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Bromoalkane production by Antarctic ice algae

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ABSTRACT

Ice microalgae, collected from the underside of annual sea ice in McMurdo Sound, Antarctica, were found to contain and release to seawater a number of brominated hydrocarbons. These included bromoform, dibromomethane, mixed bromochloromethanes, and methyl bromide. Atmospheric measurements in the McMurdo Sound vicinity revealed the presence of bromoform and methyl bromide in the lower atmosphere, with lowest concentrations inland, further indicating that biogenic activity in the Sound is a source of organic bromine gases to the Antarctic atmosphere. This may have important implications for boundary layer chemistry in Antarctica. In the Arctic, the presence of bromoform has been linked to loss of surface ozone in the spring. We report here preliminary evidence for similar surface ozone loss at McMurdo Station.

1. Introduction

Bromo- and bromochloromethanes are known to occur in high concentrations in the arctic atmosphere during late winter and early spring (Berg et al., 1984; Cicerone et al., 1988; Bottenheim et al., 1990). Photolysis of these compounds, in particular bromoform (tribromomethane, $CHBr_3$), has been cited as a possible cause of the surface ozone loss observed in the Arctic (Barrie et al., 1988; Oltmans et al., 1989) and, to a lesser extent, the Antarctic (Schnell et al., 1991). However, the exact origin of these brominated compounds has remained unexplained, although biogenic emissions from ice microalgae have been suspected, since these undergo an intense bloom beginning with first light in both polar regions (Palmisano and Sullivan, 1983; Cota, 1985).

We have collected samples of sea ice microalgae and analyzed the sea water matrix in which they were stored for evidence of release of volatile bromoalkanes. We have also examined the algal cellular content for bromoalkanes. Ambient atmospheric samples were collected to confirm that the McMurdo Sound area is a source of bromoalkanes to the antarctic atmosphere.

2. Sampling and analysis

During November 1989, samples of ice algae from the southernmost reaches of the Ross Sea at McMurdo Sound, Antarctica (Fig. 1) were retrieved by ice corer from the platelet ice layers located at the ice-seawater interface beneath 2 to 2.5 m of congelation ice. The samples were brought to the surface under a darkened tent to prevent photoinhibition, and then sealed in polyethylene carboys, after dilution with seawater to lessen osmotic shock to the cells as the ice melted. The diluent seawater was collected at depth at the McMurdo aquarium water inlet, filtered, and stored at -2°C in the dark for 1–5 days before use. The cell suspension was subsequently stored at 10–20 μE m^{-2} s^{-1} (an irradiance representative of under-ice illumination) and at 0 to -1.5°C.

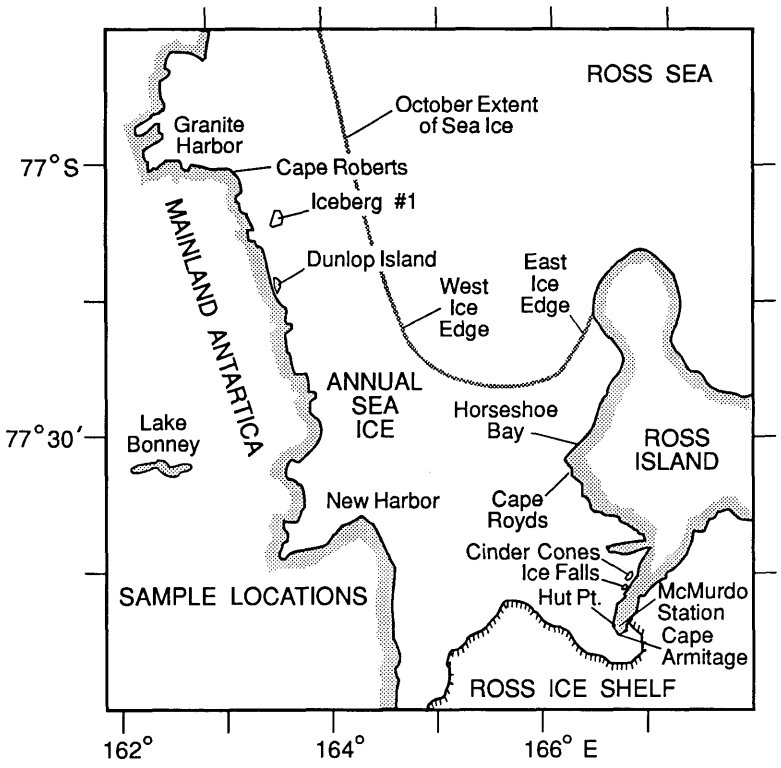

Fig. 1. Map of air sampling locations on and around McMurdo Sound.

