Vertical Profiles of Bromoform in Snow, Sea Ice, and Seawater in the Canadian Arctic

William T. Sturges
Glenn F. Cota
Old Dominion University
Paul T. Buckley

Follow this and additional works at: https://digitalcommons.odu.edu/ccpo_pubs
Part of the Oceanography Commons

Repository Citation
Sturges, William T.; Cota, Glenn F.; and Buckley, Paul T., "Vertical Profiles of Bromoform in Snow, Sea Ice, and Seawater in the Canadian Arctic" (1997). CCPO Publications. 283.
https://digitalcommons.odu.edu/ccpo_pubs/283

Original Publication Citation

This Article is brought to you for free and open access by the Center for Coastal Physical Oceanography at ODU Digital Commons. It has been accepted for inclusion in CCPO Publications by an authorized administrator of ODU Digital Commons. For more information, please contact digitalcommons@odu.edu.
Vertical profiles of bromoform in snow, sea ice, and seawater in the Canadian Arctic

William T. Sturges
School of Environmental Sciences, University of East Anglia, Norwich, England

Glenn F. Cota
Center for Coastal Physical Oceanography, Old Dominion University, Norfolk, Virginia

Paul T. Buckley
Cooperative Institute for Research in Environmental Sciences, University of Colorado, Boulder

Abstract. Bromoform (CHBr₃) was measured in vertical profiles from the snow surface through the snowpack, sea ice, and water column to the seafloor at Resolute Bay, Canada, in the spring of 1992. Elevated concentrations of bromoform were observed in both the ice (32-266 ng L⁻¹ by liquid water volume) and seawater (~20 ng L⁻¹) at the ice-water interface, associated with bromoform emission from ice microalgae. A surprising finding was a second horizon of high bromoform concentrations (336-367 ng L⁻¹) in sea ice at the snow-ice interface. Chlorophyll and salinity were also elevated in this upper ice layer, although chlorophyll was much lower than in the basal ice microagal layer. We speculate that this upper bromoform-enriched layer may have originated from scavenging of the surface water layer by frazil ice during initial ice formation in the preceding autumn. Equally unexpected was the occurrence of yet higher bromoform concentrations in snowpack immediately overlying the sea ice (492-1260 ng L⁻¹), declining in concentration (by about a factor of 2 or more) toward the snow surface. Snow of very recent origin, however, contained as little as 2 orders of magnitude less bromoform than the older snowpack. Possible origins for elevated bromoform in the snowpack include diffusion out of the bromoform-enriched upper ice layer and gradual concentration of bromoform out of the atmosphere by adsorption on to ice crystals. These are considered in turn. In one scenario, photolysis of bromoform from snow is considered, which might help account for atmospheric bromine-ozone chemistry. The possible contributions from snow, sea ice, and seawater to atmospheric bromoform levels during both the winter and spring are also considered, and it is concluded that surface seawater presents the most significant reservoir for atmospheric bromoform.

1. Introduction

There has been considerable interest in the occurrence of bromoform (CHBr₃) in the Arctic environment since high concentrations were first measured in the lower Arctic troposphere [Berg et al., 1984; Barrie et al., 1988; Cicerone et al., 1988] and in surface waters of the Arctic Ocean [Fogelqvist, 1985; Krysell, 1991]. Indeed, bromoform together with methyl bromide, evidently dominates the atmospheric budget of gaseous bromine in the Arctic troposphere [Sturges et al., 1993]. While methyl bromide displays relatively invariant concentrations year round [Cicerone et al., 1988], bromoform has been shown to have a strong inverse correlation with surface ozone concentrations during Arctic spring [Bottenheim et al., 1990; Yokouchi et al., 1994]. This led to initial speculation that bromine radicals released by the photolysis of atmospheric bromoform might be responsible for the episodic destruction of surface ozone [Barrie et al., 1988; Oltmans, 1991]. More recently there has been compelling evidence from hydrocarbon measurements that bromine chemistry does indeed play a central role in the Arctic spring ozone loss [Jobson et al., 1994], but the source (or sources) of the bromine has remained obscure. Tang and McConnell [1996] have been able to model the polar sunrise ozone loss by invoking a bromine source from sea salt-laden snowpack, coupled with photolytic production of "seed" bromine from bromoform.

In addition to the variability of bromoform in the spring, there is also a pronounced seasonal cycle in the Arctic, with a concentration minimum in June and July and a maximum between December and February [Cicerone et al., 1988; Yokouchi et al., 1996]. This is in antiphase to solar flux and is therefore believed to reflect higher photolytic removal rates in summer, rather than changing source strengths.
The origins of bromoform itself in the Arctic atmosphere are unclear. Gschwend et al. [1985] have shown that macrophytes are a significant global source, and Moore et al. [1993] have indicated that macrophytes could be an important source of bromoform in certain open-water areas near the Arctic Ocean. Macrophytes are, however, restricted to the shallow waters of suitable coastal zones (not ice covered or ice scoured, and nondepositional, rocky environments), and usually contribute very little (<1%) to total primary productivity in the Arctic [e.g., Welch et al., 1992]. It is therefore doubtful that macrophytes growing within the Arctic could alone account for the magnitude of bromoform concentrations observed in the Arctic atmosphere.

In earlier work we made direct measurements of spring bromoform production by microalgae inhabiting the underside of annual sea ice in the Arctic [Sturges et al., 1992]. It was estimated that only 2-19% of this under-ice microalgal production would need to be transferred to the atmosphere to account for observed concentrations. Venting of bromoform from natural cracks and drill holes in the sea ice was indeed observed at the same location, but later flux measurements over drill holes fell short of the required rate [Sturges and Cota, 1995].

As part of the second spring season of field experiments to examine biogenic bromoform production at Resolute Bay, Canada, we made measurements of the vertical profiles of bromoform from the surface atmosphere, through recent snow drifts, annual snowpack, sea ice, and the water column. We hoped to gain insight into the spatial and temporal distribution of bromoform production in the Arctic and potential pathways for its transport to the atmosphere.

