Methyl bromide, other brominated methanes, and methyl iodide in polar firn air

W. T. Sturges,[1] H. P. McIntyre,[1] S. A. Penkett,[1] J. Chappellaz,[2]
J.-M. Barnola,[2] R. Mulvaney,[3] E. Atlas,[4] and V. Stroud[4]

Abstract. We report measurements of brominated, bromochlorinated, and iodinated methanes in air extracted from deep firn at three polar locations (two Antarctic and one Arctic). Using a firn diffusion model, we are able to reconstruct a consistent temporal trend for methyl bromide from the two Antarctic sites. This indicates a steady increase by about 2 ppt from the midtwentieth century to 8 ppt today. The Arctic firn, however, contained extremely high levels of methyl bromide as well as numerous other organic gases, which are evidently produced in situ. The other brominated species (dibromomethane, bromochloromethane, bromodichloromethane, dibromochloromethane, and bromoform) showed little or no long-term trend in Antarctic firn and therefore are evidently of entirely natural origin in the Southern Hemisphere. A clear seasonal trend was observed in the upper firn for the shortest-lived halocarbons (notably bromoform and methyl iodide). The same species were present at lower abundance at the higher altitude and more inland Antarctic site, possibly due to their origin from more distant oceanic sources.

1. Introduction

Organic bromine gases are responsible for carrying bromine to the stratosphere where, on a per-atom basis, bromine is 50–60 times more effective in depleting ozone than chlorine [*Kurylo et al.*, 1999]. Methyl bromide (CH_3Br) is the single largest carrier of bromine to the stratosphere [*Butler*, 2000], followed by the sum of long-lived halon (bromofluorocarbon) compounds that are of entirely anthropogenic origin [*Fraser et al.*, 1999]. There is growing evidence, however, that short-lived bromoalkanes can also collectively contribute to stratospheric reactive bromine (Br_y). Aircraft measurements have shown the presence of several bromo- and bromochloro-carbons in the upper troposphere and lower stratosphere [*Schauffler et al.*, 1999; 1998; 1993; *Wamsley et al.*, 1998]. *Dvortsov et al.* [1999] singled out bromoform as a hypothetical "missing" precursor of stratospheric bromine, while *Sturges et al.* [2000] showed evidence for its presence in the stratosphere from balloon samples. The latter authors attributed 65% of Br_y in the lowermost extratropical stratosphere (mean age of air <1 yr) to CH_3Br, 15% to halons, and 20% to the short-lived bromo and bromochlorocarbons also reported in this paper. It has, further, been suggested that some bromine (perhaps 10% of the stratospheric budget) may enter the stratosphere in the form of Br_y, and this is likely to have originated from tropospheric breakdown of the same short-lived organic precursors [*Dvortsov et al.*, 1999; *Pfeilsticker et al.*, 2000].

There has also been recent interest in the possible influence of iodine on ozone in the upper troposphere and lower stratosphere. The present consensus is that the effect is unlikely to be significant [*Ravishankara et al.*, 1999], although it has been suggested that enhancement of ClO by cirrus clouds might boost the efficiency of ozone removal by iodine [*Solomon et al.*, 1997]. Iodocarbons have, however, been directly implicated in destruction of ozone in the marine boundary layer through production of IO radicals, which have themselves been positively identified in the boundary layer [*Alicke et al.*, 1999; *Carpenter et al.*, 1999; *Stutz et al.*, 1999].

Whereas the origins and recent trends of the halons are now well established [*Fraser et al.*, 1999], the same is not true of the other bromocarbons, nor of methyl iodide. There has been particular attention given to CH_3Br, which is known to have both anthropogenic and natural origins, although the relative contributions of each are still poorly constrained. The only direct measurements of the long-term trends of CH_3Br are those of *Khalil et al.* [1993] which showed a latitudinally weighted global increase of 0.15±0.08 ppt yr^{-1} between 1983 and 1992. No direct long-term records are available for the other compounds reported here. Reconstructed trends of CH_3Br from Antarctic firn have been published by *Butler et al.* [1999] from two locations (South Pole and Siple Dome) which suggest a rate of growth increasing from about 0.01 ppt yr^{-1} in the early 1900's to 0.05–0.06 ppt yr^{-1} during the 1970's and 1980's. None of the other bromo or iodocarbons reported here were measured in the *Butler et al.* study. A concern in their paper was the observation of very large increases in CH_3Br at their third, Northern Hemispheric (NH) site (Tunu, Greenland). This was clearly not an atmospheric signal, and cast some doubt on the validity of the Antarctic records as a true representation of past atmospheric composition.

