Is cloud seeding in coastal Antarctica linked to bromine and nitrate variability in snow?

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Abstract
Considering the significance of methanesulfonate (MSA) in the sulfur cycle and global climate, we analyzed MSA and other ionic species in snow from the coastal Larsemann Hills, East Antarctica. MSA concentrations recorded were high (0.58 ± 0.7 μM) with ice-cap regions showing significantly higher concentrations (df = 10, p < 0.001) than ice-free regions. High nutrient concentration in ice-cap snow appears to have favored algal growth (7.6 × 10^2 cells l^-1) with subsequent production of brominated compounds. The consequent elevated Br^- (3.2 ± 2.2 μM) in the ice-cap region could result in the release of Br atoms through photoactivated reactions on aerosols and the snow surface. Activated Br atoms in the atmosphere could react with ozone leading to BrO enhancement with subsequent dimethylsulfide (DMS) oxidation and production of sulfur aerosols. Since BrO based DMS oxidation is much faster than the OH/NO3 pathway, elevated Br^- in ice-cap snow could contribute more than ice-free sites towards formation of cloud condensation nuclei at the expense of ozone.

Keywords: bromide, methanesulfonate, snow, nitrate, algae, Antarctica

1. Introduction

On a global scale, marine biogenic activity has been recognized as a primary contributor of dimethylsulfide (DMS) to the atmosphere (Saltzman et al 1983, Ayers et al 1986). DMS is formed from enzymatic cleavage of precursor dimethylsulphoniopropionate which is produced by certain species of marine algae, phytoplankton and benthic diatoms (Trevena et al 2000). Once emitted into the atmosphere, DMS is oxidized by OH radicals, NO3 radicals (at night) and BrO/IO, forming aerosol sulfates via methanesulfonate (MSA) and SO2 (Nguyen et al 1983, Saltzman et al 1983). DMS oxidation by OH and halogen radicals yields MSA and SO2 while the reaction with NO3 radicals yields only SO2. These products of DMS oxidation are of particular interest because of their potential climate-forcing effects. Charlson et al (1987) suggested that sulfate aerosols from DMS oxidation are capable of acting as cloud condensation nuclei (CCN), which enhance cloud albedo or directly affect the earth atmosphere radiative balance by absorbing and scattering solar radiation. This in turn would cause a climate feedback mechanism resulting in reduced algal growth through the effects of reduced sunlight. Although this hypothesis is widely debated, the idea has evolved over the years and still continues to be pursued as a paradigm.

Recent studies on the chemical mechanisms of DMS oxidation have become increasingly detailed and complex. However, biological factors controlling DMS oxidation remains a major uncertainty in our understanding of the contribution of these processes in regulating the formation of MSA and other sulfur aerosols. It is well known that algae emit DMS, which is oxidized in the atmosphere to form sulfur aerosols. What is little understood is that algae not only contribute to CCN formation via production of DMS but
also through formation of halogen radicals that contribute to the rapid oxidation of DMS to sulfuric and methanesulfonic acids. Atmospheric regulation of DMS oxidation through biogenic production of halogen radicals has been largely overlooked. Although the complexity of the physicochemical and atmospheric processes controlling the oxidation of DMS is becoming increasingly evident, the biogenic processes controlling DMS oxidation are still vaguely understood. While there exist uncertainties in the magnitude of most biogenic sources of bromine, measurements of biogenic bromine in the atmosphere (Sturges et al. 1992) indicate that the presence of these compounds seems to have been underestimated. In this study, we investigate the factors responsible for the high concentrations of MSA in the snow deposited along a transect within the Ingrid Christensen Coast in East Antarctica and provide new insight on the possibility of biogenic bromine mediated oxidation of DMS.