2. Methods

Samples were collected during April and May of 1992 from shore-fast annual ice near Resolute Bay, Canada (74°39.9N, 94°55.2W). Samples were mostly collected and processed at our own ice camp (site 1) over about 10 m of seawater, with additional seawater samples being collected from a deeper water ice camp (125 m) operated by a joint Canadian/Japanese group (site 2).

Snow was collected from excavated pits directly into glass sparging vessels. Ice samples were collected with a motorized SIPRE Teflon-coated stainless steel corer. Seawater samples were collected with Niskin bottles lowered down hydroholes at the two ice camps. The samples were immediately processed at our ice camp. Ice and snow samples were first allowed to melt in glass sparging vessels in a water bath. The samples (50-100 mL) were sparged at 40°C with about 3 L of purified nitrogen (high-purity nitrogen passed through a heated palladium catalyst). The sparge effluent was passed through nitrogen countercflow Nafion drier and then through one or more 15 x 0.65 cm OD stainless steel tubes filled with Tenax-TA (a porous polymer) at about 20°C. The Tenax tubes had been previously cleaned by purging with purified helium at 220°C. The tubes were tightly sealed before and after sampling with Swagelok end caps.

The Tenax tubes were analyzed within 1-3 days at the shore-based laboratory by direct thermal desorption into a Hewlett Packard 5890A gas chromatograph fitted with an electron capture detector. The tubes were fitted into a specially modified capillary injection port. Purified helium carrier gas was diverted through the tube, and a heater block at 200°C was clamped around the tube for 5 min. The desorbed compounds were separated with a 75-m J&W DB624 0.53-mm-OD capillary column. The column oven temperature was programmed from 35°C to 200°C. An important feature of the system was that subambient cooling was not required, since cryogenic coolants could not be transported to the site. Numerous brominated and chlorinated compounds were observed, including a suite of brominated alkanes ranging in elution time from CH₂BrCl to CHBr₃. Bromoform was by far the most abundant of these, and discussion will be limited, in the present report, to this compound.

Calibrations were made by injecting standards, diluted in hexane from an UltraScientific DWM-540 standard mixture in methanol, into the upstream end of clean Tenax tubes, and desorbing as above. Sparging efficiency was determined by successively sparging actual samples, and collection efficiency was determined by measuring the breakthrough to one or more additional Tenax tubes. These efficiencies averaged 91 and 95%, respectively. Successive desorption of sample-containing Tenax tubes indicated 100% desorption efficiency. Blanks were assessed by sparging degassed deionized water. The concentrations reported here have been corrected for collection efficiency, sparging efficiency, and blank level. Analytical precision was about ±5% (10 standard deviation).

Salinities were measured with a refractometer (±1%). Chlorophyll was measured according to the fluorometric method of Holm-Hansen et al. [1965].

3. Results

Figure 1 shows bromoform and chlorophyll profiles in seawater at the two ice camps. The chlorophyll measurements at the deep water site were made by another group (M. Gosselin, personal comment, 1992). Chlorophyll levels were measurable but much lower than those found in bottom ice, which can reach thousands of micrograms per liter (see below). At the deep water site (site 2) there did appear to be a corresponding increase in both bromoform and chlorophyll near the top of the profile on May 11, but the higher chlorophyll levels encountered on May 14 at the shallow water site (site 1) were not accompanied by elevated bromoform. It is our belief that it was the influence of bromoform emissions from the under-ice microalgal community that produced the higher near-surface concentrations at the deep water site, and the rapid diminution with depth to almost constant levels below about 20 m. These measurements at the deep water site are in good agreement with measurements made in parallel at Resolute by another group [Moore et al., 1993], which showed concentrations of about 10-18 ng L⁻¹ in the 10 m of water below the ice, and about 5-8 ng L⁻¹ in the deeper water. The concentrations in the lower part of the deep water profiles were similar to those reported by Dyrrsen and Fogelqvist [1981] and Fogelqvist [1985] for open waters in the Arctic Ocean (6-13 ng L⁻¹), while the concentrations just under the ice were greater than those reported under Arctic sea ice by Fogelqvist [1985] (9.6 ng L⁻¹). Much higher concentrations again (9-370 ng L⁻¹) have been reported nearshore and over macrophyte beds in Arctic waters [Dyrrsen and Fogelqvist, 1981].
deep water camp (site 2). The concentration scales are the same for both graphs, but the depth scale has been expanded.

Figure 1. Bromoform and chlorophyll concentrations in seawater at (a) the shallow water camp (site 1) and (b) the deep water camp (site 2). The concentration scales are the same for both graphs, but the depth scale has been expanded in Figure 1a.

1981; Schall and Heumann, 1993), and concentrations in excess of 400 ng l⁻¹ have been reported by Moore et al. [1993].

The shallow water site showed relatively uniform concentrations of bromoform with depth, indicating well-mixed conditions. The concentrations were similar to those observed in the uppermost 10 m at the deep water site. Sources of bromoform to the shallow water would have included microalgae in the overlying sea ice and scattered kelp plants underlying the site, whereas chlorophyll levels in the water column itself were low. Both the ice algae and the kelp (Agarum cribosum) were shown to have been actively producing bromoform at this time [Cota and Sturges, 1997]. Because of the degree of mixing, however, it is not possible to discern from the profiles the relative contributions of these two sources. Macrophytes would not have occurred in the depths of the chemical and chlorophyll measurements do not match exactly. In both profiles, bromoform in the bottom ice layer was measured in the very lowest ice layer and therefore accurately represents the concentrations in the bulk of the ice algal layer. The chlorophyll measurements, on the other hand, refer to the ice just above this. More detailed chlorophyll measurements conducted on other cores showed that there was a strong chlorophyll gradient in the bottom few centimeters of ice. Chlorophyll has been observed to increase by as much as 2 to 3 orders of magnitude within the first 2 cm of ice [Cota and Smith, 1991, and Cota unpublished data, 1993]. The chlorophyll values reported here for the lower ice are therefore lower limits.