In this work we have examined firn air from two further Antarctic drilling sites in Dronning Maud Land (DML) and on Dome Concordia (Dome C), and at one Arctic site (Devon Island, Canada) to compare the reconstructed CH_3Br trends with those of the earlier *Butler et al.* [1999] study. We have also examined trends of a more extensive suite of short-lived bromo, bromo-

[1]School of Environmental Sciences, University of East Anglia, Norwich, England, United Kingdom.
[2]Laboratoire de Glaciologie et Geophysique de l'Environnement, CNRS, Saint Martin d'Heres Cedex, France.
[3]British Antarctic Survey, Natural Environment Research Council, Cambridge, England, UK.
[4]Atmospheric Chemistry Division, National Center for Atmospheric Research, Boulder, Colorado.

Table 1. Characteristics of the Arctic and Antarctic Firn Drilling and Extraction Sites

Site	Date	Latitude, Longitude	Elevation, m	Mean Annual Temperature, °C	Transition depth, m	Snow Accumulation Rate, cm water equivalent yr^{-1}
Devon Island, Canada	April 1998	75°N, 82°W	1800	-23	59	30
Dronning Maud Land (DML), Antarctica	January 1998	77°S, 10°W	2300	-35	73.5	10
Dome Concordia (Dome C), Antarctica	December 1998 to January 1999	75°S, 123°E	3240	-53	99.6	3

chloro, and iodocarbons not previously reported. We have given further consideration to the issue of possible "artefact" effects on the reconstructed atmospheric trends of CH$_3$Br. All of the compounds reported here were indeed clearly affected by in situ processes at Devon Island, so we will concentrate primarily on results from the two Antarctic sites. Measurements at Devon Island are used in an attempt to constrain the possible artefact in the Antarctic records.

2. Sampling and Analysis

2.1. Firn Air Sampling

Firn air was sampled at three locations, as detailed in Table 1. Firn air was extracted by pumping on a sealed borehole, using a modified version of the firn extraction equipment described by *Schwander et al.* [1993]. The main modifications were as follows. The lower plate was reengineered to incorporate two closely spaced circular baffle plates, slightly smaller than the core hole diameter. Sampling tubes were swaged directly on to the end plate to reduce leakage. These tubes were continuous lengths (no intermediate connections) of up to 110 m connecting the bottom of the core hole with the surface pumping system. The bottom sensor switch was not incorporated in to this design, to minimize contamination. The seal was either a 5 m long sleeve of synthetic latex (DML and Devon Island) or a 3 m long sleeve of natural latex (Dome C). The sample lines were either 3/8 inch ID PFA (DML and Dome C) or 1/4 inch ID Dekabon polyethylene laminated tubing (Devon Island). A 1/4 inch ID nylon tube was connected through the top plate of the assembly to inflate the sleeve and so seal the bottom of the core hole.

The pumping system comprised a metal bellows pump (Metal Bellows Corporation) for sample collection and seal inflation, and a piston compressor (RIX Industries) used both for "waste" flow and for filling high-pressure. The compressor pulled air from the upper "chamber" between the lower end plate and upper baffle, and flushed any trace contaminants coming from the sleeve, or from leakage around the seal, away to waste. The "clean" sample line penetrated the upper baffle and pulled air from the lower chamber. This double-pumping arrangement was first used by M. Bender, Princeton University, to whom we are indebted for the idea.

A nondispersive infrared analyser (LI-COR) continuously monitored CO$_2$ concentrations in the sample line, and samples were not collected until a low, stable CO$_2$ reading was obtained. This indicated that "old" firn air, uncontaminated by contemporary air, was being extracted from the core hole. At this stage a suite of flasks of various types, for use in both this and other parallel studies, were filled to pressures of about 3 bar. In this study, the containers used consisted of 3 and 6 L fused-silica lined stainless steel (Restek "SilcoCans"), 3 L electropolished stainless

steel (Meriter canisters), 2 L custom-made electropolished canisters from the Max Plank Institute (MPI) in Mainz, and similar custom-made canisters from the National Center for Atmospheric Research (NCAR) in Boulder. The SilcoCans, Meriters, and MPI canisters were flushed three times using pressure from the metal bellows pump and vacuum from a diaphragm pump, before the final filling. The SilcoCans and Meriters had been previously cleaned by repeated evacuation and flushing with clean nitrogen at 180°C, conditioned by filling with humid marine air at a rural coastal location, and shipped pressurized with clean nitrogen. The NCAR flasks were similarly cleaned and shipped with humidified nitrogen. During sampling, the NCAR flasks were pumped out only once before filling, to preserve some moisture in the sample, and a subsequent dilution correction was made.