2. Sampling and analytical methods

The Larsemann Hills (69°20’S to 69°30’S and 75°55’E to 76°30’E) are a relatively ice-free area located approximately midway between the eastern extremity of the Amery Ice Shelf and the southern boundary of the Vestfold Hills on the Ingrid Christensen Coast, East Antarctica (Figure 1). Surface snow samples were collected from this region during 8–11 March 2007, along an ice-free to ice-cap transect. Soft, surface snow samples were collected up to a depth of ~10 cm using fresh, sterile, powder-free and polymer-coated latex gloves. Ambient day time temperatures during the sampling days were −5 to −10°C. The prevailing wind at the time of collection of samples was almost parallel to the coast. Twelve samples were selected from the ice-free region (Grovnes) which represents the bare rock area of the ice edge and 25 samples from the ice-cap. The sampling transects covered ~18 km and had an elevation ranging from 2.7 m asl (above sea level) to about 526 m asl. A distance of about 2.5 km from the coast represented the ice-free sampling area. The samples from the ice-free area were collected at an elevation ranging from 2.7 to about 12.5 m asl. Visual observation suggested that the snow structure was essentially the same at all sites, as fresh surface snow was collected from both ice-free and ice-cap area. Since the samples were predominantly soft snow
deposits and were collected during the late summer period, we consider that the samples studied here could represent a single season (summer). The snow samples were stored in well sealed, labeled and pre-cleaned LDPE bags and kept frozen in clean expanded polypropylene boxes. The samples were shipped in −20 °C conditions and were stored in such condition until the sample processing and analysis. Sample preparation, processing and analysis were carried out with adequate precautions and clean techniques. All labware and glassware used during sample processing were cleaned with ultra-pure nitric acid and MilliQ Element (Millipore) water. Samples were melted at room temperature in a Class 100 clean room. MSA (CH$_3$SO$_3^-$), Na$^+$, Cl$^-$, Br$^-$, NH$_4^+$, PO$_4^{3-}$ and NO$_3^-$ concentrations were measured using reagent-free ion chromatograph techniques (Dionex ICS-2500 with EG50 Eluent Generator Module and CD25 Conductivity detector) in a Class 100 clean room. Determination of I$^-$ was carried out by anion-exchange chromatography (Dionex ICS 3000) with Pulsed Amperometric Detection and an Ionpac AS-12A/Ionpac AG-12A column. All reagents used were of ultra-pure grade. Calibrations for CH$_3$SO$_3^-$, Na$^+$, Cl$^-$, Br$^-$, NH$_4^+$, PO$_4^{3-}$ and NO$_3^-$ were carried out using standards from Inorganic Ventures, USA and for I$^-$ from Merck, Germany. In order to confirm the quality of measurements, chromatographic standards were analyzed on a daily basis throughout the study. Blanks were also run periodically to check the quality of the data. The instrumental detection limits were better than 1 µg l$^{-1}$ for MSA, Na$^+$, Br$^-$ and 250 ng l$^{-1}$ for I$^-$. The analytical precision obtained based on the daily analysis of the international chromatographic standards is better than ±5% for the ions reported here.

3. Results and discussion

3.1. MSA and sulfate distribution in the surface snow

The mean MSA concentration in the Larsemann region was 0.58 ± 0.7 µM ($n = 37$), which is higher than that recorded in snow samples elsewhere in Antarctica. An exception is Western Dronning Maud Land where reported values for coastal snow samples were higher, with values ranging from 0.7 ± 0.7 to 4.5 ± 0.2 µM (Kárkás et al. 2005). Concentrations of MSA measured elsewhere in Antarctic snow have been reported to range from 0 to 0.46 µM with a mean value of 0.07 µM (Maupetit and Delmas 1992) and from 0.07 to 0.14 µM (Legrand et al. 1992). Several studies have shown that MSA concentration is higher at coastal sites and shows a decreasing trend towards inland regions and with increasing elevation (Propositio et al. 2002, Bertler et al. 2005, Kárkás et al. 2005). Since MSA is derived exclusively from oxidation of marine plankton derived DMS (Saltzman et al. 1983, Ayers et al. 1986), the high values observed in this study could indicate enhanced biological activity in the surrounding ocean and ice. In the study region, MSA levels were significantly higher in snow samples collected from ice-cap areas compared to the samples from the ice-free region ($df = 10$, $p < 0.001$). MSA values ranged from ND to 0.07 µM (mean 0.02 ± 0.02 µM, $n = 12$) in the ice-free region. In the ice-cap areas, the concentrations ranged from 0.1 to 3.6 µM with a mean value of 0.8 ± 0.7 µM ($n = 25$) (figure 2).