Two horizons of high bromoform and salinity were evident: one at the base of the ice, and one at the top. The lower horizon clearly corresponds to the ice algal layer. The discovery of an upper horizon, however, was unexpected, although Moore et al. [1993] have also now reported the existence of both a lower and upper bromoform horizon in sea ice at Resolute. They, on the other hand, did not find as great a degree of enrichment as we report here, with bromoform concentrations of only around 60 ng L⁻¹. Precise sampling details, however, were not given regarding depth or thickness of the ice sections examined, which might affect the comparability of our results if the enriched layers are very thin. In both profiles in Figure 2, bromoform levels were similar or even higher in the upper horizon than in the basal ice, despite the much lower levels of chlorophyll in the upper horizon.

The elevated salinity in the upper horizon was almost certainly a remnant of the process of ice formation in the preceding autumn. As the surface waters cool, “frazil ice” crystals form in the upper part of the water column in response to slight supercooling (reviewed by Makyut [1985]). These ice crystals float to the surface and consolidate into a layer about 1-10 cm thick under quiescent conditions, thicker again under wind- and- wave induced turbulence. Once a critical density of frazil ice in the surface water occurs, sintering and regelation between crystals reduces their mobility, and the transition to a solid surface begins. After the initial solidified frazil ice layer forms, subsequent ice formation takes place in response to heat loss from the ice surface, resulting in accretion of new ice to the underside of the ice layer. This new ice grows downward as “platelet” ice, entrapping brine pockets between platelets, and so giving rise to the characteristic columnar crystal structure of bulk sea ice.

As seawater freezes, impurities in the water are excluded from the solid ice into the surrounding brine. As the temperature drops, solid salts begin to precipitate out of the brine, beginning with sodium sulfate at ~8.2°C. Sodium chloride precipitates out at ~22.9°C. In the first instance, the amount of brine trapped is a function of the speed of ice formation and is thus greatest at the surface, yielding typical salinities of 10-20%, consistent with our observations of 10 and 13% in the upper ice. There should therefore be a roughly monotonic decrease in salinity with depth in the ice, since growth rates slow with time and ice depth. In practice, a C-shaped profile, as we observed, is typical of first-year ice. This is due to progressive desalination of the platelet ice as brine pockets become interconnected into brine channels and drain under the influence of temperature gradients within the ice and the increasing hydrostatic head. The sharp upturn in salinity we observe at the base of the ice was common for newly formed skeletal layer ice.
It is notable that although the processes of brine exclusion and drainage during ice formation had reduced the salinity from about 32% in the original seawater to the 5-6% we observed in the sea ice, the bromoform levels in this ice were not dissimilar to those in the deep (>20 m) seawater (Figure 1b). This difference in the ratio of salinity to bromoform between seawater and the ice implies that the two are not fractionated in the same way during ice formation and desalination. Melnikov [1997] found a ratio of 0.7 for dissolved organic carbon in young sea ice versus seawater, so it appears that a large fraction of organic solutes are incorporated into sea ice.

Figure 3 presents the bromoform profiles (note the logarithmic scale) measured in snowpack and snow drifts from different locations within walking distance of our ice camp. "New" snow refers to one day-old snow in deep drifts overlying higher-density, wind-packed snow. Results from the new snow are shown in Figures 3a and 3b. The remaining four panels are profiles through the "old", consolidated snowpack, mostly comprising snow deposited during the preceding autumn and winter. In Figure 3e the result from loose, freshly deposited, powder snow has also been plotted. The depth of snow sampled was approximately 5 cm in most cases and is represented by the width of the bars in Figure 3.

Bromoform concentrations in new snow were much lower, by as much as 2 orders of magnitude, than in the old snowpack. The lowest concentrations of all (22 ng L⁻¹) were in the fresh powder snow sample. Nevertheless, these values in new snow are not insignificant compared with the seawater concentrations, indeed, they were all at least as high, on a liquid water basis, as seawater concentrations at the shallow water site (Figure 1a). There was slightly more bromoform in the bottom of the new snow than in the top, but significantly so only in profile 3a. In contrast to the new snow, there appeared to be a distinct gradient of bromoform concentration in the old snowpack. Bromoform concentrations in the lower snow were very large indeed: exceeding 1 µg L⁻¹ in one case. This is higher than levels in either the upper sea ice horizon or the basal ice algal layer (Figure 2).

Moore et al. [1993] also reported elevated bromoform in snow at Resolute and other Arctic locations, although only for surface snow scrapes. Their results, ranging from 48 to 201 ng L⁻¹ at Resolute and Tuktoyaktuk and up to 538 ng L⁻¹ in the Beaufort Sea, are in good agreement with our observed surface snowpack values of 88-616 ng L⁻¹. They reported much lower values (0-20 ng L⁻¹) at Alert, although these were evidently mostly from a snow collector and are therefore likely to be more comparable with our new snow and powder snow values.

Clearly, it is important to give due consideration to the type and age of snow studied, given the orders of magnitude differences in bromoform concentrations we have observed between new and old snow. Exact details of the nature of the
snow examined are not given in the Moore et al. [1993] paper. It may be that the type of snow is of overriding importance in explaining their results and provides an alternative to their hypothesis of progressive precipitation scavenging of bromoform in northward tracking air masses. Our results for freshly fallen snow at Resolute would, furthermore, seem to argue against sufficiently high scavenging ratios for such a mechanism. In addition, there appears to be no systematic difference in springtime atmospheric bromoform concentrations between Resolute and Alert [Sturges and Cota, 1995; Yokouchi et al., 1994; Hopper et al. 1994]. Particularly telling in this respect is a comparison of bromoform measurements by Cicerone et al. [1988] at Barrow, Alaska (71°N) and by Yokouchi et al. [1996] at Alert (82°N). Allowing for the apparent calibration factor difference of 2.5 between the two studies [Bottenheim et al., 1990] the annual cycles of bromoform at these two locations are almost identical in trend and magnitude.