After storage for a given period, bromoalkanes in the seawater matrix were sampled in one of two ways: (1) the headspace in the carboy was drawn into 2.6 l capacity evacuated stainless steel canisters for later gas chromatography/mass spectrometry (GC/MS) analysis, or (2) a subsample of the suspension was placed into an airtight bottle and charcoal-filtered air was sparged through the seawater/melted ice to drive off dissolved gases through Tenax polymer-filled absorbent tubes, for later thermal desorption/gas chromatography (GC) analysis with electron capture detection (ECD). The Tenax tubes are inefficient at collecting methyl bromide (bromomethane), but measurements of methyl bromide were made by the canister-GC/MS technique. The canister sampling technique has not at yet been calibrated for dibromomethane or the mixed bromochloromethanes. Sampling and analytical methodologies and calibration procedures for both the GC/MS and the thermal desorption/GC techniques are described in detail elsewhere (Cicerone et al., 1988 and Sturges et al., 1992). Detection limits for the Tenax/GC-ECD method were better than 10 pg dm^{-3}, and analytical precision 2–4%, depending on compound. The GC/MS measurements had detection limits of 1.2 and 0.4 ppt, and analytical precision of 10 and 15%, for methyl bromide and bromoform respectively. Chlorophyll-a was determined in the samples by fluorometric techniques on acetone extracts of particulate material from the ice meltwater (Palmisano and Sullivan, 1983).

Further samples of the sea ice diatom *Porosira pseudodenticulata* collected from the platelet ice layers at Cape Royds were either filtered through 0.45 μm Millipore filters or centrifuged for 10 min at 3000 g, and frozen in liquid nitrogen for shipping to the University of Colorado. An estimate of the cellular content of bromoalkanes was determined by suspending the now ruptured cells in distilled-deionised water and collecting sparged

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samples, as described above, for GC analysis. The diluent contained undetectable amounts of the bromoalkanes. Each individual result shown is the sum of a sequence of three or four consecutive spargings and analyses, first at room temperature, and then at 85–90°C. In all cases significantly more bromoalkanes were released at elevated temperature.

In addition to the algal experiments, steel canister samples of whole ambient air were collected at various locations on the annual and shorefast ice of McMurdo Sound and at an inland site. The sampling locations are shown in Fig. 1.

3. Results

Sea ice algal communities were sampled at three different sites: two contained predominantly *Nitzschia stellata* (a pennate diatom), and the third was a virtual monoculture of *Porosira pseudodenticulata* (a centric diatom). A surface seawater sample was also collected from the ice edge where the mean flow was northward from beneath the ice. The results are shown in Fig. 2. Bromochloromethane (CH_2BrCl) concentrations were at most 0.02 ng dm^{-3}, and the results have not been plotted in the Figure. Experiments 2 and 3, and 4 and 5, were conducted with subsamples of the two Nitzschia collections respectively whilst experiment 6 was performed with the *Porosira* collection. Also shown in Fig. 2 are literature results for mid-Atlantic (6°W, 6°W) seawater (Class and Ballschmiter, 1988).

Comparison of the mid-Atlantic results with the ice edge seawater indicate that the latter was enriched in several of the bromoalkanes, presumably due to emissions from the under-ice algal communities. There were marked variations in bromoalkane emission from the different algal samples. The results were reasonably consistent between subsample analyses, but there were large differences between the results from different *Nitzschia* collections. The two subsamples of *Nitzschia* #53 gave rise to similar concentrations to the ice-edge sample (experiment 1), with the exception of higher dibromomethane. Dibromomethane and bromoform dominated in these algal samples. *Nitzschia* #24 exhibited higher concentrations of all the bromoalkanes; predominantly