3.2. Distribution of nutrients in snow

The distribution of inorganic nutrients such as NH$_4^+$, NO$_3^-$ and PO$_4^{3-}$ were also determined in Larsemann snow. PO$_4^{3-}$ values ranged from ND to 4.4 µM in the ice-free samples and from 0.6 to 9.8 µM in the ice-cap region. NO$_3^-$ concentration in the ice-cap areas was 3.04 ± 2.7 µM, which is five times higher than that observed in the ice-free area. NH$_4^+$ was below the detection limit in most of the ice-free snow samples, while in the ice-cap region concentration ranged up to 4.68 µM.

Jones and Pomeroy (1999) reported that during summer, when snow melts, soluble nutrients like NH$_4^+$ and NO$_3^-$ promote abundant growth of snow algae, which reproduce within the melt water retained by snow. The abundant concentration of nutrients in snow observed in this study raised the possibility that they could promote the growth of algae in snow. In order to confirm this, we examined a few snow samples under a scanning electron microscope (JEOL JSM-6360) to check for the presence of algae. This revealed the presence of several diatom frustules. However, most of the frustules were not intact. These diatoms were present even in samples collected from an elevation of about 513 m asl. In the ice-free sample the diatom population was about 3 times higher than the ice-cap samples collected from an elevation of about 513 m asl. In the ice-free sample the diatom population was about 3 times higher than the ice-cap samples collected from an elevation of about 513 m asl. In the ice-free sample the diatom population was about 3 times higher than the ice-cap samples collected from an elevation of about 513 m asl.
phosphate, pyruvate etc (Decho 1990). Their importance as a nutrient source has been reviewed by Decho (1990) and Verdugo et al (2004).

3.3. Bromide concentration in snow: key player in regulating MSA level?

Analyses of Br\(^-\) in Larsemann snow samples revealed that its concentration along an ice-free area to the ice-cap region ranged from ND to 6.9 \(\mu\)M (figure 3). The values measured here are exceptionally high compared to values reported for any coastal Antarctic site (Kalnajs and Avallone 2006). Within the ice-cap region, Br\(^-\) values steadily increased with increasing distance from the coast, with a mean concentration of 3.2 ± 2.2 \(\mu\)M (n = 24). The concentration of Br\(^-\) was found to be negatively correlated with Na\(^+\) (\(r = -0.428, p < 0.01, n = 36\)). This observed anti-relation may be mainly because: (i) unlike Na\(^+\), whose deposition in snow indicates marine influence, the presence of Br\(^-\) in snow may not be dominated by deposition of sea salt aerosol (Simpson et al 2005) or (ii) elevated Br\(^-\) levels in inland region from brominated organic compounds produced by snow algae.

Bromine is released from the snow pack through heterogeneous chemical reactions. This is indicated by its presence in high concentrations within snow packs as compared to the air above (Foster et al 2001). Atmospheric Br\(_2\) is recycled by a mechanism which involves the uptake of gaseous HOB\(_r\) on snow followed by its reaction with Br\(^-\) to form more Br\(_2\) and BrCl that are subsequently photolyzed to form reactive halogen atoms (McConnell et al 1992). The reactions involved in this process are outlined by Fickert et al (1999). Other mechanisms involve transformation of halide ions to trihalide ions such as I\(_2\)Br\(^-\) and IBr\(_2\) due to freezing with subsequent release of bromine atoms (O’Driscoll et al 2006). The bromine atoms react with ozone in the atmosphere to form BrO. BrO has been recognized as a major route for oxidation of DMS to MSA via DMSO (Toumi 1994, Saiz-Lopez et al 2007). The rate of oxidation of DMS by BrO has been reported to be an order of magnitude faster than that of DMS by OH even at a BrO concentration of parts per trillion levels (Saiz-Lopez et al 2007). In addition to BrO, IO, which is formed from the reaction of I atoms with O\(_3\), has also been implicated in the oxidation of DMS (Nakano et al 2003). I\(^-\) is also known to efficiently catalyze the oxidation of Br\(^-\) to Br\(_2\), thus playing an important role in the release and recycling of Br atoms (Enami et al 2007, Vogt et al 1999) and further enhancing the impact of DMS oxidation by BrO. In this study, the concentration of I\(^-\) in most of the snow samples was found to be below the detection limit, except two samples in the ice-free region where the concentration was recorded as 2.3 and 2.7 nM. Although, we cannot completely rule out the role of iodine in the oxidation of DMS, the apparently very low values of I\(^-\) in the snow samples studied here may suggest that IO mediated DMS oxidation is less significant in the study region as compared to BrO.