2.2. GC-MS Analysis

The majority of the measurements reported in this paper were made at the University of East Anglia (UEA) using a Micromass Autospec gas chromatograph - trisector mass spectrometer (GC-MS) combination. Details of analytical techniques are given more fully elsewhere [e.g., *Fraser et al.*, 1999; *Oram et al.*, 1995]. In brief, 400 mL aliquots of air from the samples were cryogenically focused using liquid argon, then desorbed and separated on a DB-5 capillary column. Compounds eluting from the column were subject to electron impact ionization and mass separation in single ion mode. Detection limits were around 0.001 ppt. Instrumental drift correction was made by alternating sample analyses with aliquots from a high-pressure cylinder filled with dried air from Niwot Ridge, Colorado.

Measurements at NCAR were made with a GC-quadrupole MS system. The analytical and calibration techniques are described fully by *Schauffler et al.* [1999].

The Niwot Ridge air had been calibrated for the compounds of interest and was used to determine concentrations in the firn air samples analyzed at UEA. The calibrations derive from various sources. The CFC-12 and CH$_3$Br calibrations come from the National Oceanic and Atmospheric Administration-Climate Monitoring and Diagnostics Laboratory (NOAA-CMDL) scale, based on gravimetric gaseous standard preparation. CHBr$_3$, CH$_2$Br$_2$, CHClBr$_2$, and CH$_3$I were cross-referenced to a separate Niwot Ridge air standard. The latter was calibrated at UEA using a technique involving the evaporation of methanolic solutions of the compounds of interest into a helium sweep gas, and analyzed with a quadrupole GC-MS system [*Carpenter et al.*, 1999]. Calibrations for the other compounds were calculated from relative peak areas. A comparison of nine firn air samples from a range of depths at DML (20 to 73.5 m) analyzed at both UEA and at NCAR, on their respective instrumentation and concentration scales, gave average ratios [UEA:NCAR] of 0.98 for CH$_3$Br, 0.70 for CH$_2$BrCl, 0.79 for CH$_2$Br$_2$, 1.15 for CHBr$_2$Cl, 1.23 for CHBr$_3$,

and 2.09 for CH_3I. No comparison data were obtained for $CHBrCl_2$. Given the difficulty of preparing standards of these relatively reactive, low-volatility compounds with high affinities for surfaces, we consider these comparisons to show very good agreement (except for CH_3I). In this paper we will reference all quoted concentrations to the UEA "scale." These are then compatible with boundary layer, free tropospheric, and stratospheric measurements reported previously by the UEA group [e.g., *Carpenter et al.*, 1999; *Pfeilsticker et al.*, 2000; *Sturges et al.*, 2000; *Sturges et al.*, 1999]. The above conversion factors can be used to compare the measurements with tropospheric and stratospheric measurements reported by the NCAR group [e.g., *Schauffler et al.*, 1999; 1998; 1993].

2.3. Sample Stability

Stability of gases in the sample containers was investigated in a number of ways. At DML, three different types of containers (SilcoCans, MPI, and NCAR canisters) were used to collect firn air, while at Devon Island, SilcoCans, Meriters, and NCAR canisters were used. There was no evidence of either systematic losses or gains for one type of container compared with another (see Results). Moreover, pairs of samples collected sequentially at four different firn depths at DML (5, 67, 70, and 73.5 m) showed no, or barely significant, mean differences above the 1-sigma combined standard deviations of the means (Figure 1a). These differences could also have arisen from small differences in the original sample collected, rather than storage effects.

Storage tests were also conducted on individual samples in SilcoCans as shown in Figures 1b-1e. These comprised two firn air samples from different depths (40 and 90 m) at DML, analyzed 3 and 6 months after collection, and two aliquots of the Niwot Ridge standard air (which had been chemically dried during collection) analyzed within a few days and again after 6 months. Sample pressures were all below 3 bar. There were almost no consistent changes during storage that were significant above the accumulated analytical uncertainty, except for $CHBr_3$ and CH_3I. The latter compounds showed significant losses of, at worst, 7% for both the firn air and ambient air samples (we believe the "growth" of CH_3I in the firn air to be unrepresentative due to the very low concentrations and low precisions for these samples).

