

## Organic trace gases of oceanic origin observed at South Pole during ISCAT 2000

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### Abstract

Volatile organic compounds (VOCs) were measured at the South Pole (SP) from late Austral spring to mid-summer 2000 as part of the Investigation of Sulfur Chemistry in the Antarctic Troposphere Program (ISCAT-2000). This paper focuses on VOCs that are directly emitted from the ocean, specifically dimethyl sulfide (DMS), methyl nitrate ( $\text{CH}_3\text{ONO}_2$ ), methyl iodide ( $\text{CH}_3\text{I}$ ) and bromoform ( $\text{CHBr}_3$ ). A partial seasonal cycle of these gases was also recorded during the year following ISCAT-2000. During the summer, the SP periodically receives relatively fresh marine air containing short-lived oceanic trace gases, such as DMS ( $\tau \approx 1$  day). However, DMS was not detected at the SP until January even though DMS emissions from the Southern Ocean typically start peaking in November and elevated levels of other ocean-derived VOCs, including  $\text{CH}_3\text{ONO}_2$  and  $\text{CHBr}_3$ , were observed in mid-November. We speculate that in November and December most of the DMS is oxidized before it reaches the SP: a strong correlation between  $\text{CH}_3\text{ONO}_2$  and methane sulfonate (MSA), an oxidation product of DMS, supports this hypothesis. Based on a limited number of samples taken over the course of one year,  $\text{CH}_3\text{ONO}_2$  apparently accumulates to a quasi-steady-state level over the SP in winter, most likely due to continuing emissions of the compound coupled with a lower rate of photochemical destruction. Oceanic emissions were concluded to be the dominant source of alkyl nitrates at the SP; this is in sharp contrast to northern high latitudes where total alkyl nitrate mixing ratios are dominated by urban sources. © 2004 Elsevier Ltd. All rights reserved.

**Keywords:** Oceanic emissions; DMS; South pole; Methyl iodide; Bromoform; Alkyl nitrates; Photochemistry

### 1. Introduction

The ISCAT Program was originally established to investigate sulfur chemistry on the Antarctic plateau (Davis et al., this issue). However, due to the unexpected finding during ISCAT 1998 that there were major buildups of NO within the planetary boundary layer (PBL) at the South Pole (SP) (e.g., due to  $\text{NO}_x$  emissions

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from the snowpack), the research direction of the ISCAT program was subsequently shifted. Thus, ISCAT 2000 became more focused on photochemical processes, specifically  $\text{NO}_x$ – $\text{HO}_x$  chemistry. This paper discusses a related area of the revised ISCAT 2000 program, specifically how photochemistry impacted the concentrations of DMS and other VOCs of oceanic origin, including  $\text{CH}_3\text{ONO}_2$ ,  $\text{CH}_3\text{I}$  and  $\text{CHBr}_3$  at the SP. The chemical lifetime of each of these species is controlled directly by photolysis or reaction with OH.

As noted by Davis et al. (this issue) and extensively discussed in earlier literature, the source of DMS to Antarctica is well established to be phytoplankton blooms in the surrounding Southern Ocean. However, the mechanisms by which DMS is oxidized to end products such as sulfate ( $\text{SO}_4^{2-}$ ), dimethylsulfoxide (DMSO), and methane sulfonate (MSA) via its reaction with OH radicals is only partially understood (Berresheim et al., 1998). More generally, it has also not been established with certainty how the various gas- and aerosol-phase DMS oxidation products arrive at the SP, and are eventually deposited in the snow surface.

Alkyl nitrates are also known to be formed and released from marine waters, predominantly in the  $\text{C}_1$ – $\text{C}_3$  forms (Atlas et al., 1993; Blake et al., 2002; Chuck et al., 2002). Although their formation mechanisms are not entirely known, their main emissions appear to be associated with upwelling regions, such as the equatorial Pacific and the Southern Ocean surrounding Antarctica (Blake et al., 2002). The other primary source of alkyl nitrates has been shown to be photochemical oxidation of alkanes in the presence of nitrogen oxide (NO); these photochemical reactions produce predominantly  $\text{C}_3$  and higher alkyl nitrates (Atkinson et al., 1982; Roberts, 1990).

Bromoform is predominantly emitted from macro algae and planktonic ocean sources (Quack and Wallace, 2003, and references therein). It is the second largest natural reservoir of bromine in the atmosphere after  $\text{CH}_3\text{Br}$  (Schauffler et al., 1999). Similarly,  $\text{CH}_3\text{I}$  is the dominant alkyl iodide species in the atmosphere and is also emitted from the ocean. It represents the primary source of iodide transported from the ocean through the atmosphere to terrestrial regions (Lovelock and Maggs, 1973). Field measurements have shown that phytoplankton (Moore et al., 1996; Tokarczyk and Moore, 1994; Zafriou, 1975), as well as algae and kelp (Carpenter et al., 1999; Class and Ballschmiter, 1986; Schall and Heumann, 1993) release  $\text{CH}_3\text{I}$  in large quantities. There is also evidence that  $\text{CH}_3\text{I}$  is photochemically generated in marine surface waters (Moore and Zafriou, 1994).

## 2. Experimental

From 12 November 2000, to 1 January 2001, personnel associated with the ISCAT project collected

105 samples of whole air in evacuated 2-l stainless-steel canisters. Additional samples were collected from 12 January 2001–23 February 2001 (22 samples), 21–27 June 2001 (4 samples), and 18 September to 25 October 2001 (20 samples). For most samples, the air within the canisters was pressurized to 30 psi using a single bellows pump connected to a stainless-steel inlet line attached to a sampling tower atop the Atmospheric Research Observatory (ARO). The inlet was  $\sim 16$  m above the snow surface. Only one sample a day was collected during most of the ISCAT 2000 intensive period; however, on occasion when unusual weather conditions developed or other special studies were taking place, multiple daily samples were collected. Sampling was typically avoided when the wind was blowing from directions outside of the clean air sector (see Davis et al. this issue, for details), particularly when it was aligned with the camp generators and living quarters. Within 1 month after the ISCAT intensive, the first 105 samples were returned to the University of California, Irvine (UCI) for analysis. Samples collected after the intensive period, spanning much of the 2001 calendar year, were returned to UCI for analysis after 1 year of residence at the SP.