Salinity and chlorophyll measurements were available for just one of the snowpack profiles Figure 3f). This profile has been replotted in Figure 4 along with these additional measurements (note the linear concentration scale in this case). The salinity in the lower snow was similar to that of the underlying sea ice (Figure 2). Salinity then dropped sharply towards the surface, although not to zero. The high salinity at depth would have been at least partly due to capillary rise of seawater ("brine wicking") through snow deposited on the newly formed sea ice during the previous autumn. Brine wicking should, however, be effective only through the bottom few centimeters of snow [Takizawa, 1985]. Salinity in the upper snow may have arisen from deposition or precipitation scavenging of atmospheric sea salt particles [Davidson et al., 1991]. The decline in bromoform levels did not follow the same trend as salinity and is therefore probably unrelated.

Chlorophyll concentrations were relatively uniform throughout the snowpack, and similar to those in seawater at
the shallow water site. Absorption spectra of acetone extracts of untreated snow particulates did not, however, show absorption peaks characteristic of algal pigments. Further work is needed to establish whether detrital pigments, dissolved organic matter, or other fluorescent material interfered with the fluorometric analysis of chlorophyll. We do not, however, expect there to be significant numbers of active algal cells in the snow at this time of year.

In Figure 5 the majority of the foregoing data have been compiled into a composite picture of a profile from the snow surface to the seafloor. The single measurement for fresh powder snow (bromoform only) has been plotted at the top of the profile. Below this are shown mean values for the surface and base of the new snow; and the surface, midprofile, and base of the old snow, plotted at their approximate respective depths. (It should be noted that the new snow occurred in individual drifts, not as continuous coverage.) The chlorophyll and salinity data in old snow are from a single profile (Figure 4) and were not available for new snow. The sea ice section is the mean of the two profiles in Figure 2 for approximately corresponding depths. Since the snow and ice samples were all collected in the vicinity of the shallow water site, only the seawater values from this same site have been plotted (mean of the three profiles in Figure 1a). Note the contracted depth scale for the seawater section of the profile. This figure will be the main point of reference in the discussion (section 4).

The bromoform measurements from Figure 5 have been further summarized in Table 1 as estimated integrated column amounts in different parts of the profile. In this case a typical average depth profile for this area has been used. This table provides an indication of the relative sizes of bromoform reservoirs in the air, snow, ice, and seawater compartments. The atmospheric concentration was derived from our own measurements at Resolute during the springs of 1991 and 1992, averaging 2.6 and 1.3 pptv (parts per trillion by volume) in each respective year [Sturges and Cota, 1995]. A constant concentration of 2 pptv has been adopted to the top of a 400-m-high surface inversion layer (consistent with Sturges et al. [1992]), to yield a column amount of 9 μg m⁻². To convert the snow and ice concentrations (in units of mass per liquid water volume) to column amounts, corrections for approximate bulk density were applied. Specific densities were assigned as follows: new snow, 0.25; old snow, 0.3; ice, 0.9; and seawater, 1.0. Approximate layer depths were assigned, as shown in Table 1.

It is notable from Table 1 that the atmospheric burden of bromoform was relatively small in comparison with the amounts stored in snow and ice, which together totalled about five times the atmospheric amount. Also, despite the much greater thickness of the sea ice, more of the bromoform resided in the snow than in the ice. The largest reservoir, however, was surface seawater, which exceeded the atmospheric burden by a factor of 10-20.

![Figure 5](image-url)
Table 1. Integrated Column Amounts of Bromoform for a Typical Depth Profile Through the Lower Atmosphere, Snow, Sea Ice, and Seawater at Resolute Bay in May 1992

<table>
<thead>
<tr>
<th>Layer</th>
<th>Sub-Division</th>
<th>Depth interval</th>
<th>CHBr₃, µg m⁻²</th>
</tr>
</thead>
<tbody>
<tr>
<td>Surface Inversion</td>
<td></td>
<td>400 m</td>
<td>9.0</td>
</tr>
<tr>
<td>New snow</td>
<td>upper</td>
<td>3 cm</td>
<td>0.2</td>
</tr>
<tr>
<td></td>
<td>lower</td>
<td>7 cm</td>
<td>6.4</td>
</tr>
<tr>
<td>Snowpack</td>
<td></td>
<td>7 cm</td>
<td>6.4</td>
</tr>
<tr>
<td></td>
<td></td>
<td>7 cm</td>
<td>18.0</td>
</tr>
<tr>
<td>Sea ice</td>
<td>surface</td>
<td>2 cm</td>
<td>6.7</td>
</tr>
<tr>
<td></td>
<td>bulk</td>
<td>1.5 m</td>
<td>11.0</td>
</tr>
<tr>
<td></td>
<td>ice algal</td>
<td>2 cm</td>
<td>2.8</td>
</tr>
<tr>
<td></td>
<td>site 1</td>
<td>10 m</td>
<td>180.0</td>
</tr>
<tr>
<td></td>
<td>(shallow)</td>
<td>10-15 m</td>
<td>90-135</td>
</tr>
<tr>
<td></td>
<td>site 2</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

4. Discussion

4.1. Bromoform in the Under-Ice Algal Layer

Of the features of Figure 5, the most readily explained is the bromoform and chlorophyll maximum in the bottom ice layer, which is due to the presence of the ice microalgal layer. The mean ice algal production rate from incubation experiments (n=12) at Resolute Bay during this field mission was 75 ± 134 µg CHBr₃ (g chlorophyll⁻¹ h⁻¹) [Cota and Sturges, 1997]. The mean chlorophyll concentration in basal ice from Figure 5 equates to an areal concentration for a 2 cm layer of 4.4 mg chlorophyll m⁻². As was mentioned in the earlier discussion of basal ice chlorophyll levels, this figure underestimates the true chlorophyll concentration in the ice algal layer. We will apply a conservative correction factor of 5, to give an algal chlorophyll concentration of about 22 mg chlorophyll m⁻². As applied in the earlier discussion of basal ice chlorophyll levels, this figure underestimates the true chlorophyll concentration in the ice algal layer. We will apply a conservative correction factor of 5, to give an algal chlorophyll concentration of about 22 mg chlorophyll m⁻² (this compares with the "typical" range of 10-100 mg chlorophyll m⁻² for Arctic ice algae [Cota and Smith, 1991]. Applying this to the bromoform production rate given above yields an areal ice algal production rate of 1.7 µg CHBr₃ m⁻² h⁻¹. This is sufficient to produce the observed amount of bromoform in bottom ice (2.8 µg m⁻³ from Table 1) in under 2 hours. It can therefore be concluded that the transfer of algal-produced bromoform from the bottom ice to the underlying seawater must be rapid, most likely due to movement of seawater through the skeletal ice.

