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Arctic tropospheric chemistry: an overview

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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). It is underlain by the flat Arctic Ocean from which it is separated by a crack-ridden ice membrane 3 to 4 m thick. Ocean-to-atmosphere exchange of heat, water vapour and marine biogenic gases influence the composition of the reactor. 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 stabily stratified. This hinders vertical mixing and dry deposition of atmospheric chemicals. Precipitation in the high arctic winter and spring is very low, approaching desert conditions (10 mm H_2O equivalent per month). Thus, precipitation scavenging of chemicals is at a minimum.

In this winter environment, chemical reactions involving sunlight as well as removal rates of aerosols are much slower than further south. Thus, it is not surprising to find the abundance of photochemically-reactive compounds and aerosols in the atmosphere high at polar sunrise. However, there are exceptions to the rule of slower reactions in the arctic troposphere than further south. Perhaps the most spectacular is the destruction of lower tropospheric ozone accompanied by the production of filterable bromine and iodine. About a decade ago, tropospheric ozone depletion at polar sunrise was reported by Oltmans and Komhyr(1986) at Point Barrow Alaska and by Bottenheim et al. (1986) at Alert Canada. It 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 (Solberg et al., 1996). There are strong indications that a very similar phenomenon occurs at polar sunrise in Antarctica. Apparently, ozone depletion only occurs after polar sunrise during the period mid-March to the end of May when sunlight is present and the arctic is still frozen. Ground-based ozone mixing ratios decrease from the mid-winter mean of 30 to 40 ppbv to <1 ppbv. These processes appear to have few or no parallels in other parts of the troposphere. They may have natural causes, but arctic haze sulphate aerosols and gaseous pollutants advected from Europe, Russia and to a lesser extent, North America, may also contribute.

A striking anti-correlation between ozone and bromine collected on cellulose aerosol filters at Alert Canada led to the hypothesis of halogen catalysed reaction cycles (Barrie et al., 1988) leading to particulate Br production. In addition, organic di-carboxylic acids, ketoacids and dicarbonyl particulate matter is formed (Kawamura et al., 1995, 1996). Subsequent, photochemical modelling and laboratory studies have suggested the involvement in polar sunrise chemistry of Br/BrO, ClO/Cl and possibly IO/I acting individually or in combination, as well as the important rôle of heterogeneous reactions on ice or acid aerosols (McConnell et al., 1992; Fan and Jacobs; 1992, LeBras and Platt, 1995) in ozone destruction. In an intensive international study, Polar Sunrise Experiment 1992 (PSE92) at Alert (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 ozone destruction (Jobson et al., 1994) and that BrO was unequivocally present in the lower Arctic troposphere (Hausmann and Platt, 1994). New observa-

tions in that study raised questions regarding the chemical mechanism of tropospheric ozone loss, the rôle of halogen oxide radicals in this phenomenon, the rôle of anthropogenic chemicals and the environmental consequences of arctic tropospheric ozone loss.

A key outstanding issue is the source of reactive halogen species (RHS). The observation that total bromine (i.e., the sum of inorganic and organic gas-phase Br compounds and aerosol Br) increases during low ozone 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 for RHS during arctic spring are degradation of organohalogen compounds of anthropogenic or natural origin, or 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., bromochloroalkanes such as CH_3Br, $CHBr_3$, $CHBr_2Cl$), under polar springtime conditions, the first source is unlikely.

There are several possible heterogeneous mechanisms to oxidize the sea salt halides phase (sea salt contains by weight 55.7% Cl, 0.19% Br, and 0.00002% I) to reactive halogen species (e.g., Cl_2, Br_2), that can be released to the gas. 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, strong evidence is now emerging (Tang and McConnell, 1996, Vogt et al., 1996, Ariya et al., this issue; Sander et al., this issue) that atmospheric reactions involving oxidants lead to auto-catalytic liberation of reactive bromine from sea salt. Once a reaction cycle of this type has started, there is an exponential growth of the RHS concentration. This can be called a "bromine explosion".

In order to address outstanding questions raised in PSE92, the ARCtic Tropospheric Ozone Chemistry (ARCTOC) project was organized by European scientists (Platt and Lehrer, 1996). It consisted of three components.

(1) Two field studies during spring 1995 and 1996 at Ny-Ålesund/Spitsbergen with measurements including O_3, halogen oxides (Tuckermann et al., this issue), volatile organic compounds (Ramacher et al., this issue), and the aerosol chemical composition (Lehrer et al., this issue) supplemented by about two years of continuous ozone measurements at three Greenland sites (Thule, Scoresbysund, and Søndre Strømfjord).

(2) Laboratory kinetic investigations of relevant homogeneous (Birebach et al., this issue) and heterogeneous reactions at arctic temperatures. This includes in particular reactions of Br atoms with unsaturated hydrocarbons as well as interactions of NO_y with sea salt.

(3) Modelling studies of the underlying chemical mechanisms and the large-scale development of the phenomenon.

In this special issue, results from ARCTOC as well as measurements in Søndre Strømfjord (Miller et al., this issue) are highlighted.

This research has greatly increased our knowledge of polar tropospheric chemistry. We are now more confident that the observed polar boundary layer O_3 depletion events are caused by catalysis by BrO and ClO under meteorological 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 ozone depletion.