The amount of Br\(^-\) in snow is the limiting factor in the liberation of Br\(_2\) and BrCl (Piot and von Glasow 2007). Sources that contribute to Br\(^-\) accumulation in snow include frost flowers (Kaleschke et al 2004), anthropogenic inputs and brominated organic compounds produced by snow algae and phytoplankton (Tokarczyk and Moore 1994, Schall et al 1996). Since frost flowers cannot account
Figure 4. A simplified scheme of possible Br production mechanisms and photochemical reactions involved in generation of MSA and their climate link. ↑ in the box indicates high concentration and ↓ indicates low concentration.

for the high Br\(^-\) concentrations in ice-cap regions and anthropogenic inputs in East Antarctica are negligible, the observed concentrations could be due to bromocarbons released by an enhanced snow algal population. Snow algae are important sources of brominated organic compounds. Some of the brominated organic compounds produced by algae include CHBr\(_3\), CHBrCl\(_2\), CH\(_2\)Br, CH\(_3\)Br\(_2\) and CHBr\(_2\)Cl. Sturges et al (1993) have measured a number of brominated hydrocarbons produced by microalgae in Antarctic ice. These algae were reported to be responsible for the high bromoform concentrations observed in the overlying atmosphere. Additionally, marine exopolymers, which are found in high concentrations over biologically productive oceans, are known to be enriched in halogens like Cl (Decho 1990, Bigg et al 2004, Leck and Bigg 2005) and may also be an important source of Br in the snow pack. The conversion of Br\(^-\) present on the snow surface to gas-phase Br\(_2\) with consequent photolytic release of Br atoms suggests a high probability of increased Br\(_2\) levels over this region. The ensuing reaction of BrO + DMS in the atmosphere would subsequently lead to enhanced MSA levels. This would lower the burden on the DMS + OH and DMS + NO\(_3\) pathways. The subsequent scavenging of MSA and unutilized gaseous nitrate from the atmosphere may explain the observed abundant nitrate and MSA values in snow from the ice-cap area. In the ice-free region, since the concentration of Br\(^-\) is low, the magnitude of DMS oxidation by BrO would be less, resulting in a greater contribution of OH and NO\(_3\) as a sink for DMS. The ensuing reaction with NO\(_3\) would result in the loss of gaseous nitrate, which is reflected in the low concentrations measured in snow samples from the ice-free areas. Hence, in addition to DMS oxidation by OH/NO\(_3\), the reaction with BrO could be a major path for formation of MSA in the Larsemann Hills. The sulfur aerosols generated during DMS oxidation would result in formation of cloud condensation nuclei. Bromine is also of interest due to its well-known ozone depletion capabilities. A scheme for some Br\(^-\) related reactions and other processes involved in MSA generation and their climate link are demonstrated in figure 4. In addition to BrO, marine exopolymers may also contribute to CCN creation, as they have been found to act as sites for the deposition of oxidation products of DMS leading to the formation of sulfur containing CCN (Leck and Bigg 2005, 2008).

This biogeochemical cycle involving marine exopolymers, biogenic bromine and oxidation of DMS to MSA via BrO, OH and NO\(_3\) could have a profound influence on the earth’s climate, since sulfur containing aerosols serve as cloud condensation nuclei leading to the reflection of solar radiation and thus limiting the amount of sunlight reaching the earth’s surface. Thus, enhanced concentrations of Br\(^-\) in the ice-cap snow in coastal Antarctica could contribute to the formation of cloud condensation nuclei in addition to being a strong sink for DMS, at the expense of ozone depletion.

