice (see Snow section below).

At Alert, concentrations of particulate LMW diacids correlated positively with particulate Br and I (Kawamura *et al.*, 1995b), which are involved in ozone depletion (see the article by Barrie, Platt, and Shepson, this issue; Barrie *et al.*, 1988, 1994). This indicates that the production of small diacids occurs simultaneously with production of particulate Br during ozone depletion at polar sunrise. Although TC and WSOC contents tended to decrease from the winter to summer season, they peaked in early spring. WSOC comprises 30-72% of TC with higher values in April, indicating that Arctic organic aerosols are highly water
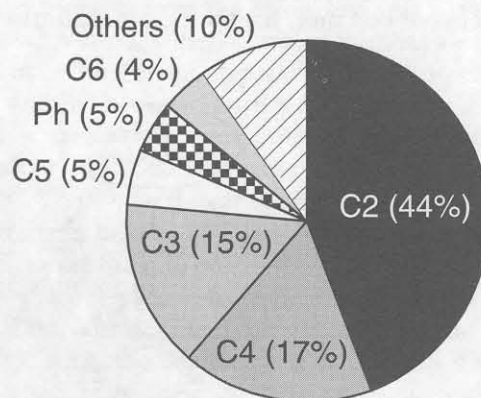
Alert Aerosols (Feb. to Jun., 1991)

Figure 1. The average relative contributions of individual dicarboxylic acids to the total diacids mass (C$_2$-C$_{11}$) detected in Arctic aerosols at Alert, Canada (February to June, 1991). C$_2$: oxalic acid, C$_3$: malonic acid, C$_4$: succinic acid, C$_5$: glutaric acid, C$_6$: adipic acid, Ph: phthalic acid (Kawamura *et al.*, 1995a).
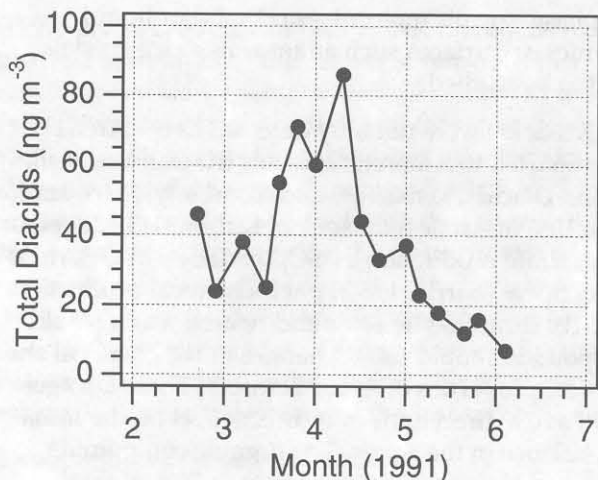
Figure 2. Concentration change of LMW diacids (C_2-C_{11}) in Arctic aerosols at Alert, 1991 (Kawamura et al., 1995a).

soluble and that water soluble organics are produced at polar sunrise.

Lipid class compounds were also detected in Arctic aerosols, including n-alkanes (C_{18}-C_{35}), polynuclear aromatic hydrocarbons (PAHs), n-alcohols (C_{13}-C_{30}), fatty acids (C_7-C_{32}), and long-chain α,ω-dicarboxylic acids (C_6-C_{26}). Although the concentrations are generally less than that of LMW dicarboxylic acids (Table 1), their molecular distributions sometimes provide useful information on anthropogenic/biogenic source strength, source regions, and types of organisms which produce organic matter. For example, a significant increase in the concentrations of long-chain dicarboxylic acids which are produced in soils by microbial ω and ω-1 oxidation of plant-derived fatty acids was observed about one month after the polar sunrise

(Kawamura et al., 1996c). Their distributions are characterized by low even/odd carbon number ratios (1.6-2.7), which are different from fresh soils (ratios >4). This indicates that long-chain diacids are derived from aged soils. The even/odd ratios are similar to those of aged soil (Holocene) samples from China, suggesting that atmospheric transport of Chinese loess is very likely the source which caused high concentrations of long-chain diacids. Air parcel trajectory analysis showed that in late April to May, air masses originating from the arid area in China were transported to the northern North Pacific and then across Alaska and the western Arctic to Alert (Kawamura et al., 1996c).

Snow

Formic and acetic acids represent major contributors to the acidity of natural precipitation over the world, even in remote regions. Direct emissions from vegetation and from its combustion, as well as atmospheric oxidation of various biogenic hydrocarbons are thought to be the main sources of these light carboxylic acids in the natural atmosphere. Human activities, through direct emissions from combustion as well as secondary production from anthropogenic hydrocarbon emissions, may also contribute to their budgets. However, it remains difficult to estimate the relative importance of each of these processes. Recent polar ice core chemistry studies have provided useful information on the atmospheric cycles of these species at high latitudes at present and during the past.

The study of carboxylic acids present in Greenland snow deposits revealed that large spikes of formate are associated with marked increases of the ammonium and carbonaceous aerosol contents (Legrand et al., 1992; Legrand et al., 1995). Large forest fires in circumpolar regions may be the cause of these large perturbations.
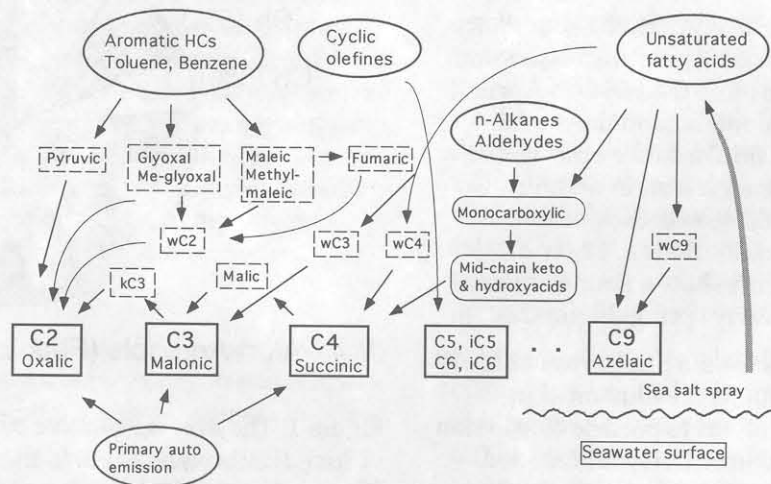

Figure 3. Possible photochemical production of oxalic (C_2), malonic (C_3), succinic (C_4) and azelaic (C_9) acids in the atmosphere (Kawamura et al., 1996b). kC_3 and wC_2 are ketomalonic acid and glyoxylic acid, respectively.