The figure for algal bromoform production calculated above may then be taken as equivalent to the net under-ice release rate. If the mean concentration at depths below 30 m at the deep water site (7 ng L⁻¹ from Figure 1b) is taken as indicative of the "background" concentration, then the mean seawater concentration at the shallow water site (18 ng L⁻¹) was elevated above the background by 11 ng L⁻¹. An under-ice emission rate of 1.7 µg CHBr₃ m⁻² h⁻¹ into a 10-m water column would achieve an increase in concentration of 11 ng L⁻¹ in just 2.8 days under static conditions. This emission rate is consistent with in situ experiments conducted by Moore et al. [1995] at Resolute in 1993 using an under-ice incubation cup. The three experiments they conducted yielded under-ice emission rates of 0.6, 1.1, and 5.2 µg CHBr₃ m⁻² h⁻¹. This gives us confidence that our incubation experiments, conducted in incubators at the ice camp, genuinely represented actual in situ conditions.

4.2. Bromoform in the Upper Sea Ice

The origin of the bromoform-enriched upper sea ice horizon is much less apparent. It was evidently formed at or around the time of initial ice formation in the previous autumn (see discussion on ice formation in the section 3). The exact timing of freeze-up varies widely between years and locations. At Resolute in late 1992, freezing of inshore waters would likely have started in October when air temperatures were consistently below 0 °C (Figure 6).

Three possible explanations present themselves: biogenic production by an autumn microalgal bloom, in situ biogenic production by an autumn microalgal bloom, in situ biogenic production by an autumn microalgal bloom, in situ biogenic production by an autumn microalgal bloom, in situ biogenic production by an autumn microalgal bloom, in situ biogenic production by an autumn microalgal bloom, in situ biogenic production by an autumn microalgal bloom, in situ biogenic production by an autumn microalgal bloom, in situ biogenic production by an autumn microalgal bloom, in situ biogenic production by an autumn microalgal bloom, in situ biogenic production by an autumn microalgal bloom, in situ biogenic production by an autumn microalgal bloom, in situ biogenic production by an autumn microalgal bloom, in situ biogenic production by an autumn microalgal bloom, in situ biogenic production by an autumn microalgal bloom, in situ biogenic production by an autumn microalgal bloom, in situ biogenic production by an autumn microalgal bloom, in situ biogenic production by an autumn microalgal bloom, in situ biogenic production by an autumn microalgal bloom, in situ biogenic production by an autumn microalgal bloom, in situ biogenic production by an autumn microalgal bloom, in situ biogenic production by an autumn microalgal bloom, in situ biogenic production by an autumn microalgal bloom, in situ biogenic production by an autumn microalgal bloom, in situ biogenic production by an autumn microalgal bloom, in situ biogenic production by an autumn microalgal bloom, in situ biogenic production by an autumn microalgal bloom, in situ biogenic production by an autumn microalgal bloom, in situ biogenic production by an autumn microalgal bloom, in situ biogenic production by an autumn microalgal bloom, in situ biogenic production by an autumn microalgal bloom, in situ biogenic production by an autumn microalgal bloom, in situ biogenic production by an autumn microalgal bloom, in situ biogenic production by an autumn microalgal bloom, in situ biogenic production by an autumn microalgal bloom, in situ biogenic production by an autumn microalgal bloom, in situ biogenic production by an autumn microalgal bloom, in situ biogenic production by an autumn microalgal bloom, in situ biogenic production by an autumn microalgal bloom, in situ biogenic production by an autumn microalgal bloom, in situ biogenic production by an autumn microalgal bloom, in situ biogenic production by an autumn microalgal bloom, in situ biogenic production by an autumn microalgal bloom, in situ biogenic production by an autumn microalgal bloom, in situ biogenic production by an autumn microalgal bloom, in situ biogenic production by an autumn microalgal bloom, in situ biogenic production by an autumn microalgal bloom, in situ biogenic production by an autumn microalgal bloom, in situ biogenic production by an autumn microalgal bloom, in situ biogenic production by an autumn microalgal bloom, in situ biogenic production by an autumn microalgal bloom, in situ biogenic production by an autumn microalgal bloom, in situ biogenic production by an autumn microalgal bloom, in situ biogenic production by an autumn microalgal bloom, in situ biogenic production by an autumn microalgal bloom, in situ biogenic production by an autumn microalgal bloom, in situ biogenic production by an autumn microalgal bloom, in situ biogenic production by an autumn microalgal bloom, in situ biogenic production by an autumn microalgal bloom, in situ biogenic production by an autumn microalgal bloom, in situ biogenic production by an autumn microalgal bloom, in situ biogenic production by an autumn microalgal bloom, in situ biogenic production by an autumn microalgal bloom, in situ biogenic production by an autumn microalgal bloom, in situ biogenic production by an autumn microalgal bloom, in situ biogenic production by an autumn microalgal bloom, in situ biogenic production by an autumn microalgal bloom, in situ biogenic production by an autumn microalgal bloom, in situ biogenic production by an autumn microalgal bloom, in situ biogenic production by an autumn microalgal bloom, in situ biogenic production by an autumn microalgal bloom, in situ biogenic production by an autumn microalgal bloom, in situ biogenic production by an autumn microalgal bloom, in situ biogenic production by an autumn microalgal bloom, in situ biogenic production by an autumn microalgal bloom, in situ biogenic production by an autumn microalgal bloom, in situ biogenic production by an autumn microalgal bloom, in situ biogenic production by an autumn microalgal bloom, in situ biogenic production by an autumn microalgal bloom, in situ biogenic production by an autumn microalgal bloom, in situ biogenic production by an autumn microalgal bloom, in situ biogenic production by an autumn microalgal bloom, in situ biogenic production by an autumn microalgal bloom, in situ biogenic production by an autumn microalgal bloom, in situ biogenic production by an autumn microalgal bloom, in situ biogenic production by an autumn microalgal bloom, in situ biogenic production by an autumn microalgal bloom, in situ biogenic production by an autumn microalgal bloom, in situ biogenic production by an autumn microalgal bloom, in situ biogenic production by an autumn microalgal bloom, in situ biogenic production by an autumn microalgal bloom, in situ biogenic production by an autumn microalgal bloom, in situ biogenic production by an autumn microalgal bloom, in situ biogenic production by an autumn microalgal bloom, in situ biogenic production by an autumn microalgal bloom, in situ biogenic production by an autumn microalgal bloom, in situ biogenic production by an autumn microalgal bloom, in situ biogenic production by an autumn microalgal bloom, in situ biogenic production by an autumn microalgal bloom, in situ biogenic production by an autumn microalgal bloom, in situ biogenic production by an autumn microalgal bloom, in situ biogenic production by an autumn microalgal bloom, in situ biogenic production by an autumn microalgal bloom, in situ biogenic production by an autumn microalgal bloom, in situ biogenic production by an autumn microalgal bloom, in situ biogenic production by an autumn microalgal bloom, in situ biogenic production by an autumn microalgal bloom, in situ biogenic production by an autumn microalgal bloom, in situ biogenic production by an autumn microalgal bloom, in situ biogenic production by an autumn microalgal bloom, in situ biogenic production by an autumn microalgal bloom, in situ biogenic production by an autumn microalgal bloom, in situ biogenic production by an autumn microalgal bloom, in situ biogenic production by an autumn microalgal bloom, in situ biogenic production by an autumn microalgal bloom, in situ biogenic production by an autumn microalgal bloom, in situ biogenic production by an autumn microalgal bloom, in situ biogenic production by an autumn microalgal bloom, in situ biogenic production by an autumn microalgal bloom, in situ biogenic production by an autumn microalgal bloom, in situ biogenic production by an autumn microalgal bloom, in situ biogenic production by an autumn microalgal bloo