2.4. Firn Modeling

To interpret firn air profiles in terms of historical concentration trends in the atmosphere, it is necessary to account for gravitational settling and diffusion rates of individual compounds. To do this, a diffusion model was employed [*Rommelaere et al.*, 1997]. The model was run in the forward (direct) mode; that is, hypothetical scenarios were entered into the model yielding depth profiles for comparison with actual measured profiles. The model requires, amongst other parameters, knowledge of the firn tortuosity profile for each site, and this was determined by inverse modeling of the CO_2 profiles [*Fabre et al.*, 2000]. Diffusion coefficients of other molecules relative to CO_2 were estimated from Le Bas molecular volumes [*Fuller et al.*, 1966]. No thermal fractionation effects were included in this model.

3. Results

3.1. Arctic Firn Air Results

As mentioned earlier, all of the halocarbons reported here (other than CFC-12) showed anomalous profiles at the Arctic site (Devon Island). It was therefore not possible to derive any realis-
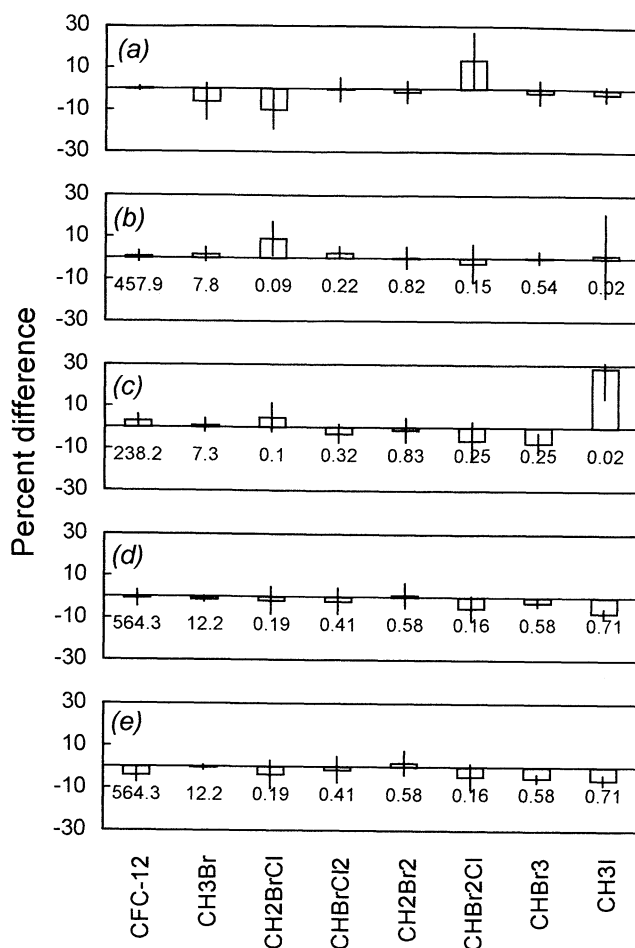

Figure 1. Various tests of compound stability in sample containers: (a) mean difference between 3 L SilcoCans and 3 L MPI canisters cocollected at four different depths at DML; change in concentration after 3 months storage of firn air collected in 3 L SilcoCans from (b) 40 m and (c) 90 m at DML; and (d) and (e) change in concentration after 6 months storage of dried ambient air in two identical 1 L SilcoCans. Bars represent the percentage change in concentration, with the initial concentration (in ppt) shown below (not in Figure 1a), which was for a range of concentrations). Error bars are the combined standard deviations of the means in Figure 1a, and combined analytical uncertainties (1-σ) of the initial and final measurements in Figures 1b–1e.

tic temporal trends from these data and, as a consequence, we are unable to provide any information on their past concentrations in the NH. We will, therefore, consider the Devon Island profiles first, and then consider the Antarctic data separately and by individual halocarbon species.