Aside from sporadic high concentration events, it was found that the background level of formate in Greenland ice was five times lower at the end of the last glacial age (~20,000 years before present) than during the last 10,000 years (Legrand and De Angelis, 1996). An increase in formate in Greenland ice occurring 5,000 years after the glaciers retreated from North America is consistent with high-latitude vegetation being a significant source of these light carboxylic acids. In other words, not until vegetation was established on the ice-free continent did the formate levels in Greenland ice increase (Legrand and De Angelis, 1996). Finally, the remarkable lack of formate trend in Greenland snow deposited over the last decades (see article by Delmas and Legrand, this issue) suggests that anthropogenic emissions do not yet dominate the present-day budget of formic acid at high northern latitudes.

Although it is present at similar concentrations to those of formate in present-day Greenland snow deposits, acetate exhibits a weaker response to the last great climatic transition, suggesting that an additional marine source may contribute to its natural budget at high northern latitudes (Legrand and De Angelis, 1996). These first studies of light carboxylates trapped in Greenland ice have opened up a powerful new avenue of ice core research dedicated to organic ice chemistry and its use to better understand the role of natural biogenic processes in influencing atmospheric composition.

References

Barrie, L.A., J.W. Bottenheim, R.C. Schnell, P.J. Crutzen, and R.A. Rasmussen, Ozone destruction and photochemical reactions at polar sunrise in the lower Arctic atmosphere, *Nature*, **334**, 138-141, 1988.

Barrie, L.A., R. Staebler, D. Toom, B. Georgi, G. den Hartog, S. Landsberger, and D. Wu, Arctic aerosol size-segregated chemical observations in relation to ozone depletion during Polar Sunrise Experiment 1992, *J. Geophys. Res.*, **99**, 25,439-25,451, 1994.

Kawamura, K., and K. Ikushima, Seasonal changes in the distribution of dicarboxylic acids in the urban atmosphere, *Environ. Sci. Technol.*, **27**, 2227-2235, 1993.

Kawamura, K., H. Kasukabe, and L.A. Barrie, Concentration changes of dicarboxylic acids, water soluble organic carbon and total carbon in Arctic aerosols: Polar sunrise 1991, WMO Global Atmospheric Watch No. 107 (Extended Abstracts of Papers Presented at the WMO-IGAC Conference on the Measurement and Assessment of Atmospheric Composition Change, Beijing, October 9-13, 1995), 190-194, 1995a.

Kawamura, K., H. Kasukabe, O. Yasui and L.A. Barrie, Production of dicarboxylic acids in the arctic atmosphere at polar sunrise, *Geophys. Res. Lett.*, **22**, 1253-1256, 1995b.

Kawamura, K., H. Kasukabe, and L.A. Barrie, Source and reaction pathways of dicarboxylic acids, ketoacids and dicarbonyls in arctic aerosols: one year of observations, *Atmos. Environ.*, **30**, 1709-1722, 1996a.

Kawamura, K., R. Sempere, Y. Imai, M. Hayashi, and Y. Fujii, Water soluble dicarboxylic acids and related compounds in the Antarctic aerosols, *J. Geophys. Res.*, **101**, 18,721-18,728, 1996b.

Kawamura, K., A. Yanase, T. Eguchi, T. Mikami and L.A. Barrie, Enhanced atmospheric transport of soil derived organic matter in spring over the high Arctic, *Geophys. Res. Lett.*, **23**, 3735-3738, 1996c.

Legrand, M., and M. De Angelis, Light carboxylic acids in Greenland ice: A record of past forest fires and vegetation emissions from the boreal zone, *J. Geophys. Res.*, **101**, 4129-4145, 1996.

Legrand, M., M. De Angelis, T. Staffelbach, A. Neftel, and B. Stauffer, Large perturbations of ammonium and organic acids contents in the Summit-Greenland ice core: Fingerprint from forest fires?, *Geophys. Res. Lett.*, **19**, 473-475, 1992.

Legrand, M., M. De Angelis, H. Cachier, and A. Gaudichet, Boreal biomass burning over the last 80 years recorded in a Greenland ice core, in: *Ice Core Studies of Global Biogeochemical Cycles*, NATO ASI Ser., vol. 30, edited by R. Delmas, pp. 347-360, Springer-Verlag, New York, 1995.

Air-Snow Transfer Function: Where Are We?

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1. Introduction

Contrary to what was generally believed some ten years ago, the translation of ice records in terms of atmospheric concentrations is not always straightforward. The validity of this fundamental assumption of simple air-snow-glacial ice relationships has not yet been established for most of the chemical species of interest in glaciochemical studies. One of the major recommendations of PASC in 1990 was to improve the understanding of the transfer mechanisms of atmospheric impurities (aerosol particles or trace gases of various kinds) to the polar ice.

The transfer function between the atmosphere and glacial ice involves multiple physical and chemical processes which can be summarized very briefly as:

- the various processes controlling removal of material from the atmosphere and its incorporation into the snowflakes at cloud level or into fog at low elevation

- the deposition mechanisms in polar conditions, in particular dry vs. wet deposition, including snow ventilation, ice crystal metamorphism, etc.