Previous studies by the UCI group have determined that many analytes are stable for months to years if enough water is present to passivate the active canister surfaces. We added  $\sim 2.4$  kPa of purified water to all evacuated canisters just before they were sent to Antarctica. Additionally, cold temperatures such as those encountered at the SP typically increase analyte stability within the canisters. Studies of DMS stability in the canisters at subzero temperatures showed no degradation with time. DMS remained at  $100 \pm 3$  pptv over a four month duration.

Each sample was analyzed for more than 50 trace gases, including hydrocarbons, halocarbons, dimethyl sulfide (DMS), and alkyl nitrates. The analytical procedure is described in detail by Colman et al. (2001), and Sive (1998). Briefly, a 2-l sample of air is preconcentrated on glass beads in a stainless-steel trap immersed in liquid nitrogen, then warmed by  $80^\circ\text{C}$  water and flushed into a carrier flow where it is quantitatively split into five streams. Each of these streams is directed to a different gas chromatograph with a specific column and detector combination, as described below. The sample is in contact with stainless steel from the sample canister to the 5-port splitter, and is then transported to each of the GC columns via Silcosteel tubing (0.53 OD; RESTEK Corporation). The columns are all cryogenically cooled during sample injection and then heated following the temperature ramp programs described in Colman et al. (2001). This sample splitting process has been found to be highly reproducible as long as the specific humidity of the injected air is above  $2$  g  $\text{H}_2\text{O}/\text{kg}$  air.

Methyl nitrate,  $\text{CH}_3\text{I}$ , and  $\text{CHBr}_3$  were analytically separated employing three of the five column-detector combinations. The first combination (abbreviated as ‘DB5ms/MSD’) was a DB-5ms column (J&W; 60 m, 0.25 mm I.D., 0.5  $\mu\text{m}$  film thickness) whose output went to a quadrupole mass spectrometer detector (MSD) (Hewlett Packard, HP-5973). The second combination (Restek1701/ECD) consisted of a RESTEK 1701 column (60 m, ID 0.25 mm, film 0.5  $\mu\text{m}$ ) the output of which was directed into an electron capture detector (ECD). A third combination (DB5-Restek1701/ECD) was made up of a DB-5 (J&W 30 m, I.D. 0.25 mm, film 1  $\mu\text{m}$ ) column connected in series to a RESTEK 1701 column (5 m, I.D. 0.25 mm, film 0.5  $\mu\text{m}$ ), with the output again going to an ECD. The DB5ms/MSD, Restek1701/ECD, and the DB5-Restek1701/ECD combinations received 10.1%, 7.2%, and 6.8% of the sample flow, respectively. Dimethyl sulfide was also analyzed on the DB5ms/MSD. The other two columns used flame ionization detection to analyze for hydrocarbons, an analysis that is not reported as part of this investigation. The typical alkyl nitrate detection limit (DL) was 0.02 pptv (0.01 pptv for  $\text{CH}_3\text{ONO}_2$ ) and the precision was  $\pm 5\%$  at mixing ratios above 5 pptv and  $\pm 10\%$  below 5 pptv (Blake et al., 2002; Colman et al., 2001). The detection limits for  $\text{CH}_3\text{I}$ ,  $\text{CHBr}_3$ , and DMS were 0.01, 0.01, and 2 pptv, respectively. The precision limits for  $\text{CH}_3\text{I}$  and  $\text{CHBr}_3$  were 1.1% and 1.6%, respectively (Colman et al., 2001). For DMS, the precision was approximately 3% at mixing ratios  $> 25$  pptv, and 1 pptv or 15%, whichever was higher, at mixing ratios  $< 10$  pptv (Simpson et al., 2001). Methane sulfonate samples were collected by high volume filters and then

analyzed by ion liquid-chromatography as discussed by Arimoto et al. (this issue).

### 3. Results

#### 3.1. DMS, $\text{CHBr}_3$ , $\text{CH}_3\text{I}$ , and $\text{CH}_3\text{ONO}_2$

Dimethyl sulfide mixing ratios were below their detection limit ( $\sim 2$  pptv) in all 105 samples collected during the Austral spring and mid-summer field study (Fig. 1). A measurable concentration of 2.4 pptv was first recorded on 12 January, with a maximum seasonal concentration of 7.3 pptv on 1 February, 2001 (Fig. 2). Very large DMS concentrations, ranging from hundreds of pptv to a few ppbv, have been measured at numerous coastal sites in Antarctica (e.g., Pszenny et al., 1989; Prospero et al., 1991; Berresheim et al., 1998; Curran and Jones, 2000; Jourdain and Legrand, 2001). The low mixing ratios measured at the SP in late summer/early fall combined with the absence of detectable DMS in spring to early summer seems remarkable considering the magnitude of the Southern Ocean source strength for DMS. The absence of DMS in the samples collected in November and December is examined in greater detail in Sections 4.1 and 4.3.

MSA was present throughout ISCAT (Fig. 1) and its presence indicates the air mass originally contained DMS (Arimoto et al., this issue). Bromoform and  $\text{CH}_3\text{I}$  were also present throughout ISCAT, and exhibited a relatively steady decrease from the beginning to the end of the ISCAT-2000 field experiment. The aerosol values for MSA decreased through the beginning of ISCAT

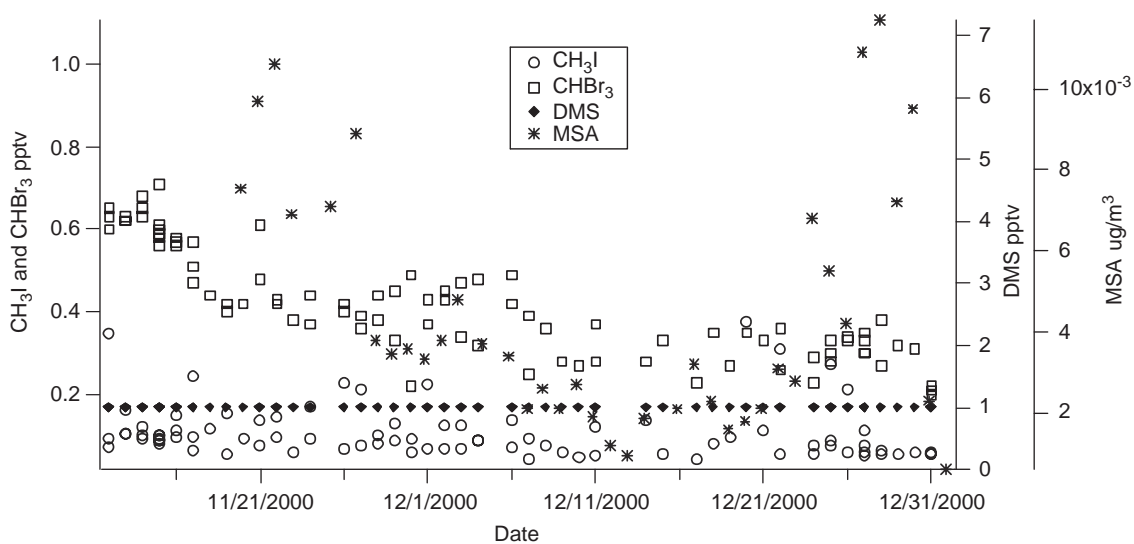


Fig. 1. Trends during the ISCAT intensive for  $\text{CHBr}_3$  (open squares),  $\text{CH}_3\text{I}$  (open circles), DMS (solid diamonds; right y-axis), and MSA (asterisk, 2nd right y-axis). The DMS mixing ratio never reached its 2 pptv limit of detection.