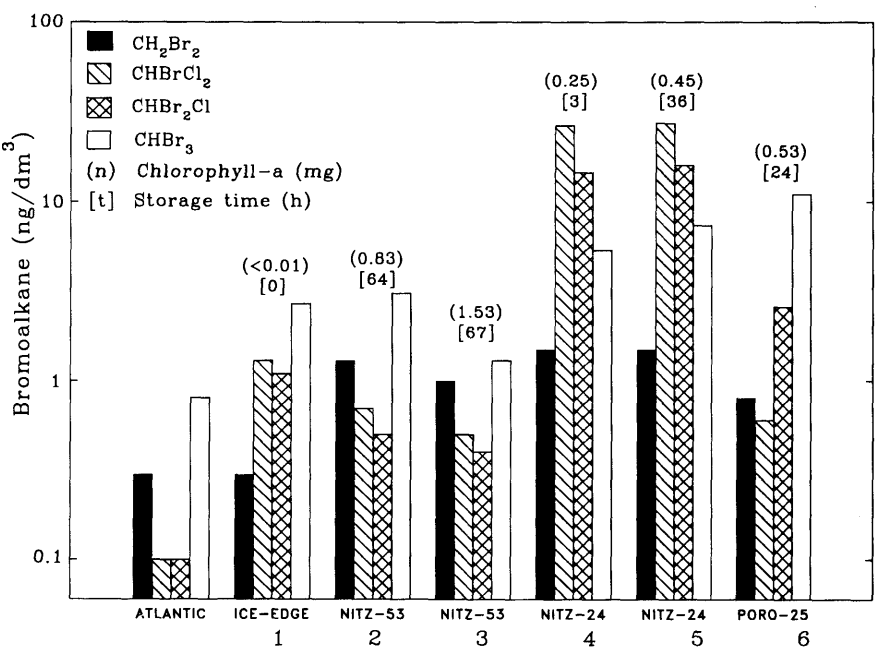

Fig. 2. Summary of seawater and algal suspension sparging experiments. Sample names are given along the bottom axis, with experiment numbers underneath (NITZ = *Nitzschia* samples, PORO = *Porosira* samples). Also shown are literature data for mid-Atlantic seawater (Class and Ballschmiter, 1988).

Table 1. *Cellular content of bromoalkanes in frozen Porosira samples returned from McMurdo Sound (ng compound per g dry algal mass)*

Br compound	Filter samples mean ± sd	*n*	Paste samples mean ± sd	*n*
CH_2BrCl	7 ± 7	3	1 ± 1	2
CH_2Br_2	255 ± 249	2	301 ± 207	2
$CHBrCl_2$	20 ± 9	2	0.4 ± 0.6	3
$CHBr_2Cl$	36 ± 22	3	10 ± 6	3
$CHBr_3$	21 ± 5	3	15	1
Total bromoalkane	339		327	

bromodichloromethane and dibromochloromethane. The subsample of algae #24 stored for 36 h did not show proportionately greater concentrations than the short storage experiment. This is consistent with experiments with arctic *Nitzschia* cultures (Sturges and Cota, 1991) which showed diminished bromoalkane production after several hours incubation. This may also partly explain, along with losses to the headspace and vessel walls, the lower concentrations for the *Nitzschia* #53 samples which were stored for 64–67 h.

The *Porosira* sample produced mostly bromoform and lesser amounts of dibromomethane and the mixed bromochloromethanes. Phase contrast microscopy of this algal sample revealed evidence of hypotonic shock, thus the results presented here may have been influenced by release of intracellular material.

Table 1 presents the results from measurements of *Porosira* cellular bromoalkane content. Summing the bromoalkanes gave a total which falls within the range reported by Gschwend et al. (1985) for a variety of red, brown and green macroalgae (178–529 ng Br-compounds per g dry algal mass). The same general pattern of compound distribution was found in both paste (centrifuged) and filter samples, although the levels were lower for most of the compounds in the paste sample, for reasons which are not clear. The most abundant cellular brominated compound was dibromomethane, although this was not reflected in the in-situ experiments, where the mixed bromochloromethanes and bromoform dominated. No definitive answer can be given as to whether this was due to preferential release of some bromoalkanes, reactions in seawater, differential loss to headspace, or reactions during storage of the cellular material. In this respect it may be significant that Wever et al. (1991) have reported the ability of certain seaweeds to brominate exogenous organic matter, thus intra- and extracellular concentrations would not be expected to be the same.

Independent confirmation of ice algal production of bromoform was given by the two headspace samples from a carboy containing a suspension of *Nitzschia stellata* (Table 2). After 1 h storage the concentrations in the headspace were only slightly higher than the simultaneously sampled ambient air. After a further 5 h the concentrations of bromoform had increased significantly. There was also evidence that methyl bromide had increased in the latter headspace sample relative to both the initial concentration and the ambient air concentration.