- the post-depositional processes affecting the chemical characteristics of the records until pore close-off and even, in some cases, in the ice itself.

Deposition mechanisms differ markedly according to the species (gas or aerosol-associated compound). We will have to introduce the notion of "reversibly" -deposited species (RDS) for the case of non-aerosol impurities.

Two NATO workshops (see references) have been devoted in 1993 and 1995 to the discussion of the data obtained from several coordinated atmospheric, snow pit, and ice core field studies conducted in Greenland (Summit) and Antarctica (South Pole, Vostok Station), where particular attention was paid to the transfer function issue. Summit experiments are more specifically discussed by Jaffrezo *et al.* (1995), Dibb (1996) and Dibb and Jaffrezo (1997). The reader is asked to consult these reviews for more details. In this paper, we will focus our attention on a limited number of results of interest for the IGAC community.

A general conclusion of the studies is that the problems are important and many are still presently unsolved. However, despite these difficulties which may make questionable some ice core data, we should not "throw out the baby with the bathwater".

2. Deposition mechanisms of aerosols in central Greenland

Experiments on aerosol and snow composition were performed during the period May-July of 1993 at Summit in order to quantify the relative importance of deposition processes for several major aerosol components, in particular sulfate, the main aerosol anion. The contributions of snow, fog, and dry deposition were estimated from the data as 58 ± 6, 25 ± 4, and 17 ± 7 percent, respectively (Bergin *et al.*, 1995). Therefore, considering that snow and fog are two components of wet deposition, dry deposition appears to be a minor process, at least for this time of the year which represents only 16% of the annual sulfate inventory.

Dry deposition velocity of sulfate particles was found to be 0.041 ± 0.012 cm s^{-1}, a value 60% greater than earlier measurements. As a priority, future efforts should involve year-round measurements.

Fischer *et al.* (in press) used an extensive net of shallow cores in Northern Greenland to study the influence of snow accumulation rate on the respective importance
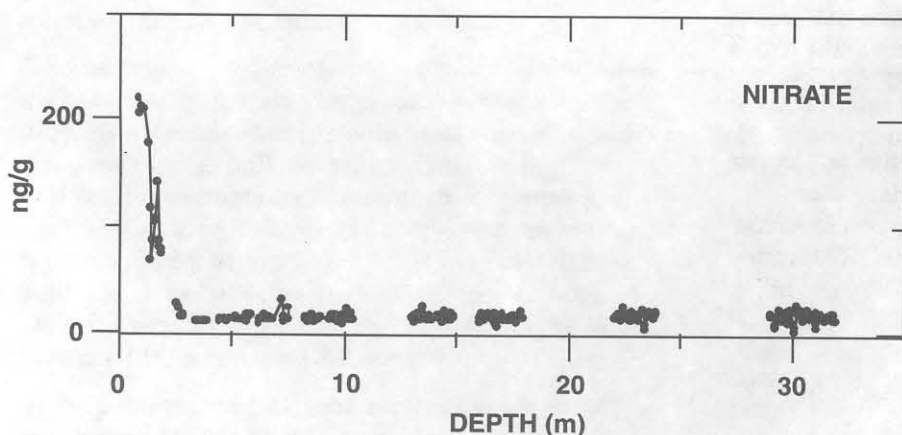

Figure 1. Nitrate profile at Vostok Station (East Antarctic plateau) in the upper 32 m firn layers showing a sharp decrease of concentrations in the shallowest layers (Wagnon *et al.*, in press). Very similar trends are observed for chloride and methanesulfonate ions. This postdepositional dramatic loss of acid gas species at low accumulation sites is linked to snow metamorphism (see text).

of dry and wet deposition in these regions. They conclude that recent sulfate concentrations are governed by wet deposition, but that the increase of pollution sulfate is mainly due to an increase of dry deposition, which increased two times more rapidly than wet deposition over recent decades.

3. Deposition of reversibly deposited species (RDS)

The relationships between air and snow concentrations for species that are predominantly in the gas phase are certainly more complex, and thus in some ways more interesting, than those for aerosol-associated species. These RDS continue to exchange between air and snow for some time after deposition.

3.1. Hydrogen peroxide

In polar regions, H_2O_2 is thought to be co-deposited with water vapor onto the snow surface. A University of Arizona team has been focusing on H_2O_2 as the archetypal RDS and has combined field and laboratory measurements to build models describing the forward transfer function (from air into snow). A lumped parameter model has been successfully tested against Summit snow pit records [McConnell et al., 1997a] while a more fundamental physically-based model has shown promise when applied to the greatly different conditions at South Pole and the coastal Antarctic site Siple Dome (McConnell et al., 1997b; McConnell et al., 1998). At Summit, firnification processes lead to a loss of H_2O_2 concentration in the uppermost meter of the firn due to diffusion and recrystallization processes. After the first 1-2 years the H_2O_2 profile continues to smooth as a consequence of snow metamorphism (evaporation, gas phase diffusion, and recondensation processes). Deeper layers show an overall slight loss of H_2O_2 limited to a few percent per century. The amount of H_2O_2 stored in the ice depends mainly on the local accumulation rate and the temperature.

At South Pole, measurements in the atmosphere and in the snow demonstrate that the surface snow acts as an excellent archive of atmospheric H_2O_2 and suggest that snow temperature is the dominant factor determining atmosphere-to-surface snow transfer (McConnell et al., 1997b). We can therefore now be more confident in the value of the temporal trend detected at Summit for this compound (see paper by Delmas and Legrand, this issue).