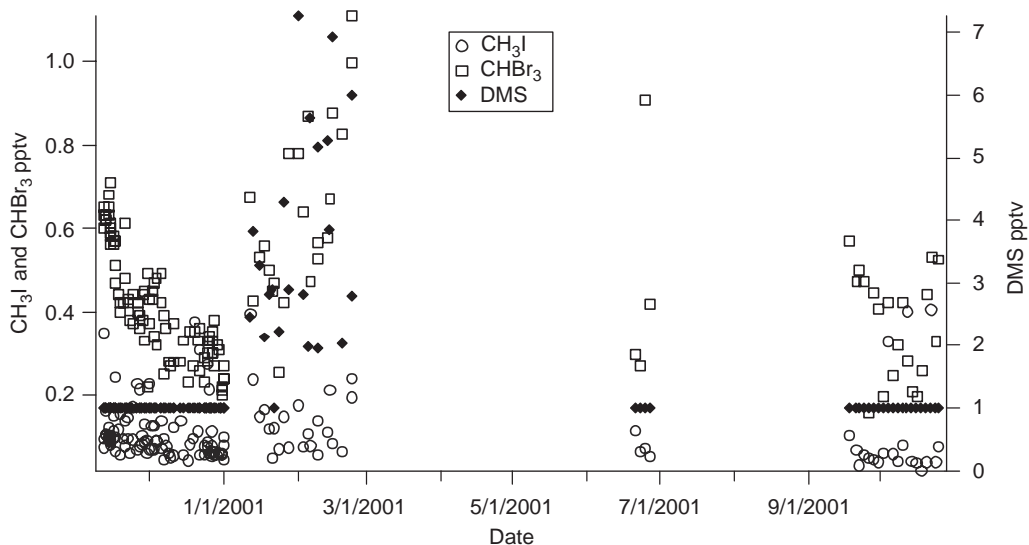


Fig. 2. Partial seasonal trends for DMS (solid diamonds; y-axis), CHBr<sub>3</sub> (open squares) and CH<sub>3</sub>I (open circles). 12 January, 2001 was the first sample collection at SP that had a DMS mixing ratio above its 2 pptv limit of detection.

along with the other trace gases, but MSA also showed a significant increase late in December that was not seen in the trace gases. The MSA increase in late December is consistent with meteorological analysis showing weak circulation over the plateau with episodic upslope flow on 16–17, 21–22, December and short-lived periods from 25–31 December (A. Hogan, unpublished results). The sampling frequency creates some difficulty in attempting to interpret the trend in the aerosol filter samples, which are averages over 24 h, compared to the trace gases, which are collected within 10 min. However, the trends up to the last 8 days of ISCAT are very similar for MSA, CHBr<sub>3</sub> and CH<sub>3</sub>I.

Although bromoform decreased steadily through the ISCAT intensive, it then increased again in late summer (January–February) when DMS was also first observed. The increasing DMS and CHBr<sub>3</sub> mixing ratios in late summer were correlated with increases in CH<sub>3</sub>ONO<sub>2</sub>, with  $r^2$  values of 0.64 and 0.81, respectively. (We note that CH<sub>2</sub>Br<sub>2</sub> also correlates with CHBr<sub>3</sub> throughout the year. The yearly average concentration of CH<sub>2</sub>Br<sub>2</sub> was  $0.92 \pm 0.12$  pptv.)

In contrast to the other ocean-derived VOCs, the CH<sub>3</sub>I concentrations are relatively constant year round, with a mean of  $0.11 \pm 0.08$  pptv. Although nine sporadic increases of CH<sub>3</sub>I occurred during the study, reaching 0.2–0.4 pptv, these were not correlated with increases in any of the other measured trace gases. These sporadic increases might be associated with fluxes from the snowpack, which has been shown to be a source of CH<sub>3</sub>I (Swanson et al., 2002a), but this source was not examined in detail during the ISCAT 2000 study. Interestingly, when the 9 samples out of 105 above

0.2 pptv are not considered, CH<sub>3</sub>I shows a decrease from  $0.108 \pm 0.032$  to  $0.065 \pm 0.014$  pptv during the November–December ISCAT intensive. However, due to the non-marine sources of CH<sub>3</sub>I at the SP, relatively little discussion of its significance at the SP has been included in this analysis.

During the steady decrease of CHBr<sub>3</sub> through the spring and mid-summer, there were several short episodes of increasing mixing ratios that suggest that fresh maritime air had reached the SP. Several of these events can be seen in Fig. 1 and 3, such as on 21 November where the mixing ratio of CHBr<sub>3</sub> increases from  $0.42 \pm 0.05$  to  $0.61 \pm 0.01$  pptv. Events such as that on 21 November have been described as rapid upslope flow that resulted in fresh maritime air reaching the SP (A. Hogan, unpublished results). However, it was concluded that upslope flow was infrequent and short-lived during the ISCAT 2000 study, and that the predominant flow pattern during ISCAT remained within the interior of Antarctica over the ice.