Table 3 summarizes the ambient air measurements of bromoform and methyl bromide in the McMurdo area. Bromoform concentrations were similar from both ice edge and annual ice sites. Three of the four lowest values at the ice edge sites occurred with air flow over the ice; the remainder

Table 2. *Bromoform and methyl bromide in whole air canister samples from the headspace above a suspension of Nitzschia stellata*

Sample	Time in carboy (h)	Bromoform (pptv)	Methyl bromide (pptv)
Carboy headspace‡	1	2.2	7.9
Carboy headspace‡	6	5.3	11.2
ambient air¶		1.6	9.1

‡ 10 dm^3 of a 1.0 mg chl-a dm^{-3} algal suspension (~10% ice) placed in a 20 dm^3 carboy (i.e., headspace of 10 dm^3) at around 0°C. Canister samples were ~2.6 dm^3.

¶ Ambient air sample collected at the ice coring site on the same day.

Table 3. *Bromoform and methyl bromide in ambient air samples from the McMurdo Sound area*

Location	*n*	Bromoform (pptv)			Methyl bromide (pptv)		
		mean	median	range	mean	median	range
ice edge	7	1.3 ± 0.7	1.2	0.47–2.8	9.5 ± 0.8	9.3	8.6–11.2
annual ice	10	1.5 ± 0.4	1.6	0.84–2.0	9.1 ± 0.8	9.0	8.0–10.7
tidal crack	2	2.0	—	1.8–2.2	8.1	—	7.9–8.2
Lake Bonney	1	0.36	—	—	7.5	—	—

were collected in calm air or with air from open water. The highest concentration of all was collected under calm wind conditions at the ice edge (2.8 pptv). One of the ice edge samples was collected in the presence of a prolific bloom of *Phaeocystis* phytoplankton, and one of the annual ice samples was collected directly over a surface infiltration pond containing microalgae. In neither case were elevated bromoform or methyl bromide concentrations observed. Samples collected near a tidal crack showed relatively high bromoform concentrations, but not significantly higher than the other sea ice sites. Venting of bromoform from cracks in sea ice has, however, been observed in the Arctic (Sturges and Cota, 1991).

One sample collected at Lake Bonney, in the Dry Valleys inland of McMurdo, with air flowing down from the polar ice sheet, showed a very much lower bromoform content (Table 3). Although it is highly speculative to make any conclusions based on this one sample, it would appear that bromoform was emanating from the sea ice of the Ross Sea, and not from the antarctic continent. Methyl bromide (Table 3) showed similar results, and the same conclusions apply.

Is surface ozone loss observed at McMurdo in the spring, as it is in the Arctic in the presence of organobromine compounds? Fig. 3 shows the lowest 2 km of three ozone soundings from McMurdo Station (Deshler et al., 1990). Ozone