3.2. Chemical changes in the firn at central Antarctic sites of very low accumulation rates

Snow pit and firn core measurements carried out at Vostok Station (accumulation rate 2.2 g cm^{-2} a^{-1}) indicate that the concentrations of four species (NO_3^-, Cl^-, MS^- (=methanesulfonate), and F^-) suffer very serious post-deposition changes in the shallow layers, most probably in relation with the snow metamorphism

(Wagnon et al., in press). Whereas $SO_4^=$ and Na profiles exhibit no trend as a function of depth, concentrations of the 4 species drastically decrease by a factor 5 to 10 from the surface to about 5-6 meter depth (Figure 1), then they stabilize. The study points out for the first time the possible deposition of gaseous MSA in central Antarctica. The three other species are already known to be partly deposited as gases, contrary to $SO_4^=$ and Na which are in the aerosol phase.

Data indicate also that these compounds accumulate in shallowest snow layers, suggesting that, after deposition, these compounds tend to migrate to the surface in the gaseous phase and to partly redeposit in upper layers. The redeposited fraction, which depends on the compound, is presently unknown.

In the upper layers, the escape of the gases to the free atmosphere is possible whereas in deeper firn layers the redeposition process probably predominates. It can be expected therefore that, in ice, volatile acids are located partly in the solid phase, partly in the bubbles. Time is a parameter to take into account since such processes need decades to develop (about 60-80 years at Vostok). At relatively high accumulation sites, the snow is buried before they can occur. They are particularly well marked in central Antarctica where accumulation is lower than about 5 g cm^{-2} a^{-1}. The Antarctic ice sheet is a net, but only extremely weak, sink for acid gases. However, as these species are expelled back to the troposphere after deposition, firn can also be regarded as a source for the pristine Antarctic atmosphere.

As already recommended, physico-chemical processes occurring in the firn for these gases have to be experimentally and theoretically investigated, as it has been the case recently for the non-interacting greenhouse gases. Laboratory studies are currently being developed to obtain fundamental information about the interaction and deposition mechanisms of such atmospheric trace gases (in particular HCl and HNO_3) with ice surfaces in polar conditions (Thibert and Dominé, 1997; 1998).

Until it is demonstrated that, for these RDS, equilibrium is reached between concentrations recorded in ice and atmospheric concentrations, caution must be exerted in the interpretation of such records.

3.3. Impact of acidity on the formation of ice records of reversibly-deposited species

In Greenland and Antarctic ice cores, the chemical analysis of the acid layers corresponding to volcanic eruptions of global concern reveals that profiles of RDS (HNO_3, H_2O_2, HCl, HF, carboxylic acids, etc.) exhibit drops or "holes" associated with the H_2SO_4 deposits. Considering only the case of nitrate, some authors concluded that atmospheric nitrate concentra-

are reduced (in some cases nearly to zero) during the time of the eruption, due to photochemical processes. Could the effect be atmospheric and due to a lowering of the incorporation of these species in the snowflakes caused by unusual high acidity? This mechanism has been put forward to evaluate the role of the acidity in the uptake of carboxylic acids (in particular formic acid) from the gas phase into the precipitation (Legrand and De Angelis, 1996). It has an important implication in the interpretation of the trends observed for carboxylic acids in Greenland ice cores in relation with increasing anthropogenic acidity (see paper on "Trends", this issue). For other RDS, this conclusion is less obvious. Moreover, as shown for fluoride deposition accompanying volcanic eruptions at Summit (De Angelis and Legrand, 1994), fluoride expelled from the volcanic layer is redeposited in the adjacent layers. In Vostok firn, where snow metamorphism is a process taking decades, RDS are slowly released into the interstitial air and seem also to partly redeposit in nearby firn layers (Wagnon et al., in press). Rather than an atmospheric effect, as generally proposed in the past, we are therefore most probably dealing in such cases with a long-lasting post-deposition glaciological process. In any case, these findings demonstrate that increased acidity (of volcanic or anthropogenic origin) is capable of lowering the already very low incorporation of volatile species in ice and markedly influencing the concentrations of these compounds in ice cores.

4. Identification of some N-bearing compounds in the polar atmosphere

Nitrate is a major component of ice core chemical composition, but its origin and deposition mechanism are still discussed. As deposition mechanisms are expected to be different for gaseous HNO_3 and aerosol nitrate, it is of primary interest to determine the nature of nitrate-bearing species present in the polar atmospheres. Measurements at Summit suggest that HNO_3 is not the only reactive nitrogen species exchanging with surface snow, and it may not be the dominant source of NO_3^-. Speculation centers on the role of one or more organic nitrate species (e.g., PAN and alkylnitrates) which must account for a significant fraction of the measured total reactive nitrogen (NO_Y). Measurements of NO_Y in the air at Summit have shown the mixing ratios to be surprisingly high, averaging nearly 1000 pptv during summer 1995. This was about 50% greater than similar measurements in the mid-troposphere over the Arctic basin (Dibb et al., 1998). Both HNO_3 and NO_Y flux into and out of the snow have been documented, with the direction of exchange changing on time scales of hours (Munger et al., submitted). In nearly half the cases, HNO_3 and NO_Y fluxes were in opposite directions, with more of these showing HNO_3 leaving the snow against an NO_Y flux into the snow than the reverse. This finding is difficult to reconcile with the standard atmospheric chemistry "model" which considers HNO_3 to be the main fraction of NO_Y which could be lost by deposition to the surface, and also calls into question the glacio-chemical assumption that NO_3^- in snow reflects atmospheric inorganic nitrate deposition. The magnitudes of bidirectional fluxes observed were too small (HNO_3) or much too large (NO_Y) to account for observed changes in the nitrate content of surface snow.

It thus appears that other members of the NO_Y family must be considered as sources of nitrate in the snow, with organic species (particularly peroxyacetyl nitrate) the most likely candidates. In the Antarctic also, in the air above G. von Neumayer Station, it appears that inorganic nitrate accounts for only a very minor fraction of reactive nitrogen oxides (Jones et al., submitted), suggesting that, at least in coastal locations, alkyl nitrates must be considered in addition to the peroxyacyl nitrates when interpreting ice cores.