### 3.2. Alkyl nitrates

The C<sub>1</sub>–C<sub>3</sub> (methyl, ethyl, and *i*-propyl) alkyl nitrate mixing ratios exhibited a steady decrease from 12 November to 1 January (Fig. 3). The sum of C<sub>1</sub>–C<sub>4</sub> alkyl nitrates (including *n*-propyl- and 2-butyl nitrate) decreased from approximately 12–4 pptv. There was no evidence of alkyl nitrates >C<sub>4</sub> (at DL ~0.02 pptv) during the ISCAT intensive or later in the winter samples. 2-Butyl- and *n*-propyl nitrate mixing ratios remained very low, averaging  $0.15 \pm 0.12$  and  $0.12 \pm 0.10$  pptv, respectively. The episodic upslope flow

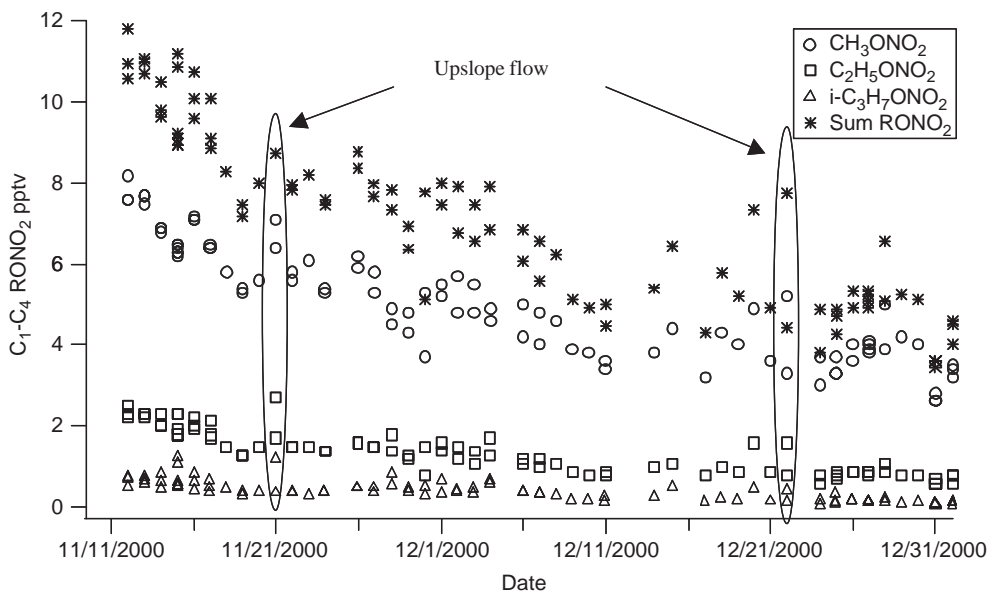


Fig. 3. Trends during the ISCAT intensive for alkyl nitrates. As mentioned in the text, several upslope flow events showing stronger oceanic influence are highlighted in circles.

of maritime air mentioned above was also seen in the total alkyl nitrate levels, which increased from around 8 to as high as 12 pptv on 21 November. Total alkyl nitrates were dominated by methyl and ethyl nitrate, which equaled  $91 \pm 1\%$  of the total throughout the year. This distribution is consistent with that known to arise from ocean emissions, particularly the equatorial Pacific and Southern Ocean (e.g., Blake et al., 1999, 2002) and Antarctic coastal areas (Jones et al., 1999). The Southern Ocean and associated seas surrounding Antarctica constitute 20% of the total world ocean area, and thus represent a dominant source region for marine emitted trace gases reaching the Antarctic continent (Curran and Jones, 2000).

The seasonal sampling data shown in Fig. 4 are quite sparse during the fall–winter with only four measurement days in June and no samples collected from March through May, or July through August. Therefore, the trends seen over the fall–winter season must be considered interpolations, and thus, represent best estimates of the seasonal distributions of these trace gases. Keeping this tentative nature of the seasonal distributions in mind, the speciation of the alkyl nitrates is dominated by  $\text{CH}_3\text{ONO}_2$  which maintains a concentration between 8–10 pptv throughout the winter (Fig. 3). The mixing ratios of ethyl and *i*-propyl nitrate tend to track the shifts seen in  $\text{CH}_3\text{ONO}_2$  during the fall, although the ratios of  $\text{CH}_3\text{ONO}_2/\text{C}_2\text{H}_5\text{ONO}_2$  ( $C_1/C_2$ ) and  $\text{CH}_3\text{ONO}_2/i\text{-C}_3\text{H}_7\text{ONO}_2$  ( $C_1/i\text{-C}_3$ ) increase into the spring–winter consistent with the fact that  $\text{CH}_3\text{ONO}_2$  has a longer lifetime relative to the  $C_2$ – $C_3$  alkyl nitrates.

## 4. Discussion

### 4.1. Oceanic air mass origin

The beginning of the ISCAT intensive study in mid-November was marked by high mixing ratios of  $C_1$ – $C_2$  alkyl nitrates and  $\text{CHBr}_3$ , suggestive of recent oceanic input. However, as shown in Fig. 1 and 3, their mixing ratios decreased steadily during summer, suggesting a parallel decrease in the mass transport of marine emissions to the plateau. Quite interestingly, the concentration of MSA on aerosol (Arimoto et al., this issue) was correlated with the alkyl nitrates and  $\text{CHBr}_3$  up until 14 December ( $r^2 = 0.73$ ). This tight correlation then dropped precipitously (to  $r^2 = 0.1$ ) at the end of December 2000 as MSA increased significantly without a corresponding increase in the oceanic gases. The earlier correlation supports a common origin, transport pathway and photochemical processing, while the trend over the last days of December imply either different source or sink processes during transport.

At first glance, a November inflow of marine emissions would seem to conflict with the SP observations that all DMS values during November and December of 2000 were below the  $\sim 2$  pptv detection limit (see Fig. 1). Possible explanations for why DMS was absent in earlier November 2000 could include: (1) that the biota responsible for DMS production were not active in the region of the Southern ocean from which the alkyl nitrates and  $\text{CHBr}_3$  originated, or (2) that all three species were released nearly simultaneously (i.e.,