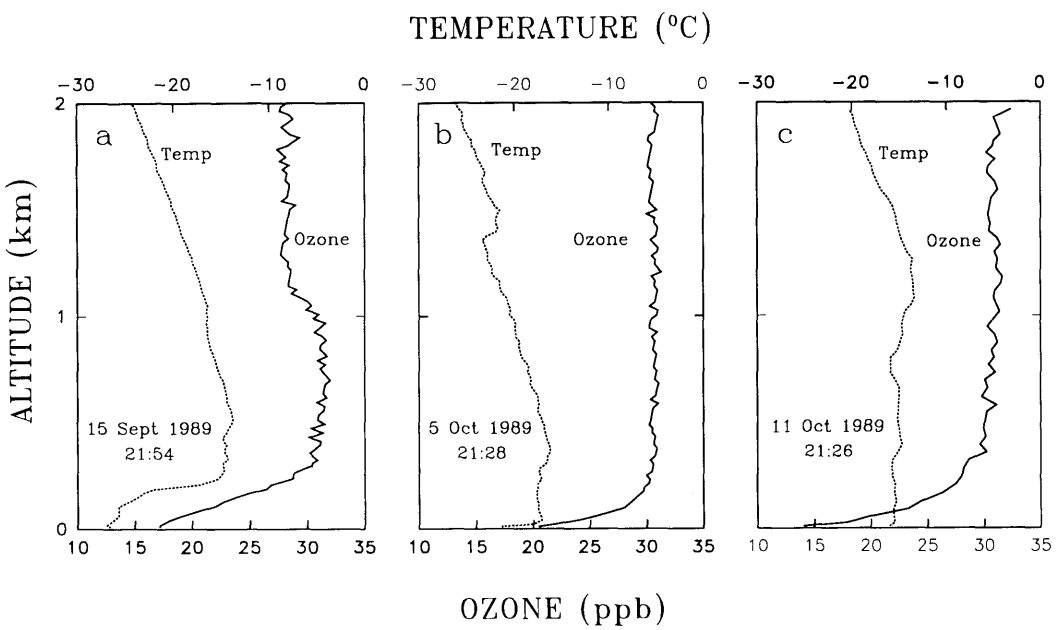

Fig. 3. Three selected ozone and temperature profiles from balloon sondes released from McMurdo Station.

reductions of as much a 15 ppbv occurred close to the surface, within a layer of limited vertical mixing on the order of 200 m thick. This is similar to observations of surface ozone loss in the Arctic (Oltmans et al., 1989), except that ozone concentrations in the Arctic may reach zero throughout a few hundred meters. Such events are relatively rare at McMurdo, whereas they occur frequently in the arctic spring, probably as a result of the lower frequency of strong surface inversions at the antarctic coast compared to the arctic. Although reductions in near-surface ozone on the order of a few ppbv (<10) were commonly observed at McMurdo; of the 39 ozone profiles measured at McMurdo in 1989 (23 August to 30 October), only 5 showed surface ozone depletions of more than 10 ppbv at the surface.

4. Discussion

For decades it has been known that many temperate and tropical macroalgae, and a few marine bacteria, can synthesize numerous brominated organic compounds; bromoform perhaps being the most prolific (Siuda and DeBernardis, 1973 and Faulkner, 1984). Yet, to our knowledge, there have been no previous positive findings of bromine production by marine microalgae (cf. Gschwend et al., 1985). Ice algae, in particular, have been practically unstudied in terms of their possible role in biogeochemical cycling. We believe that these are the first measurements of bromoalkane production by sea ice microalgae.

In this study we did not address the possibility that bacteria, and not the algae, were responsible for the organobromine production. In our later studies (Sturges and Cota, 1991) of arctic ice algae (also predominantly *Nitzschia*) we found no affect on bromoform production after adding a procaryotic inhibitor, but virtual cessation after adding either eucaryotic or photosynthetic inhibitors. We therefore have confidence in attributing the organobromine production observed here to microalgal activity.

Another question is whether macroalgae in McMurdo Sound could contribute to the observed atmospheric levels. This is less readily answered due to the sparsity of data on both microalgal and macroalgal distributions and densities. However, it should be noted that ice algae are present under virtually all annual and pack ice, and can achieve high carbon production rates (5–23 g C m^{-2} y^{-1} during a 60–90 day bloom: Grossi et al., 1987; Cota et al., 1991), whereas macroalgae are found only in suitable shallow water environments. Pelagic and surface ice algae did not appear to produce large amounts of bromoform or methyl bromide in this study. Pelagic algal blooms in McMurdo Sound generally occur later in the year than the ice algal bloom, after ice break-up.

Sturges and Cota (1991) measured bromoform production rates by ice algae, and found that they could account for observed arctic atmospheric levels with less than 20% of the estimated emission to seawater by ice algae. Furthermore estimates of annual bromoform release by ice algae at both poles exceeded that of global macroalgae production. Better knowledge of the relative production by micro- and macroalgae is required to address this issue. Alternatively, year round monitoring of atmospheric bromine chemistry at McMurdo Sound would indicate if seasonal variations exist which match the ice algal production cycle.

5. Conclusions

The *diatoms Nitzschia stellata* and *Porosira pseudodenticulata*, that inhabit the underside of annual ice in McMurdo Sound, synthesize, and release to the surrounding seawater, substantial amounts of bromoalkanes; bromoform, dibromomethane, and mixed bromochloromethanes (and possibly methyl bromide). The relative and absolute amounts of the bromoalkanes produced varies between, and even within, different algal assemblages. This biogenic source of bromoalkanes undoubtedly has an impact on the atmospheric composition immediately overlying the coastal antarctic areas, as we have demonstrated from measurements of relatively high bromoform at a number of locations across the annual ice in McMurdo Sound compared with an inland location. There was also some evidence for higher methyl bromide concentrations over the sea ice.

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