References

Bergin, M.H., J.-L. Jaffrezo, C.I. Davidson, J.E. Dibb, S.N. Pandis, R. Hillamo, W. Maenhaut, H.D. Kuhns, and T. Makela, The contribution of snow, fog, and dry deposition to the summer flux of anions and cations at Summit, Greenland, J. Geophys. Res., 100, 16,275- 16,288, 1995.

Dibb, J.E., Overview of field data on the deposition of aerosol-associated species to the surface snow of polar glaciers, in: Chemical Exchange Between the Atmosphere and Polar Snow, NATO ASI Ser. I, vol. 43, edited by E. Wolff and R. Bales, pp. 249-274, Springer-Verlag, New York, 1996.

Dibb, J.E., and J.-L. Jaffrezo, Air-snow exchange investigation at Summit, Greenland: An overview, J. Geophys. Res., 102, 26,795-26,807, 1997.

Dibb, J.E., R.W. Talbot, J.W. Munger, D.J. Jacob and S.-M. Fan, Air-snow exchange of HNO_3 and NO_Y at Summit, Greenland, J. Geophys. Res., 103, 3475-3486, 1998.

Fischer, H., D. Wagenbach and J. Kipfstuhl, Sulfate and nitrate firn concentrations on the Greenland ice sheet: 1. Large scale geographical deposition changes, J. Geophys. Res., in press.

Jaffrezo, J.-L., J.E. Dibb, R.C. Bales and A. Neftel, Current status of atmospheric studies at Summit (Greenland) and implications for future research, in: Ice Core Studies of Global Biogeochemical Cycles, NATO ASI Ser. 1, vol. 30, edited by R.J. Delmas, pp. 427-458, Springer-Verlag, New York, 1995.

Jones, A.E., R. Weller, A. Minikin, E.W. Wolff, W. Sturges, and H. McIntyre, Measurements of NO_Y and its components in the Antarctic troposphere, J. Geophys. Res., submitted.

Legrand, M., and M. De Angelis, Light carboxylic acids in Greenland ice: A record of past forest fires and vegetation emissions from the boreal zone, *J. Geophys. Res.*, **101**, 4129-4145, 1996.

McConnell, J.R., R.C. Bales, J.R. Winterle, H. Kuhns, and C.R. Stearns, A five-parameter model for the atmosphere-to-snow transfer function for hydrogen peroxide, *J. Geophys. Res.*, **102**, 26,809-26,818, 1997a.

McConnell, J.R., J.R. Winterle, R.C. Bales, A.M. Thompson, and R.W. Stewart. Physically based inversion of surface snow concentrations of H_2O_2 to atmospheric concentrations at South Pole, *Geophys. Res. Lett.*, **24**, 441-444, 1997b.

McConnell, J.R., R.C. Bales, R.W. Stewart, A.M. Thompson, M.R. Albert, and R. Ramos, Physically based modeling of atmosphere-to-snow-to-firn transfer of H_2O_2 at South Pole, *J. Geophys. Res.*, **103**, 10,561-10,570.

Munger, J.W., D.J. Jacob, S.-M. Fan, A.S. Colman, J.E. Dibb, and R.W. Talbot, Concentrations and fluxes of reactive nitrogen at Summit, Greenland, *J. Geophys. Res.*, submitted.

Thibert, E., and F. Dominé, Thermodynamics and kinetics of solid solution of HCl in ice, *J. Phys. Chem. B*, **101**, 3554-3565, 1997.

Thibert, E., and F. Dominé, Thermodynamics and kinetics of solid solution of HNO_3 in ice, *J. Phys. Chem. B*, **102**, 4432-4439, 1998.

Wagnon, P., R.J. Delmas, and M. Legrand, Loss of volatile acid species from shallow snow layers at Vostok, Antarctica. *J. Geophys. Res.*, in press.

Books

Ice Core Studies of Global Biogeochemical Cycles, NATO ASI Ser. 1, vol. 30, edited by R. J. Delmas, pp. 475, Springer-Verlag, New York, 1995.

Chemical Exchange Between the Atmosphere and Polar Snow, NATO ASI Ser. I, vol. 43, edited by E. Wolff and R. Bales, pp. 675, Springer-Verlag, New York, 1996.

Trends Recorded in Greenland in Relation with Northern Hemisphere Anthropogenic Pollution

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1. Introduction

The composition of the Northern Hemisphere atmosphere has changed significantly over the last century. Emissions by fossil fuel burning of significant amounts of carbon dioxide, sulfur dioxide, nitrogen oxides, and other species are relatively well quantified, but the impact of these pollutants on the composition of the background atmosphere, in particular over the large areas located at high northern latitudes, is much more poorly documented. Anthropogenic pollution can modify radiative forcing, aerosol composition, and oxidation capacity of the atmosphere. Polar snow does not record all the parameters involved in these processes, but ice core studies are invaluable for documenting the evolution of several key atmospheric parameters since the beginning of human activities.

Over recent years, several ice cores have been recovered in Greenland and the trends of most pollutants over several centuries are now satisfactorily depicted. However, the validity of a few records may be questionable, in particular for species affected by postdepositional effects (see paper by Delmas, Jaffrezo, Gibb, and Bales, this issue).