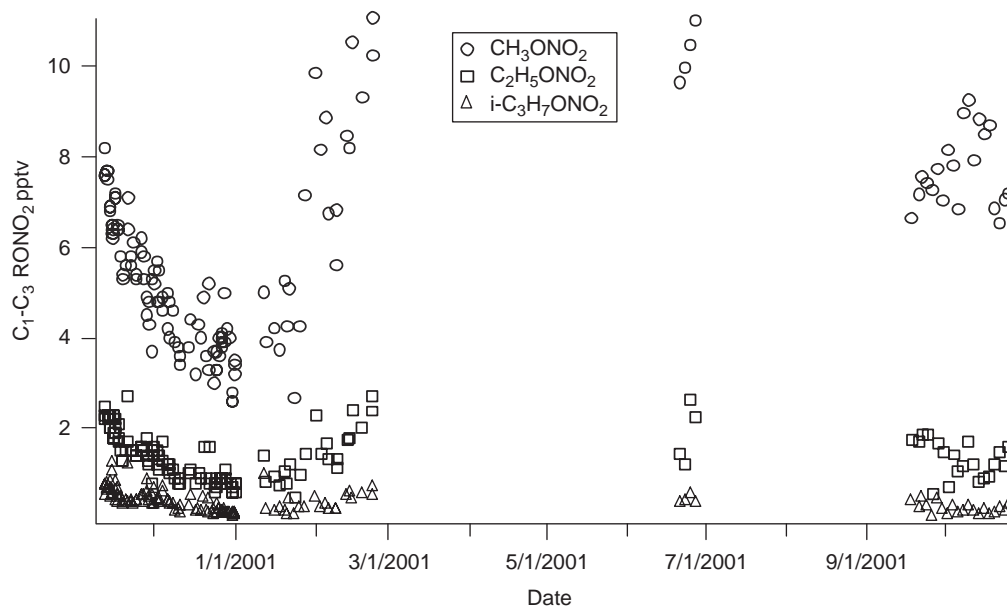


Fig. 4. Partial season cycle of methyl-, ethyl-, and *i*-propyl nitrate.

alkyl nitrates, DMS, and  $\text{CHBr}_3$ ) but that DMS was removed far more efficiently than were the alkyl nitrates and  $\text{CHBr}_3$  in transit to the SP. Concerning the first possibility, although it is well known that DMS blooms in the oceans surrounding Antarctica can be patchy (Kettle and Andreae, 2000), the absence of significant DMS emissions in marine areas that release large quantities of alkyl nitrates and  $\text{CHBr}_3$  (also related to biota levels) seems highly unlikely. Instead, the fact that the lifetime of DMS (1 day, at  $[\text{OH}] = 1 \times 10^6 \text{ mol cm}^{-3}$ ) is known to be significantly shorter than either  $\text{CH}_3\text{ONO}_2$  ( $\sim 23$  days),  $\text{CHBr}_3$  ( $\sim 12$  days),  $\text{CH}_3\text{I}$  ( $\sim 6$  days) would seem to strongly point to option (2) as the most likely, especially given that the lifetime of DMS is controlled by its reaction with OH.

The OH concentration in the Southern Hemisphere can be highly variable, and thus, the rate of DMS oxidation during transit to the SP could depend on other factors that may impact OH levels. These include season, time of day, the outflow of  $\text{NO}_x$  from the surface of the plateau into the lower free troposphere, and most importantly the geographical track followed by an air parcel during transit from the ocean to the SP. By comparison,  $\text{CHBr}_3$ , with a photolysis lifetime of 12 days, should be only modestly influenced by a 2 versus 5 day transit time to SP. Thus, given the greater photochemical sensitivity of DMS relative to other marine released trace gases, DMS levels at the SP are dependent on the integrated effects of its source strength and photochemical conditions encountered during transport. In this context, although DMS values were

undetectable from mid- to late-November 2000, a marine air mass signature is suggested by the detection of high levels of the other marine released trace gases, and elevated levels of the DMS oxidation product MSA (e.g., Arimoto et al., this issue).

The concentrations of  $\text{CH}_3\text{ONO}_2$ ,  $\text{C}_2\text{H}_5\text{ONO}_2$  and *i*- $\text{C}_3\text{H}_7\text{ONO}_2$  at the beginning of the ISCAT 2000 study (12 November), also are indicative of a strong and relatively fresh maritime air mass. We have previously made measurements of alkyl nitrates over the Southern and South Pacific Oceans, e.g., the NSF ACE-1 project in November–December 1995 ( $\text{CH}_3\text{ONO}_2$  only) (Blake et al., 1999), NASA's GTE PEM Tropics A (PTA) mission in September–October 1996, and NASA's GTE PEM Tropics B (PTB) project in March–April 1999 (Blake et al., 2002). In each of these studies a similar distribution of alkyl nitrates was observed within the marine boundary layer (MBL). The highest alkyl nitrate levels were seen near the equator and over the Southern Ocean ( $30\text{--}60^\circ\text{S}$ ) as shown in Fig. 5. The concentrations during early ISCAT 2000 of 8.2, 2.5, and 0.77 pptv for  $\text{CH}_3\text{ONO}_2$ ,  $\text{C}_2\text{H}_5\text{ONO}_2$ , and *i*- $\text{C}_3\text{H}_7\text{ONO}_2$ , respectively, are similar to measurements in the MBL over the Southern and equatorial Pacific Ocean during the aircraft campaigns.

Furthermore, the ratios of the  $\text{C}_1/\text{C}_2$  and  $\text{C}_1/i\text{-C}_3$  alkyl nitrates for MBL conditions (i.e., altitudes  $\leq 500 \text{ m}$ ) were relatively constant between the two NASA missions with medians of  $2.9 \pm 1.0$  and  $9.6 \pm 4.6$  for PTA ( $N = 466$ ) and  $2.9 \pm 0.9$  and  $9.3 \pm 5.3$  for PTB ( $N = 561$ ), respectively. These ratios differ slightly from

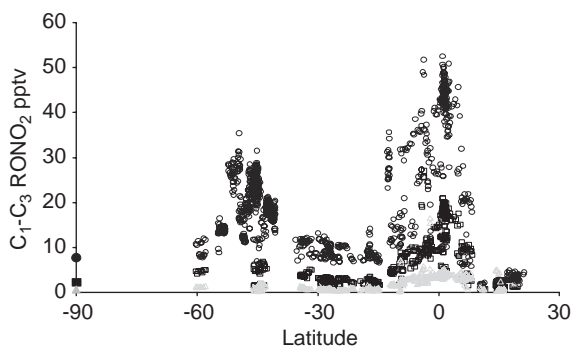


Fig. 5. Measurements in the MBL during the NASA GTE PEM Tropics A and NSF ACE-1 aircraft campaigns:  $\text{CH}_3\text{ONO}_2$  (open circles),  $\text{C}_2\text{H}_5\text{ONO}_2$  (open squares),  $i\text{-C}_3\text{H}_7\text{ONO}_2$  (open diamonds). The concentrations on 11–12 November at the SP are plotted at  $90^\circ\text{S}$  latitude for comparison:  $\text{CH}_3\text{ONO}_2$  (solid circles),  $\text{C}_2\text{H}_5\text{ONO}_2$  (solid squares),  $i\text{-C}_3\text{H}_7\text{ONO}_2$  (solid diamonds).

those presented by Blake et al. (2002) because the data considered here were stratified by placing a cut-off at 500 m and  $10^\circ\text{N}$  to ensure MBL conditions and avoid possible urban emission signatures. The ratios measured at SP for  $\text{C}_1/\text{C}_2$  and  $\text{C}_1/i\text{-C}_3$  alkyl nitrates ( $3.3 \pm 0.1$  and  $11 \pm 2$ , respectively) reflect only slight photochemical processing compared to the ratios measured during the aircraft campaigns. Bromoform concentrations at the SP of 0.65 pptv at the beginning of ISCAT 2000 are also consistent with MBL concentrations observed during the three airborne projects.