Figure 6. Monthly means of temperature, precipitation, and solar flux at the Resolute meteorological station for mid-1991 to mid-1992 (Environment Canada).
production during the winter by organisms trapped in the frazil ice layer, and scavenging of bromoform from the water column during autumn freeze-up.

In the first two cases, the low levels of chlorophyll appear to count against this explanation, especially bearing in mind that, as was discussed above, the measured chlorophyll levels in the basal ice algal layer were very much lower limits. It might be argued that even a very low biogenic production rate could produce high bromoform levels, since any amounts produced would be largely trapped within the ice, whereas bromoform produced in the basal ice algal layer is freely lost to the underlying seawater. It might also be argued that the species composition and metabolic activities in the upper ice could be quite different from the basal ice. Smith et al. [1989], for instance, have reported the presence of actively growing bacteria within sea ice, although studies employing biological inhibitors have found no evidence for bacterial production of bromoform, at least in basal ice [Cota and Sturges, 1997]. It is highly improbable that active metabolism by autotrophs or heterotrophs would have been possible in the upper ice where winter time temperatures would have declined to those of the overlying atmosphere, i.e., monthly means of below -35°C (Figure 6).

Autumn blooms of microalgae are relatively well known from the Antarctic, but there are only scattered reports from the Arctic [Horner, 1985]. Given that light levels were very low in October when the ice was forming, it is unlikely that there would have been as much bromoform production by ice algae at that time as during the spring bloom in May close to peak solar radiation levels (Figure 6). There may, however, have been some level of biogenic production by microalgae, or even macrophytes, prior to ice formation, sufficient to produce elevated bromoform levels in the seawater. Some mechanism would then be required to concentrate this bromoform into the surface ice layer. As was mentioned above, although there is clear evidence that bromoform and other dissolved organics are not excluded during seawater freezing, there is no evidence that they are actually enriched by this process. One possibility, however, might be scavenging by rising frazil ice. It is not known whether such a mechanism is possible for dissolved organics, although there is ample evidence that microorganisms are efficiently scavenged in this way [Horner, 1985].

It is also seen from our own studies that falling snow can scavenge atmospheric bromoform, albeit with low efficiency. It would not be possible to account for bromoform in the upper ice layer in terms of melting of falling snow on the newly formed ice surface (compare the column amounts of bromoform in new snow and surface ice in Table 1) given that atmospheric bromoform levels are no higher in the autumn than in the spring [Cicerone et al., 1988; Yokouchi et al., 1996]. Scavenging by frazil ice in seawater, however, if analogous to snow in air, might present a viable alternative.

The supercooling required for frazil ice production is of the order of a few tenths of a degree, whereas supercooling of 0.2°-0.4°C down to depths of a few tens of meters have been observed in the Arctic [Makyut, 1985]. Direct observations of frazil ice “billows” at depths of several meters have been reported from the Antarctic, while the common occurrence of benthic microorganisms and sediment particles in frazil ice layers argues for considerable depths of ice crystal formation [Horner and Schrader, 1982; Horner, 1985; Makyut, 1985]. For the sake of argument we will assume that a 10 m depth of water can be scavenged by frazil ice and that the bromoform concentration in the water is the same as we observed at the shallow water site, giving a column amount of bromoform of 180 μg m⁻² (Table 1). If the scavenging efficiency is 2% (compare the column amounts of bromoform in new snow and the atmospheric boundary layer in Table 1), then the frazil ice will remove 3.6 μg of bromoform from the water column. This is quite similar to the observed loading of 6.7 μg CHBr₃ m⁻² in surface sea ice (Table 1). Scavenging from seawater does therefore appear to be a credible explanation for the bromoform-enriched upper ice horizon, although time series measurements on ice throughout a seasonal cycle are required to confirm or disprove this.

4.3. Bromoform in Snowpack and Snow Drifts

A further enigma is the occurrence of high levels of bromoform in the snowpack and, in particular, the observation of higher levels in “old”, consolidated snow than in snow drifts of recent origin and in freshly deposited snow. The latter findings clearly argue against atmospheric scavenging as a major source. Chlorophyll was apparently observed in the snow (Figure 4), but there was no evidence of microalgal activity, nor would it be expected at the low temperatures experienced during the autumn and winter. Furthermore, there was no correlation between the bromoform and chlorophyll measurements. In situ production is therefore not considered to be a possibility.