2. Aerosol composition changes: Sulfate and ammonium

The extent of acid pollution to high Arctic regions was detected early, but high elevation areas were poorly documented. A preindustrial sulfate figure in the range 30-50 ng g^{-1} has been determined recently for ice at various Greenland sites, with highest values in the north (Fischer *et al.*, in press a). At Summit, mean non-sea-salt sulfate (nss-$SO_4^=$) concentration was 26 ng g^{-1} until about 1900 (see Table 1). Just after the turn of the century, SO_2 emissions by fossil fuel burning began to impact sulfate deposition in Greenland markedly. The detailed Eurocore-GRIP nss-$SO_4^=$ profile is shown Figure 1. In conjunction with several volcanic eruptions which blur the pure anthropogenic signal, nss-$SO_4^=$ concentrations start to rise during the first decade of the century (Legrand *et al.*, 1997). A break is observed in the 1930s probably in relation to the economic crisis. After World War II, a much sharper increase (5 ng $g^{-1}a^{-1}$) is found which culminates at 110 ng g^{-1} at the end of the 1960s. At Summit, the mean value for the time period 1950-1989 is 85 ng g^{-1} (Table 1). Sulfur pollution abatement measures are clearly reflected in Greenland sulfate profiles

which show a steady decreasing trend since about 1980.

Detailed measurements show that the anthropogenic impact affects mostly the dry-deposited fraction of sulfate (Fischer *et al.*, in press b). North America is proposed as the major source of pollution sulfate in Greenland for the first half of the century, Eurasia for post-war decades.

	Preindustrial	Last Decade
non-sea-salt sulfate	26	85
ammonium	5.3 ± 9.6	-
nitrate	68	120
fluoride	0.06	0.19
formaldehyde	2-3	5
hydrogen peroxide	125	255[*]
formate	7.7 ± 2.3	6.3 ± 2.4
acetate	6.5 ± 1.9	9.8 ± 3.2
methanesulfonate	2.9 ± 1.9	1.9 ± 1.05

Table 1. Comparison of pre- and post-industrial levels of various compounds determined at Summit, central Greenland. Data are from Mayewski *et al.*, 1993, De Angelis and Legrand, 1994, Legrand and De Angelis, 1996, Legrand *et al.*, 1997, Anklin and Bales, 1997. Concentrations are in ng g^{-1}. (*): mean value for the most recent 3 years (1992-94).

Interestingly, sulfate concentrations during the last glacial maximum, i.e., some 25,000 years ago (Legrand *et al.*, 1997), reached significantly higher levels than in the 1960s when pollution was at its maximum. However, during the ice age, sulfate deposition was mostly in the form of large $CaSO_4$ particles, rather than pollution sulfate which is deposited in the form of H_2SO_4 (assumed to be fine aerosol). Ca and NH_4^+ in ice cores do not show trends similar to sulfate. The former is not affected by pollution. For the latter, a 100% increase occurred during recent decades, but it is limited and affects only springtime deposition (Fuhrer *et al.*, 1996). NH_4^+ background concentration in the ice (5.3 ng g^{-1}) is contributed mainly by soil and vegetation emissions. Forest fires at high northern latitudes are a sporadic source (in the form of ammonium formate) to Greenland snow, but this contribution does not show a definite temporal trend over the last century (Legrand *et al.*, 1995). It is worth noting that in European glaciers, closer to potential NH_3 sources, ammonium concentrations started to grow already some 100 years ago, before sulfate and nitrate (Döscher *et al.*, 1996).

3. Hydrogen peroxide

H_2O_2 is the species most directly related with the oxidation capacity of the atmosphere. It is the most abundant compound found in natural polar snow, but early data were controversial. Atmospheric, snow pit, and firn core measurements at Summit using *in situ* analytical methods have shed a new light on the concentration of this species in Greenland.

Sigg and Neftel (1991) suggested at Summit a 50% increase of H_2O_2 concentration during the last 200 years, but more recent studies at the same site led to an estimate of the overall increase of 60 ± 12% since preindustrial time (Anklin and Bales, 1997), in essential agreement with the expected effect of growing emissions of CH_4, NO_X and CO. The H_2O_2 concentration profile departed from natural background fluctuations already in the middle of the last century, i.e., long before nitrate pollution. In most recent years, the increasing trend seems to be more pronounced and the amplitude between winter minima and summer maxima has tripled since 1970.

4. Carbon monoxide

The determination of CO concentrations in ice cores is difficult due to as yet poorly characterized glaciological artifacts that affect the Greenland ice in particular (Haan and Raynaud, in press). Only a few data are available up to now (Haan *et al.*, 1996). An increase of about 20 ppbv is observed between 1800 and 1950 for this compound at Summit where the preindustrial level is 90 ppbv (55-60 ppbv in the Antarctic). The figure of 90 ppbv should be regarded as an upper limit.

5. Nitrate

At Summit, nitrate concentration increases from a preindustrial mean value of 68 to 120 ng g^{-1} for the period 1950-1989. This trend, valid all over Greenland, starts markedly only since around 1950, i.e., much later than sulfate, and probably has a North American origin. A decline of this pollution is detected only for the most recent years.

This trend observed for nitrate in Greenland firn must be considered with some caution due to the reversibility of gaseous HNO_3 deposition onto snow, even in Greenland (Fischer *et al.*, in press a). Measurements carried out at various Greenland sites with different snow accumulation rates, i.e., having different depth-age relationships, lead to similar temporal changes. This suggests that postdepositional effects have only a limited impact on nitrate trends recorded in Greenland snow. However, it must be kept in mind that N-bearing species deposited in Greenland are not all yet formally identified. They may have changed since preindustrial times and in present environmental conditions, as suggested in the discussion of the transfer function (this issue).