The air arriving at the SP during 15–27 November has been described as extra-Antarctic (A. Hogan, unpublished results). It was argued that during such events, subsiding air from mid-latitude regions essentially floods the Antarctic polar region as the polar vortex is filled (A. Hogan, unpublished results). These air parcels may have had little contact with the ice and presumably spent some time in the free troposphere. This explanation is consistent with that described above for the alkyl nitrates, in that the source region is postulated to be at mid-latitudes over the Southern Ocean. In this scenario, DMS would have had ample time to react with OH and thus decrease to non-detectable levels. By contrast, significant amounts of  $\text{CHBr}_3$  and the alkyl nitrates would have survived the transit from these latitudes owing to their lower photochemical lability.

#### 4.2. Significance of the alkyl nitrate seasonal cycle

From the quasi-seasonal distribution of  $\text{CH}_3\text{ONO}_2$  (Fig. 4), it appears that the SP is nearly always exposed to air of oceanic character that has undergone various degrees of chemical/photochemical processing. This may seem obvious because the Southern Ocean encompasses

Antarctica, but the character of the air at the SP is influenced by several factors. These include stratospheric intrusions, high altitude transport from mid- to low-latitudes, storm events bringing in mid- to low-latitude air, and the presence of a very stable surface layer on the plateau, inhibiting exchange with the overlying free troposphere (Harris, 1992; Hogan, 1997). Our understanding of the aerosol composition and concentrations on the plateau, as well as the distribution/speciation of sulfur compounds that acts as chemical proxy species in ice cores, is still lacking because of a poor understanding of the transport of air masses to the SP. In the case of  $\text{CH}_3\text{ONO}_2$ , however, its presence during the winter season does not necessarily demonstrate the existence of recent marine emissions. Instead, it is more likely to reflect the long lifetime for this species under winter time conditions ( $> 1$  yr). Thus, the alkyl nitrates build up in the high southern latitudes to quasi-steady-state concentrations because of a major reduction in their photochemical loss rate. In this context, it is perhaps significant that the total alkyl nitrate concentration during the Austral summer at SP (i.e., 10–14 pptv) is quite similar to the total alkyl nitrate mixing ratio measured during the Northern Hemisphere (NH) summer at high latitudes such as Summit, Greenland, i.e., 9–12 pptv (Swanson et al., 2002b), but that winter distributions of alkyl nitrate species found at each site are distinctly different.

In the NH, due to the heavy influence of anthropogenic emissions, high concentrations of the higher ( $\geq \text{C}_3$ ) alkyl nitrates build up during winter because of stronger horizontal mixing of the lower atmosphere and a lack of removal by OH (Muthuramu et al., 1994; Swanson et al., 2002b). The influence of anthropogenic emissions in the NH continues into the summer, resulting in similar  $\text{CH}_3\text{ONO}_2$  and  $\text{C}_2\text{H}_5\text{ONO}_2$  mixing ratios of 3–4 pptv (Swanson et al., 2002b). By contrast, at the SP  $\text{CH}_3\text{ONO}_2$  is the most abundant alkyl nitrate year round. Thus, differences in the speciation of alkyl nitrates provides clear evidence that anthropogenic emissions are significant at high latitudes in the NH but small to negligible in the Southern Hemisphere at locations such as the SP. This trend is also found when examining  $\text{nss-SO}_4^{2-}$  in ice cores. This species exhibits more than a two fold increase at high latitudes in the NH due to industrial processes, but very little evidence can be found implicating anthropogenic sulfate contributions in Antarctica (Legrand, 1997; Arimoto et al., 2001, this issue).

#### 4.3. Estimation of DMS sources to the South Pole

Because the air sampled early in the ISCAT 2000 campaign contained significant marine emissions, in the form of alkyl nitrates and  $\text{CHBr}_3$ , we noted earlier that elevated levels of DMS might also be expected.

However, DMS has a lifetime of only 1 day when the 24 h average concentration of OH is  $1 \times 10^6$  molecules  $\text{cm}^{-3}$  (e.g., see Mauldin et al., this issue). Nevertheless, as discussed in Section 4.1, without knowing the paths that air parcels follow and how long they might experience different levels of OH, assigning an accurate value to the average OH concentration encountered by DMS on its transit to SP is difficult. If this average is taken to be  $1 \times 10^6$  molecules  $\text{cm}^{-3}$ , this would define 4 DMS lifetimes. Given a DL of  $\sim 2$  pptv, this suggests a starting mixing ratio of slightly over 100 pptv. In fact, results from seasonal measurements of atmospheric DMS throughout the Southern Ocean region (Bates et al., 1998; Curran and Jones, 2000; Mctaggart et al., 1995; Staubes and Georgii, 1993) and at coastal Antarctica sites (Berresheim et al., 1998; Jourdain and Legrand, 2001) indicate that DMS mixing ratios during the late Austral spring/early summer, while variable, can be equal to or even higher than this value. In the latter case, one would have expected some evidence of measurable DMS.

For an estimated transit time of 9 days, however, DMS would undergo a 9 e-fold decrease, representing a loss factor of  $\sim 8000$ . This converts to a starting concentration for DMS of nearly 16,000 pptv, a value much higher than ever reported. On the other hand, if the average OH concentration were 5 times lower than that cited above, the starting value would be lowered to  $\sim 3000$  pptv, a mixing ratio not too far removed from the maximums recently reported by Jourdain and Legrand (2001) at the coastal site of Dumont d'Urville. The above calculations indicate that a rather wide range of transit times can be accommodated with the current uncertainty in the average OH level. They also demonstrate how one might encounter air parcels that appear to have been in contact with relative fresh marine emissions of alkyl nitrates and  $\text{CHBr}_3$  and yet have undetectable levels of DMS.