4. Conclusion

Our study shows that snow from coastal ice-free and ice-cap regions show significant variability in terms of the concentration of ions such as MSA, Br\(^-\), NO\(_3^-\), NH\(_4^+\), and PO\(_4^{3-}\). The concentrations of these ions in the ice-cap sites were 1.3–31 times higher than that measured in the ice-free
area. We suggest that elevated nutrient concentrations in ice-cap snow may be responsible for the observed enhanced growth of microalgae in snow, with subsequent production of bromocarbons, which explains the high Br\(^{-}\) concentration in snow. Gaseous Br\(_2\) derived from Br\(_{-}\) through photoactivated reactions on aerosols and the snow surface would rapidly liberate Br atoms, which would subsequently react with ozone in the atmosphere forming BrO. It is a well-known fact that BrO based DMS oxidation is faster than the OH/NO\(_3\) pathway and can influence cloud seeding through the formation of sulfur based aerosols. We hypothesize that snow in elevated (>200 m) coastal ice-cap regions with a significantly higher concentration of ions such as NO\(_3\)\(^{-}\), NH\(_4\)\(^{+}\), PO\(_4\)\(^{3-}\) and Br\(^{-}\) contribute more to DMS oxidation via BrO mediated reactions than snow in coastal ice-free regions adjacent to the sea. Halogens are also of interest because of their significant effects on the atmosphere and the environment, particularly with regard to ozone depletion and climate impacts.