6. Formaldehyde

HCHO measurements in Greenland snow are scarce. Data obtained by Staffelbach *et al.* (1991) at Summit

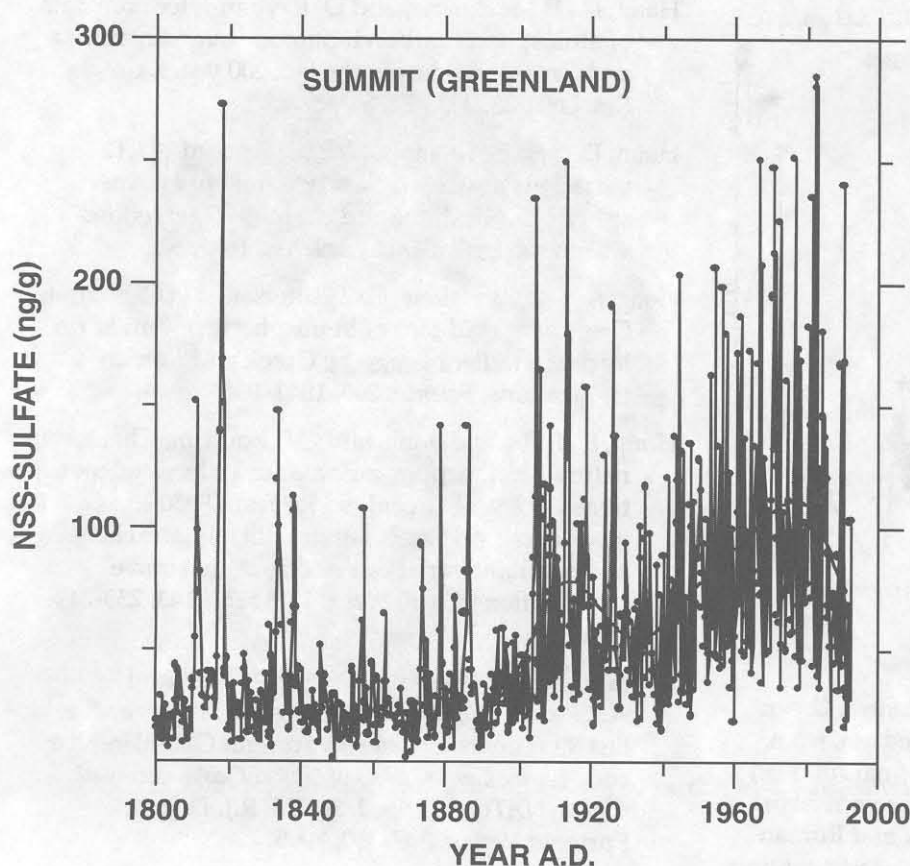**SUMMIT (GREENLAND)**

NSS-SULFATE (ng/g) vs YEAR A.D.

Figure 1. Upper part of the Eurocore-GRIP nss-sulfate profile (402 values) obtained at Summit (central Greenland) covering the two last centuries. The gray continuous curve is a running average on 3 values. In the 19th century, variability was natural: spikes were caused by large volcanic eruptions (e.g., Tambora, 1815 and Krakatoa, 1883). Note the sudden increase in the concentrations observed in 1903, linked partly to a volcanic event (most likely Santa Maria, 1902). The continuous line is a polynomial average of degree 10 including 200 values. The first "bump" on this curve is probably linked to increasing pollution, but also to sporadic volcanism. A marked decrease of pollution is observed in the last two decades.

pointed out a doubling of preindustrial concentration (about 2 ng g^{-1}) in recent years, with an acceleration of the increase in the last decades. This observation must be taken with caution, however, due the reversibility of the deposition of this species on polar snow.

7. Carboxylic acids

Light carboxylic acids in the atmosphere are linked to natural emissions by vegetation and biomass burning. Anthropogenic activities are also potential contributors, directly or indirectly, to their global budgets. Excluding sporadic biomass burning spikes, the non-biomass burning concentrations of formate and acetate at Summit over the last two centuries are 7.4 ± 2.4 and 7.2 ± 2.7 ng g^{-1}, respectively. Interestingly, a *decreasing* temporal trend in formate concentration is observed over the last century (Legrand and De Angelis, 1996), suggesting that the anthropogenic source is not dominant for this species. Moreover, it has been calculated that the increasing acidity of the snow caused by anthropogenic sulfate deposition (the incorporation of HCOOH in the snowflakes is acidity-dependant), is the most likely explanation for this decreasing trend. In contrast, the acetate profile exhibits a well-marked increase over the last three decades (Table 1), a trend presently unexplained, that could be linked with increasing deposition of peroxy-acetyl nitrate, which acts as a reservoir of acetic acid.

8. Heavy metals

It is well known that the deposition of several trace metals has increased considerably in Greenland in relation with the development of human activities (Candelone *et al.*, 1995). The ratio between preindustrial levels and those for the last 20 years is found to be significantly higher than for sulfate or nitrate. For example, factors of 2.3, 2.7, and 9 are found for Zn, Cu, and Cd, respectively. The factor is considerably higher for Pb (250) due to the use of organic lead derivates in gasoline. It is worth noting, however, that Summit studies revealed that disturbance of the natural cycle of lead began with Greek and Roman industrial activities (Hong *et al.*, 1994) and that the present level of this metal in Summit snow is just as high as it was during the last glacial maximum (Hong *et al.*, 1996) (Figure 2).

References

Anklin, M., and R.C. Bales, Recent increase in H$_2$O$_2$ concentration at Summit, Greenland, *J. Geophys. Res.*, **102**, 19,099-19,104, 1997.