Conclusions from field observations

- Levels of BrO (several 10 pptv) found in the European arctic during this study (Tuckermann et al., this issue) are comparable to those reported for arctic Canada (Alert) (Hausmann and Platt, 1994). These boundary-layer BrO concentrations are about two orders of magnitude higher than concentrations found in the stratosphere.
- The abundance of ClO which was observed in the troposphere for the first time is comparable to that of BrO (several 10 pptv) (Tuckermann et al., 1997).
- Periods of depleted O_3 in the lower troposphere generally coincide with BrO and ClO mixing ratios but not with that of IO. High BrO

and ClO concentrations were never found during periods of normal ozone concentrations.

- The bulk of the O_3 loss is most likely caused by catalysis by BrO_X (= Br + BrO), or by a combination of $BrO_X + ClO_X$, or of $BrO_X + HO_2$ (with the XO self- and cross reactions being the rate limiting steps).
- There is very good evidence that halogen catalysed troposphere ozone loss also occurs in antarctica.
- Observed halogen oxide levels are sufficiently high to destroy 1 to 2 ppbv O_3 per hour, and thus to completely eliminate 40 ppbv of initial O_3 within 1 to 2 days.
- The rapid variations in O_3 (up to 7 ppbv/h) observed at coastal baseline observatories such as Ny Alesund and Alert are almost certainly a consequence of atmospheric dynamics (i.e., advection and mixing of depleted and undepleted air masses).
- Br-atom concentrations deduced from BrO measurements and model estimates of BrO/Br ratios are consistent with concentrations derived from observations of hydrocarbon depletion (Ariya et al., 1997; Ramacher et al., 1997; Rudolph et al., 1997).
- Chlorine atom levels deduced from ClO measurements made by differential optical absorption spectroscopy frequently exceed concentrations derived from hydrocarbon depletion observations (Ramacher et al., 1997).
- Reactions involving the nitrogen oxides NO_2, NO_3, or N_2O_5 are unlikely to play a rôle in halogen release processes due to low concentrations of these nitrogen compounds in the arctic (Beine et al., this issue).
- The chemistry that maintains observed ClO_X remains unknown.
- There may be a rôle of anthropogenic arctic haze in arctic boundary layer O_3 loss, but it is not a prerequisite for the phenomenon which occurs under more natural conditions in Antarctica.

Results from the laboratory measurements

- A considerable extension has been made to the gas phase kinetic data base for the reaction of Br atoms with hydrocarbons (including alkenes, chlorinated alkenes, dienes, unsaturated carbonyls and aromatic species) (Ariya et al., 1997; Bierbach et al., 1997). The product pattern for all the alkenes investigated was similar. The yield of brominated carbonyls (retaining the original chain length) is $\approx$70–80%.
- At Br atom levels prevailing during arctic O_3 depletion episodes, competition between Br atom and OH radical-induced oxidation of unsaturated hydrocarbons is to be expected.
- Under conditions of the polar atmosphere, relatively rapid Br release from brominated oxidation products 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 sulphate aerosols are generally found to be greater at higher relative humidities.

Results from modelling studies

- Observations made during O_3 depletion events could be quantitatively reproduced by existing 3D models extended to include detailed tropospheric halogen chemistry (Ariya et al., 1997; Sander et al., 1997).
- Better results were obtained in all models of ozone depletion when heterogeneous reactions of gases on aerosol or ice surfaces were included (Tang and McConnell, 1996; Sander et al., 1997). The 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 (Shepson et al., 1996).
- Auto-catalytic release of Br (and to a lesser extent Cl), either from sea salt aerosol or salt deposits on the snow pack, possibly leading to "bromine explosions", is the most likely source of reactive halogens in the arctic. Overall, there is now a satisfactory theory of BrO_X liberation that needs to be tested (Tang and McConnell, 1996; Sander et al., 1997).

Outlook

There are still many issues that demand further investigation. In particular, future studies must explain why there appears to be no comparable halogen activation at mid-latitudes and why the phenomenon of halogen activation and ozone loss only occurs during polar springtime and not during summer or at polar sunset. Further research is also needed to elucidate the chemistry and atmospheric abundance of reactive iodine species and their possible involvement in the chemical mechanisms leading to ozone destruction.

Although the main features of O_3 depletion chemistry are quite clear, many details about the source of active halogens need further study. This is particularly true for reaction cycles occurring in deliquesced sulphate aerosols and on ice surfaces. While it is now almost certain that sea-salt is the source of reactive halogen species, it is not clear whether these are liberated from sea salt deposits on ice of refrozen leads or sea salt in the snowpack. Furthermore, the rôle of anthropogenic arctic haze pollutants in the ozone loss phenomenon needs further investigation.

Finally, recent observations in the arctic troposphere at Alert of total gas phase mercury, (TGM) consisting mostly of elemental mercury have shown that it and ozone are simultaneously destroyed at polar sunrise (Schroeder et al., 1997). TGM is converted to particulate and possibly more reactive gaseous forms of mercury that are much more rapidly deposited. Thus, as a result of ozone depletion chemistry, inputs of mercury to the Arctic Ocean ecosystem are likely enhanced. Polar ozone depletion may play a rôle in the environmental cycle of the most potentially toxic metal in the global environment by enhancing the deposition of mercury from atmosphere to arctic marine systems in spring.

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