The fact that some atmospheric scavenging evidently takes place is of considerable interest, as it is not in accord with the laboratory experiments of Hansson and Ravishankara [1993]. They exposed ice surfaces and 58% w/w sulfuric acid solution surfaces to bromoform in the gas phase at 220K. No detectable uptake on the ice surface was observed (uptake coefficient γ < 10⁻⁷). An uptake coefficient of 2 x 10⁻⁴ was observed for the sulfuric acid surface, but the bromoform was quickly released back into the gas phase after exposure ceased. They concluded that significant concentrations of bromoform cannot be stored on ice surfaces, even when acidic coatings are present. This is at odds with our observations of significant bromoform associated with new snow and very high levels indeed in old snowpack. This indicates that the behavior of real snow crystals departs significantly from laboratory models, most likely as a result of compositional differences. They certainly will contain sea salt material (note the salinity profiles in Figure 4) and may also contain crustal material [Davidson et al., 1991]. In the late winter and spring they will also incorporate, or be coated with, relatively high levels of a wide variety of pollutant materials due to the occurrence of “Arctic haze” [Barrie and Hoff, 1985]. This brings to mind two possibilities for the occurrence of high bromoform levels in the snowpack.

First, in measurements of bromoform fluxes out of holes drilled through sea ice, Sturges and Cota [1995] observed high levels of bromoform in “control” chambers placed over swept sea ice surfaces. Although not readily quantifiable, it appeared that the flux from the ice surface may have been at least as large as the flux measured from the drill holes (170 ng m⁻² d⁻¹). If such a flux had continued during the approximately 6 months between initial ice formation and the time of sampling, then a total of 31 μg CHBr₃ m⁻² would have been emitted. This is similar to the total bromoform burden in the snowpack (25 μg m⁻² from Table 1). If the bromoform in the snowpack had indeed originated from the upper ice, then unless in situ production of bromoform had occurred in the ice, the original bromoform content of the ice would
needed to have been 31 \mu g m^{-2} \text{(total of snow and surface ice from Table 1)}. This in turn would have required, say, 5 times more scavenging of seawater by frazil ice during the previous autumn. Alternatively, the bromoform might have permeated through the sea ice from the underlying seawater. Whether either of these suppositions is reasonable is by no means clear and can be resolved only by studies of seawater and sea ice composition during autumn freeze-up.

The second possibility is the slow accumulation of atmospheric bromoform in the snowpack. Because of atmospheric "pumping", air passes freely throughout the depth of the snowpack layer [Colbeck, 1989] except where impermeable meltwater layers exist (these were not observed in our profiles). Over the course of the winter, adsorption or cold-trapping of atmospheric bromoform onto the ice surfaces might lead to a substantial accumulation within the snowpack. If the snowpack had accumulated bromoform over 6 months, and if the atmospheric burden is represented by that in Table 1, then the equivalent of the bromoform content of the lowest 400 m of the atmosphere would need to be drawn down into the snowpack just once every 2 months. This could easily be achieved even with the weak level of scavenging evident in the new and powdery snow measurements.

The apparent gradient in bromoform through the snowpack could be explained in either of the cases proposed above as a diffusion profile in the case of outgassing from the sea ice, or due to the greater age, and hence exposure time, of the lower snowpack layers in the case of wind pumping. A third intriguing possibility is that it is due to photolytic loss during the spring. Although snow is highly adsorbing at longer wavelengths, its extinction coefficient is lower in blue and UV regions. An extinction coefficient for 300 nm radiation in dry snow of 0.308 has been determined by Perovich [1993]. This implies that 300-nm UV light is attenuated 12% by 40 cm of snow. This is not sufficient to account for the observed gradients in bromoform levels, where concentrations at the surface were 51-83% less than in the lower snowpack. Nevertheless, if the difference in column amounts between the upper and lower snowpack (11.6 \mu g m^{-2} \text{from Table 1}) genuinely represented photolytic loss, then this would equate to a concentration of 28 ng Br m^{-3} in a 400-m boundary layer. Comparing this with the 5 year mean spring particulate bromine concentrations at Alert, Igloolik, and Mould Bay in the Canadian Arctic of 18, 24, and 35 ng m^{-3}, respectively [Sturges and Barrie, 1988], indicates that this would not be sufficient to sustain observed particulate bromine levels throughout the spring. It is also by no means certain that photolysis-produced reactive bromine would be transported out of the snowpack without being readsorbed. Indeed, it might be instructive to examine inorganic bromine profiles through the snowpack in this respect. The comparison does, however, suggest a possible source of "seed" amounts of reactive bromine required to initiate atmospheric catalytic halogen-ozone cycles [Fan and Jacob, 1992; McConnell et al., 1992; Tang and McConnell, 1996].

4.4. Implications for Sources of Atmospheric Bromoform

What can be gleaned from the present study about the origins of bromoform in the Arctic atmosphere? Altitudinal profiles of bromoform have clearly shown that the dominant source (or sources) are surface based and are located within the Arctic itself [Barrie et al., 1988; Leaitch et al., 1994]. This points to an origin from snow, sea ice, or open seawater.