The remaining issue to be discussed is why DMS was observed in January and February when it was not detected during the ISCAT intensive. There are several possible reasons for this, (1) the air mass originally contained higher concentrations of DMS than the upslope flow events during ISCAT or, (2) the air experienced a more rapid transport time to the SP or, (3) the air experience lower concentrations of OH during transport. There was no meteorological evidence for faster transport from the coast to the SP during early 2001 versus the ISCAT upslope flow events (A. Hogan, personal communication, 2003). Additionally, there is evidence that marine emissions from the Southern Ocean generally begin to decrease heading into February (Kettle et al., 2000). However, the observations of DMS occurred as summer was progressing into fall, thus, the solar zenith angle was increasing with lower actinic fluxes reaching Antarctica so that the average

OH concentrations were decreasing. Therefore, the likely reason DMS was observed in January–February 2001 but not earlier is that the DMS lifetime increased due to a lower rate of photochemical destruction.

## 5. Conclusions

Measurements of VOCs at the SP indicate that air parcels heavily influenced by maritime trace gas emissions periodically reach the SP. However, DMS was not present during the Austral late spring or early summer SP samples. We speculate that this is most likely due to the rapid oxidation of DMS by OH relative to the much slower loss rates for the other marine gases such as the alkyl nitrates and  $\text{CHBr}_3$ . Tight correlations between  $\text{CH}_3\text{ONO}_2$ ,  $\text{CHBr}_3$ , and aerosol MSA strongly suggest that DMS was likely present in the original air mass. Additionally, late summer samples at the SP were found to contain measurable levels of DMS. Seasonal distributions of the alkyl nitrate species at the SP were different from those at high latitudes in the NH. Unlike the NH, the distribution at SP was dominated by  $\text{C}_1$  and  $\text{C}_2$  alkyl nitrates resulting from oceanic emissions, while that in the NH is dominated by secondary chemical production from urban emissions.

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## References

- Arimoto, R., Nottingham, A.S., Webb, J., Schloesslin, C.A., Davis, D.D., 2001. Non-sea salt sulfate and other aerosol constituents at the south pole during ISCAT. *Geophysical Research Letters* 28 (19), 3645–3648.
- Arimoto, R., Hogan, A., Webb, J., Grube, P., Davis, D., Schloesslin, C., Sage, S., this issue. Major Ions and Trace Elements in Aerosol Particles from the South Pole during ISCAT-2000. *Atmospheric Environment*, doi:10.1016/j.atmosenv.2004.01.049.
- Atkinson, R., Aschmann, S.M., Carter, W.P.L., Winer, A.M., Pitts, J.N., 1982. Alkyl Nitrate Formation from the Nox-Air Photooxidations of  $\text{C}_2$ – $\text{C}_8$  *N*-alkanes. *Journal of Physical Chemistry* 86 (23), 4563–4569.
- Atlas, E., Pollock, W., Greenberg, J., Heidt, L., Thompson, A.M., 1993. Alkyl nitrates, nonmethane hydrocarbons, and halocarbon gases over the equatorial pacific ocean during