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References

Ayers G P, Ivey J P and Goodman H S 1986 Sulfate and methanesulfonate in the maritime aerosol at Cape Grim, Tasmania J. Atmos. Chem. 4 173–85
Berterl N et al 2005 Snow chemistry across Antarctica Ann. Glaciol. 41 167–79
Bigg E K, Leck C and Tranvik L 2004 Particulates of the surface microlayer of open water in the central Arctic Ocean in summer Mar. Chem. 91 131–41
Charlson R J, Lovelock J E, Andreae M O and Warren S G 1987 Oceanic phytoplankton, atmospheric sulphur, cloud albedo and climate Nature 326 655–61
Decho A W 1990 Microbial exopolymer secretions in ocean environments: their role(s) in food webs and marine processes Oceanogr. Mar. Biol. Annu. Rev. 28 73–153
Enami S, Vecitis C D, Cheng J, Hoffmann M R and Colussi A J 2007 Global inorganic source of atmospheric bromine J. Phys. Chem. A 111 8749–52
Fickert S, Adams J W and Crowle J N 1999 Activation of Br\(_2\) and BrCl via uptake of HOBr onto aqueous salt solutions J. Geophys. Res. 104 23719–27
Foster K L, Plastridge R A, Bottenheim J W, Shipson P B, Finlayson-Pitts B J and Spicer C W 2001 The role of Br\(_2\) and BrCl in surface ozone destruction at polar sunrise Science 291 471–4
Jones H G and Pomeroy J W 1999 The ecology of snow and snow-covered systems: summary and relevance to Wolf Creek, Yukon Wolf Creek Research Basin: hydrology, ecology, environment Proc. Workshop (Whitehorse, Yukon, Mar. 1998) ed J W Pomeroy and R J Granger (Canada: Environment Canada) pp 1–14
Kaleschke L et al 2004 Frost flowers on sea ice as a source of sea salt and their influence on tropospheric halogen chemistry Geophys. Res. Lett. 31 L16114
Kalnajs L E and Avallone L M 2006 Frost flower influence on spring time boundary-layer ozone depletion events and atmospheric bromine levels Geophys. Res. Lett. 33 L10810
Kärkäs E, Teinila K, Virkkula A and Aurela M 2005 Spatial variations of surface snow chemistry during two austral summers in western Dronning Maud Land, Antarctica Atmos. Environ. 39 1405–16
Leck C and Bigg E K 2005 Biogenic particles in the surface microlayer and overlaying atmosphere in the central Arctic Ocean during summer Tellus B 57 305–16
Leck C and Bigg E K 2008 Comparison of sources and nature of the tropical aerosol with the summer high Arctic aerosol Tellus B 60 115–26
Legrand M, Feniet-Saigne C, Saltzmann E S and Germain C 1992 Spatial and temporal variations of methanesulfonic acid and non sea salt sulfate in Antarctica J. Atmos. Chem. 14 245–60
Ling H U 1996 Snow algae of the Windmill Islands, Antarctica J. Hydrobiolobiography 336 99–106
Ling H U and Seppelt R D 1993 Snow algae of the Windmill Islands, continental Antarctica. 2. Chloromonas rubroleosa sp. nov.(Volvocales, Chlorophyta), an alga of red snow Eur. J. Phycol. 28 77–84
Maupetit F and Delmas R J 1992 Chemical composition of falling snow at Dumont D’Urville, Antarctica J. Atmos. Chem. 14 31–42
McConnell J C, Henderson G S, Barrie L, Bottenheim J, Niki H, Langford C H and Templeton E M J 1992 Photochemical bromine production implicated in Arctic boundary-layer ozone depletion Nature 355 150–2
Nakano Y, Enami S, Nakamichi S, Alosio S, Hashimoto S and Kawasaki M 2003 Temperature and pressure dependence study of the reaction of IO radicals with dimethyl sulfide by cavity ring-down laser spectroscopy J. Phys. Chem. A 107 6381–87
Nguyen B C, Bonsang B and Gaudry A 1983 The role of the ocean in the global atmospheric sulfur cycle J. Geophys. Res. 88 C15 10903–14
O’Driscoll P, Lang K, Minogue N and Sodeau J 2006 Freezing halide ion solutions and the release of interhalogens to the atmosphere J. Phys. Chem. A 110 4615–18
Plot M and von Glasow R 2007 The potential importance of frost flowers, recycling on snow and open leads for ozone depletion events Atmos. Chem. Phys. Discuss. 7 4521–95
Proposito M, Becagli S, Castellano E, Flora O, Genoni L, Gragnani R, Stenni B, Traversi R, Udisti R and Frezzotti M 2002 Chemical and isotopic snow variability along the 1998 ITASE traverse from Terra Nova Bay to Dome C, East Antarctica Ann. Glaciol. 35 187–94
Saiz-Lopez A, Mahajan A S, Salmon R A, Bauguitte S J-B, Jones A E, Roscoe H K and Plane J M C 2007 Boundary layer halogens in coastal Antarctica Science 317 348–51
Saltzman E S, Savoie D L, Zika R G and Prospero J M 1983 Methane sulfonic acid in the marine atmosphere J. Geophys. Res. 88 10897–902
Schall C, Heumann K G, Mora S D and Lee P A 1996 Biogenic brominated and iodinated organic compounds in ponds on the McMurdo Ice Shelf, Antarctica Antarct. Sci. 8 45–8
Simpson W R, Alvarez-Aviles L, Douglas T A, Sturm M and Leck C 1997 BrCl in surface ozone destruction at polar sunrise Science 291 471–4
Sturges W T, Sullivan C W, Schnell R C, Heidt L E and Pollock W B 1993 Bromoalkane production by Antarctic ice algae Tellus B 45 120–6
Tokarczyk R and Moore R M 1994 Production of volatile organohalogens by phytoplankton cultures Geophys. Res. Lett. 21 285–8
Toumi R 1994 BrO as a sink for dimethylsulfide in the marine atmosphere Geophys. Res. Lett. 21 117–20
Trevena A J, Jones G B, Wright S W and van den Enden R L 2000 Profiles of DMSP, algal pigments, nutrients and salinity in pack ice from eastern Antarctica J. Sea Res. 43 265–73
Verdugo P, Alldredge A L, Azam F, Kirchman D L, Passow U and Santschi P H 2004 The oceanic gel phase: a bridge in the DOM–POM continuum Mar. Chem. 92 67–85
Vogt R, Sander R, Glasow R V and Crutzen P J 1999 Iodine chemistry and its role in halogen activation and ozone loss in the marine boundary layer: a model study J. Atmos. Chem. 32 375–95