From Cicerone et al. [1988] (allowing for the calibration correction discussed above) and from Yokouchi et al. [1996], it appears that average Arctic winter bromoform levels are about 4-5 pptv. The mean winter inversion height is about 600 m with a frequency of about \text{70\%} [Bradley et al., 1992]. Individual inversions may persist for many days, and the residence time of air in the Arctic in winter may be 2-3 weeks [Barrie and Hoff, 1985]. It therefore seems reasonable to assume that surface emissions of bromoform might be accumulated within a 600-m inversion layer for periods of about 10 days. We will further take the initial concentration in this layer to be the free tropospheric value of about 1 pptv measured by Leaitch et al. [1994]. It can then be shown that a final concentration of 4.5 pptv could be achieved in 10 days by a surface flux rate of 2.8 \mu g m^{-2} d^{-1}. This flux is 16 times greater than that suggested by the flux chamber studies of Sturges and Cota [1995] discussed earlier. This is likely a result, at least in part, of a deficiency in the use of static flux chambers in that study. Nevertheless, if the upper ice had consistently lost bromoform at a rate of 2.8 \mu g m^{-2} d^{-1} for the 6 months between initial freeze-up and the May sampling, then this would have required an initial reservoir in the upper ice of 518 \mu g m^{-2}. Orders of magnitude higher than the actual amounts measured in May. Similar arguments apply to the snowpack as a source. Of the possible sources of bromoform in snow discussed above, atmospheric drawdown involves the snow acting as a wintertime sink of bromoform rather than a source, while diffusion from the sea ice would again require a higher flux rate from the upper ice horizon. Venting of bromoform through leads, polynyas, fracture zones and transport through permeable ice remain as the more viable options, but further studies of escape rates are needed to ascertain this. With respect to the latter, it is worth noting that Gosink et al. [1976] determined sea ice to be between 104 and 105 times more permeable to gases than freshwater ice for gases such as methane, carbon dioxide and nitrous oxide.

The situation in the spring is even less clear. From Table 1 it can be seen that the reservoir of bromoform in snow and upper sea ice amounts to 41 \mu g m^{-2}, compared with 9 \mu g m^{-2} in the surface inversion layer. Given that the inversion persistence is about 5 days at this time of year (consistent with Sturges et al. [1992]), the total snow and ice reservoir could support the atmospheric column for only about 23 days, even assuming no atmospheric destruction. The snowpack and ice therefore are at best only marginally convincing as candidates for the atmospheric source. The most substantial reservoir is surface seawater, which is also constantly replenished by under-ice algal activity.

The question remains as to whether there is sufficient open water area in the spring, and a high enough flux rate, to account for the observed atmospheric levels. It also begs the question as to why a pulse of bromoform is not detected in the Arctic atmosphere during ice breakup in the summer. In part, this must be due to the simultaneous break up of surface inversion layers resulting from the release of latent heat and water vapor from the exposed ocean surface, thus mixing the released bromoform into a greater depth of the atmosphere. Atmospheric photolysis rates also reach an annual maximum at this time, and precipitation and cloud scavenging may play a part. A further contribution may be the abrupt cessation of
ice algal production as the cells are first photoinhibited by increasing light levels, followed by release out of the melting ice into the seawater, where they generally sink and become inactive or die [Horner, 1985]. Finally, it might also be considered that the emission rate of bromoform through sea ice even before ice breakup might in fact be considerably larger than is presently thought.

5. Conclusions
A number of conclusions can be drawn from this study. First, we have confirmed the importance of under-ice algae as a major source of bromoform in the lower sea ice, and to the surface waters of the Arctic Ocean. There now appears to be a high degree of closure between on-site laboratory incubation studies, in situ under-ice studies, profile measurements, and seawater measurements made by this and other groups. It is furthermore clear that the upper ocean is the principal reservoir of bromoform emissions to the Arctic atmosphere. It remains unclear, however, how this bromoform is transferred to the atmosphere, at what rate, and how this varies seasonally.

Profile measurements through the snow and ice showed little evidence of translocation of ice algal bromoform to the surface but instead showed the remarkable occurrence of large bromoform enrichments in the upper sea ice and snowpack. These features are probably unconnected with spring ice algal production and are in fact probably also unconnected with each other. The most likely origin of bromoform in the upper ice must be related to processes occurring during the preceding autumn when the ice layer formed. Whether it can be attributed to some form of biogenic activity in the ice layer or to seaventilation of seawater by rising frazil ice is unclear, but it is unlikely that any biogenic production would have taken place in the dark and extremely cold conditions during the polar night.

The high bromoform concentrations observed in the snowpack are perhaps even more puzzling. They are clearly at odds with laboratory experiments on pure ice and sulfuric acid surfaces which indicate that snow should not act as a reservoir for bromoform. That seaventilation can indeed take place is even indicated by small but significant bromoform concentrations in freshly fallen snow. The much higher levels in the older snowpack are, we believe, due to slow accumulation on to the ice crystals over the winter. Whether this bromoform originates from diffusion out of the underlying ice surface, from permeation of bromoform through the ice, from pumping of air through the snow, or some combination of these remains a mystery. The atmosphere, however, appears to be the largest and most obvious source.

To establish the exact mechanisms involved in all of these cases will require a seasonal study of the evolving profiles of bromoform, chlorophyll, and biogenic activity in the sea ice and snow cover from the time of initial ice formation through to the summer breakup.

Acknowledgments. This work was supported by grants from the National Science Foundation (DPP-9015614 and 9015661), with additional support from the U.S. Department of Energy (NIGEC-SERC 91UOT15). We thank M. Stafford and G. Dutton for technical support, and the Polar Continental Shelf Project of Energy, Mines and Resources Canada for logistical support in the Arctic. W.T.S. also acknowledges the additional support of the National Oceanic and Atmospheric Administration through their Global Climate Change Program (Atmospheric Chemistry Project), the Cooperative Institute for Research in Environmental Sciences at the University of Colorado through their Visiting Fellowship and Research Associateship programs, and the National Academy of Sciences (National Research Council Research Associateship).

References
Jobson, B. T., H. Niki, Y. Yokouchi, J. W. Bottenheim, J. F. Hopper, and R. L. Neish, Measurements of C-13-C-15 hydrocarbons during the...


W.T. Sturges, School of Environmental Sciences, University of East Anglia, Norwich NR4 7TT, England. e-mail: w.sturges@uea.ac.uk.
G.F. Cota, Center for Coastal Physical Oceanography, Old Dominion University, Norfolk VA 23529, USA. e-mail: cota@ccpo.odu.edu.
P.T. Buckley, Cooperative Institute for Research in Environmental Sciences, University of Colorado, Boulder, CO 80309, USA.

(Received February 12, 1995; revised November 18, 1996; accepted May 29, 1997.)