- saga-3. *Journal of Geophysical Research—Atmospheres* 98 (D9), 16933–16947.
- Bates, T.S., Kapustin, V.N., Quinn, P.K., Covert, D.S., Coffman, D.J., Mari, C., Durkee, P.A., De Bruyn, W.J., Saltzman, E.S., 1998. Processes controlling the distribution of aerosol particles in the lower marine boundary layer during the first aerosol characterization experiment (ACE 1). *Journal of Geophysical Research—Atmospheres* 103 (D13), 16369–16383.
- Berresheim, H., Huey, J.W., Thorn, R.P., Eisele, F.L., Tanner, D.J., Jefferson, A., 1998. Measurements of dimethyl sulfide, dimethyl sulfoxide, dimethyl sulfone, and aerosol ions at Palmer Station, Antarctica. *Journal of Geophysical Research—Atmospheres* 103 (D1), 1629–1637.
- Blake, N.J., Blake, D.R., Wingenter, O.W., Sive, B.C., Kang, C.H., Thornton, D.C., Bandy, A.R., Atlas, E., Flocke, F., Harris, J.M., Rowland, F.S., 1999. Aircraft measurements of the latitudinal, vertical, and seasonal variations of NMHCs, methyl nitrate, methyl halides, and DMS during the First Aerosol Characterization Experiment (ACE 1). *Journal of Geophysical Research—Atmospheres* 104 (D17), 21803–21817.
- Blake, N.J., Blake, D.R., Swanson, A.L., Atlas, E., Flocke, F., Rowland, F.S., 2002. Latitudinal, vertical, and seasonal variations of C1–C4 alkyl nitrates in the troposphere over the Pacific Ocean during PEM-Tropics A and B: Oceanic and continental sources. *Journal of Geophysical Research* 108, D2, 10.1029/2001JD001444.
- Carpenter, L.J., Sturges, W.T., Penkett, S.A., Liss, P.S., Alicke, B., Hebestreit, K., Platt, U., 1999. Short-lived alkyl iodides and bromides at Mace Head, Ireland: links to biogenic sources and halogen oxide production. *Journal of Geophysical Research—Atmospheres* 104 (D1), 1679–1689.
- Chuck, A.L., Turner, S.M., Liss, P.S., 2002. Direct evidence for a marine source of C-1 and C-2 alkyl nitrates. *Science* 297 (5584), 1151–1154.
- Class, T., Ballschmiter, K., 1986. Chemistry of organic traces in air. 5. Determination of halogenated C<sub>1</sub>–C<sub>2</sub>-hydrocarbons in clean marine air and ambient continental air and rain by high-resolution gas-chromatography using different stationary phases. *Fresenius Zeitschrift Fur Analytische Chemie* 325 (1), 1–7.
- Colman, J.J., Swanson, A.L., Meinardi, S., Sive, B.C., Blake, D.R., Rowland, F.S., 2001. Description of the analysis of a wide range of volatile organic compounds in whole air samples collected during PEM-Tropics A and B. *Analytical Chemistry* 73 (15), 3723–3731.
- Curran, M.A.J., Jones, G.B., 2000. Dimethyl sulfide in the Southern Ocean: seasonality and flux. *Journal of Geophysical Research—Atmospheres* 105 (D16), 20451–20459.
- Davis, D., Eisele, F., Chen, G. et al., 2004. An overview of ISCAT 2000. *Atmospheric Environment*, this issue, doi:10.1016/j.atmosenv.2004.05.037.
- Harris, J.M., 1992. An analysis of 5-day midtropospheric flow patterns for the South-Pole-1985–1989. *Tellus Series B—Chemical and Physical Meteorology* 44 (4), 409–421.
- Hogan, A., 1997. A synthesis of warm air advection to the South Polar Plateau. *Journal of Geophysical Research—Atmospheres* 102 (D12), 14009–14020.
- Jones, A.E., Weller, R., Minikin, A., Wolff, E.W., Sturges, W.T., McIntyre, H.P., Leonard, S.R., Schrems, O., Bauguitte, S., 1999. Oxidized nitrogen chemistry and speciation in the Antarctic troposphere. *Journal of Geophysical Research—Atmospheres* 104 (D17), 21355–21366.
- Jourdain, B., Legrand, M., 2001. Seasonal variations of atmospheric dimethylsulfide, dimethylsulfoxide, sulfur dioxide, methanesulfonate, and non-sea-salt sulfate aerosols at Dumont d’Urville (coastal Antarctica) (December 1998 to July 1999). *Journal of Geophysical Research—Atmospheres* 106 (D13), 14391–14408.
- Kettle, A.J., Andreae, M.O., 2000. Flux of dimethylsulfide from the oceans: a comparison of updated data seas and flux models. *Journal of Geophysical Research—Atmospheres* 105 (D22), 26793–26808.
- Legrand, M., 1997. Ice-core records of atmospheric sulphur. *Philosophical Transactions of the Royal Society of London Series B—Biological Sciences* 352 (1350), 241–250.
- Lovelock, J.E., Maggs, R.J., 1973. Halogenated Hydrocarbons in and over Atlantic. *Nature* 241 (5386), 194–196.
- Mauldin, R.L., Kosciuch, E., Henry, B., Eisele, F., Shetter, R., Lefer, B., Chen, G., Davis, D., Bandy, A., Thornton, D., this issue. Measurements of OH, HO<sub>2</sub> + RO<sub>2</sub>, H<sub>2</sub>SO<sub>4</sub>, and MSA at South Pole during ISCAT 2000. *Atmospheric Environment*, doi:10.1016/j.atmosenv.2004.06.031.
- Mctaggart, A.R., Burton, H.R., Nguyen, B.C., 1995. Emission and flux of DMS from the Australian Antarctic and Sub-Antarctic Oceans During the 1988–1989 summer. *Journal of Atmospheric Chemistry* 20 (1), 59–69.
- Moore, R.M., Zafriou, O.C., 1994. Photochemical production of methyl-iodide in seawater. *Journal of Geophysical Research—Atmospheres* 99 (D8), 16415–16420.
- Moore, R.M., Webb, M., Tokarczyk, R., Wever, R., 1996. Bromoperoxidase and iodoperoxidase enzymes and production of halogenated methanes in marine diatom cultures. *Journal of Geophysical Research—Oceans* 101 (C9), 20899–20908.
- Muthuramu, K., Shepson, P.B., Bottenheim, J.W., Jobson, B.T., Niki, H., Anlauf, K.G., 1994. Relationships between organic nitrates and surface ozone destruction during polar sunrise experiment 1992. *Journal of Geophysical Research—Atmospheres* 99 (D12), 25369–25378.
- Prospero, J.M., Savoie, D.L., Saltzman, E.S., Larsen, R., 1991. Impact of oceanic sources of Biogenic sulfur on sulfate aerosol concentrations at mawson, antarctica. *Nature* 350 (6315), 221–223.
- Pszenny, A.A.P., Castelle, A.J., Galloway, J.N., 1989. A study of the sulfur cycle in the antarctic marine boundary-layer. *Journal of Geophysical Research—Atmospheres* 94 (D7), 9818–9830.
- Quack, B., Wallace, D.W.R., 2003. Air–sea flux of bromoform: controls, rates, and implications. *Global Biogeochemical Cycles* 17 (1), doi:10.1029/2002GB001890.
- Roberts, J.M., 1990. The atmospheric chemistry of organic nitrates. *Atmospheric Environment Part A—General Topics* 24 (2), 243–287.
- Schall, C., Heumann, K.G., 1993. Gc Determination of volatile organoiodine and organobromine compounds in arctic seawater and air samples. *Fresenius Journal of Analytical Chemistry* 346 (6–9), 717–722.
- Schauffler, S.M., Atlas, E.L., Blake, D.R., Flocke, F., Lueb, R.A., Lee-Taylor, J.M., Stroud, V., Travnicek, W., 1999. Distributions of brominated organic compounds in the

- troposphere and lower stratosphere. *Journal of Geophysical Research-Atmospheres* 104 (D17), 21513–21535.
- Simpson, I.J., Colman, J.J., Swanson, A.L., Bandy, A.R., Thornton, D.C., Blake, D.R., Rowland, F.S., 2001. Aircraft measurements of dimethyl sulfide (DMS) using a whole air sampling technique. *Journal of Atmospheric Chemistry* 39 (2), 191–213.
- Sive, B.C., 1998. Atmospheric nonmethane hydrocarbons : analytical methods and estimated hydroxyl radical concentrations, Ph.D. Dissertation, University of California, Irvine.
- Staubes, R., Georgii, H.W., 1993. Biogenic sulfur-compounds in seawater and the atmosphere of the antarctic region. *Tellus Series B—Chemical and Physical Meteorology* 45 (2), 127–137.
- Swanson, A.L., Blake, N.J., Dibb, J.E., Albert, M.R., Blake, D.R., Rowland, F.S., 2002a. Photochemically induced production of CH<sub>3</sub>Br, CH<sub>3</sub>I, C<sub>2</sub>H<sub>5</sub>I, Ethene, and propene, within surface snow at Summit, Greenland. *Atmospheric Environment* 36, 2671–2682.
- Swanson, A.L., Blake, N., Flocke, F., Atlas, E., Blake, D.R., Rowland, F.S., 2002b. Seasonal variations of C<sub>2</sub>–C<sub>4</sub> non-methane hydrocarbons and C<sub>1</sub>–C<sub>4</sub> alkyl nitrates at the summit research station in Greenland. *Journal of Geophysical Research* 108 (D2), #4065.
- Tokarczyk, R., Moore, R.M., 1994. Production of volatile organohalogenes by phytoplankton cultures. *Geophysical Research Letters* 21 (4), 285–288.
- Zafiriou, O.C., 1975. Reaction of methyl halides with seawater and marine aerosols. *Journal of Marine Research* 33 (1), 75–81.