Candelone, J.-P., S. Hong, C. Pellone, and C. Boutron, Post-industrial revolution changes in large scale atmospheric pollution of the Northern Hemisphere by heavy metals as documented in central Greenland snow and ice, *J. Geophys. Res.*, **100**, 16,605-16,616, 1995.
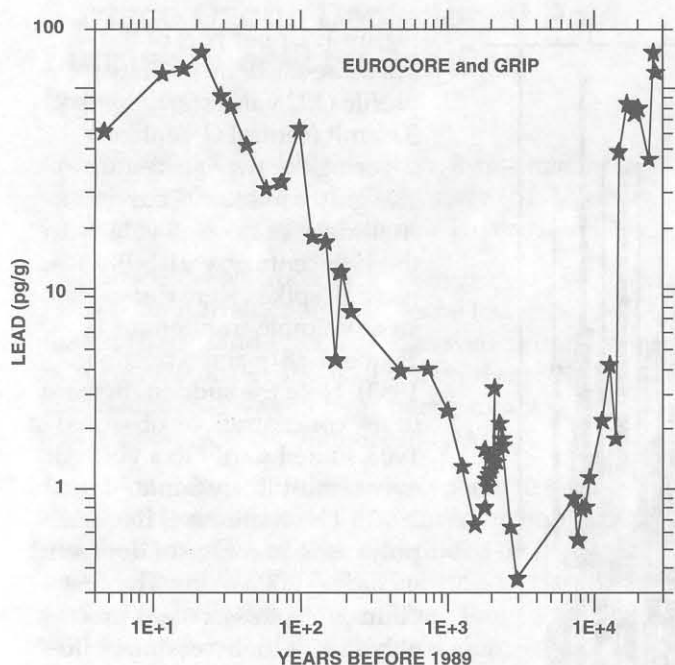
Figure 2. Lead deposition at Summit (central Greenland) over the last 30,000 years. Included are, from right to left, the decrease of the input of natural lead linked to crustal dust, a marked increase with a climax around 2,000 years ago linked to Greek and Roman mining activities (see text), thereafter a nearly continuous growth of anthropogenic pollution cluminating about 30 years ago. Since this date, a marked decreasing trend is observed linked to the use of unleaded gasoline. Data are from Hong *et al.*, 1994, 1996 and Candelone *et al.*, 1995. Note the similarity of the figures of modern (some 30 years ago) and preindustrial (about 25,000 years ago) of lead deposition.

De Angelis, M., and M. Legrand, Origins and variations of fluoride in Greenland precipitation, *J. Geophys. Res.*, 99, 1157-1172, 1994.

Döscher, A., H.W. Gäggeler, U. Schotterer, and M. Schwikowski, A historical record of ammonium concentrations from a glacier in the Alps, *Geophys. Res. Lett.*, 23, 2741-2744, 1996.

Fischer, H., D. Wagenbach and J. Kipfstuhl, Sulfate and nitrate firn concentrations on the Greenland ice sheet: 2. Temporal anthropogenic deposition changes, *J. Geophys. Res.*, in press a.

Fischer, H., D. Wagenbach and J. Kipfstuhl, Sulfate and nitrate firn concentrations on the Greenland ice sheet: 1. Large scale geographical deposition changes, *J. Geophys. Res.*, in press b.

Fuhrer, K., A. Neftel, M. Anklin, T. Staffelbach, and M. Legrand, High-resolution ammonium ice core record covering a complete glacial-interglacial cycle, *J. Geophys. Res.*, 101, 4147-4164, 1996.

Haan, D., P. Martinerie, and D. Raynaud, Ice core data of atmospheric carbon monoxide over Antarctica and Greenland during the last 200 years, *Geophys. Res. Lett.*, 23, 2235-2238, 1996.

Haan, D., and D. Raynaud, Ice core record of CO variations during the last two millennia: Atmospheric implications and chemical interactions within the Greenland ice, *Tellus*, in press.

Hong, S., J.-P. Candelone, C.C. Patterson, and C. Boutron, Greenland evidence of hemispheric pollution for lead two millennia ago by Greek and Roman civilizations, *Science*, 265, 1841-1843, 1994.

Hong, S., J.-P. Candelone, and C.F. Boutron, Changes in natural lead, copper, zinc and cadmium concentrations in central Greenland ice from 8250 to 149,100 years ago: Their association with climatic changes and resultant variations of dominant source contributions, *Earth Planet. Sci. Lett.*, 143, 233-244, 1996.

Legrand, M., M. De Angelis, H. Cachier, and A. Gaudichet, Boreal biomass burning over the last 80 years recorded in a Summit Greenland ice core, in: *Ice Core Studies of Global Geobiochemical Cycles, NATO ASI Ser. I*, 30, Ed. R.J. Delmas, Springer Verlag, 347-350, 1995.

Legrand, M., and M. De Angelis, Light carboxylic acids in greenland ice: A record of past forest fires and vegetation emissions from the boreal zone, *J. Geophys. Res.*, 101, 4129-4145, 1996.

Legrand, M., C.U. Hammer, M. De Angelis, J. Savarino, R.J. Delmas, H. Clausen, and S.J. Johnsen, Sulphur derived species (methanesulfonate and SO$_4$) over the last climatic cycle in the GRIP (central Greenland) ice core, *J. Geophys. Res.*, 102, 26,663-26,679, 1997.

Mayewski, P., L.D. Meeker, M.C. Morrison, M.S. Twickler, S.I. Whitlow, K.K. Ferland, D.A. Meese, M.R. Legrand, and J.P. Steffensen, Greenland ice core "signal" characteristics: An expanded view of climate change, *J. Geophys. Res.*, 98, 12,839-12,847, 1993.

Sigg, A., and A. Neftel, Evidence for a 50% increase in H$_2$O$_2$ over the past 200 years from a Greenland ice core, *Nature*, 351, 557-559, 1991

Staffelbach, T., A. Neftel, B. Stauffer, and D. Jacob, A record of the atmospheric methane sink from formaldehyde in polar ice cores, *Nature*, 349, 603-605, 1991.

Announcement

A workshop will be held October 7, 1998, in Lulea, Sweden on:

Measurement and Modeling of Landfill Methane Emissions and Methane Oxidation: Recent Field Data, New Techniques, and Future Trends for Global Inventories.

Co-Conveners are J. Bogner (Landfills +, Inc. and University of Illinois, Chicago, USA) and D. Savanne (Ademe, France). This workshop will be held during the Swedish Landfill Symposium 1998 (October 6-8, 1998). The workshop is a follow-up to a previous IGAC workshop held in October, 1996, at Argonne National Laboratory, Argonne, Illinois, USA. For further information, please contact Jean Bogner (landfill@ix.netcom.com).

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