The profile of CFC-12 at Devon Island (Figure 2) showed concentrations declining with depth to a minimum of 14 ppt near the close-off zone. Production of CFC-12 is known to have begun in the early 1930s [*Kaye et al.*, 1994]. Ambient air records in the Southern Hemisphere (SH) show CFC-12 concentrations of about 240 ppt in 1977, when records first began [*Kaye et al.*, 1994]. Clearly, the CFC-12 concentrations in the firn predate this CFC-12 concentration at the lower depths, but neither do they fall to zero. The oldest air therefore has a mean age between these two extremes (1930 and 1977). It is not strictly correct, however, to compare ages derived from CFC-12 with those of other molecules
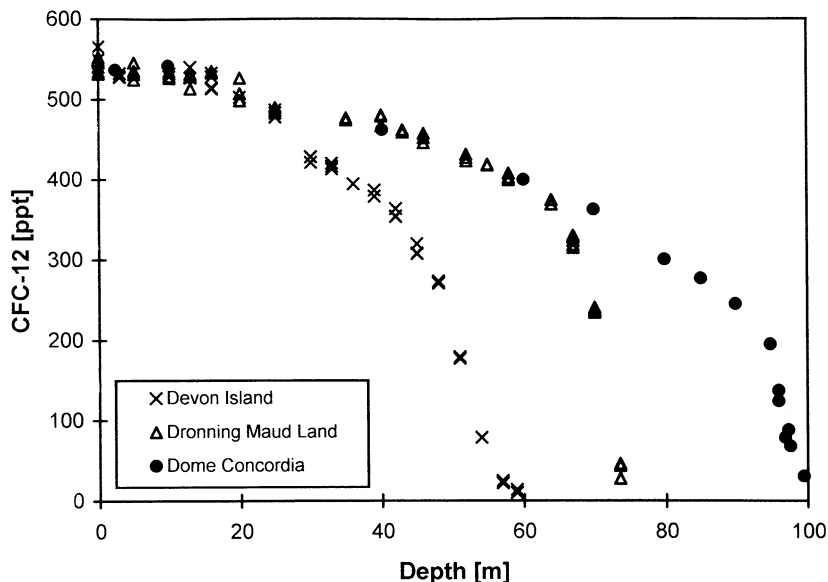
Figure 2. Depth profiles of CFC-12 in firn air at the three sampling locations.

since diffusion rates will differ between compounds depending on their firn air diffusion coefficients (generally taken as identical to the free air diffusion coefficient) and the concentration gradients within the firn. For this reason, a firn air diffusion model is required to interpret profiles in terms of reconstructed histories.

In strong contrast to the Antarctic sites (discussed later) Devon Island showed an almost exponential increase in CH₃Br concentration with depth (Figure 3, main panel). In the figure it can be seen that there was a divergence between the UEA and NCAR analyses at higher concentrations, which might have been due to a nonlinear instrumental response at these concentrations, being far beyond the normal calibrated range. At concentrations of less

than about 100 ppt of CH₃Br, however, there was excellent agreement between the two sets of analyses, and generally good agreement was observed between the three different sampling media. Near the close-off zone, CH₃Br exceeded 300 ppt, which is around 25 times the NH background ambient air concentration.

Many other species also increased similarly with depth. CH₃I near close-off was more than 200 times larger than the surface ambient air concentrations. In the inset to Figure 3 we have plotted correlations between CH₃Br and other halocarbons at Devon Island (except for CH₂BrCl which gave scattered results and was not at all correlated to CH₃Br). The strongest correlation was with CH₃I, yielding a remarkable r^2 linear correlation coefficient of
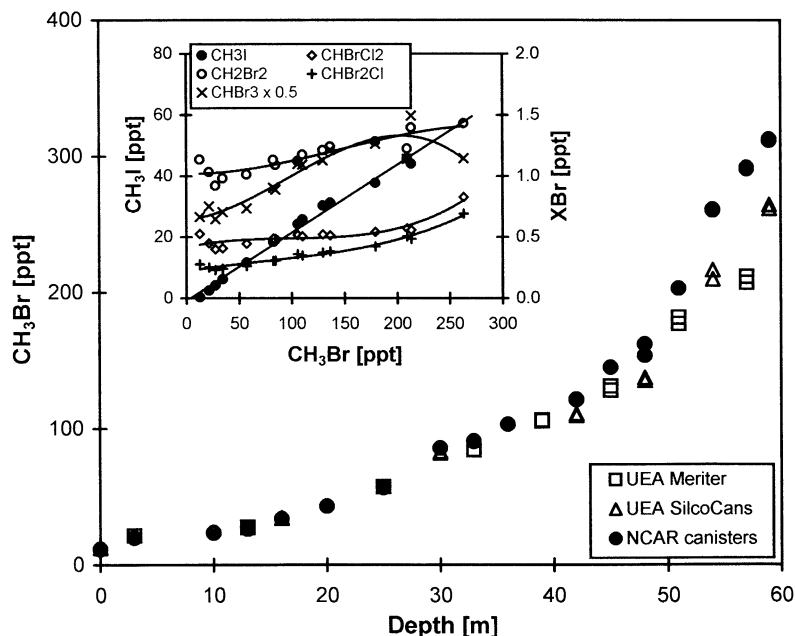

Figure 3. CH₃Br at Devon Island as a function of depth (UEA and NCAR data) and (inset) correlations between CH₃Br and other key halocarbons (UEA data only). The straight line through the CH₃Br and CH₃I data in the inset is a linear regression; the other curved lines are polynomial best fits.
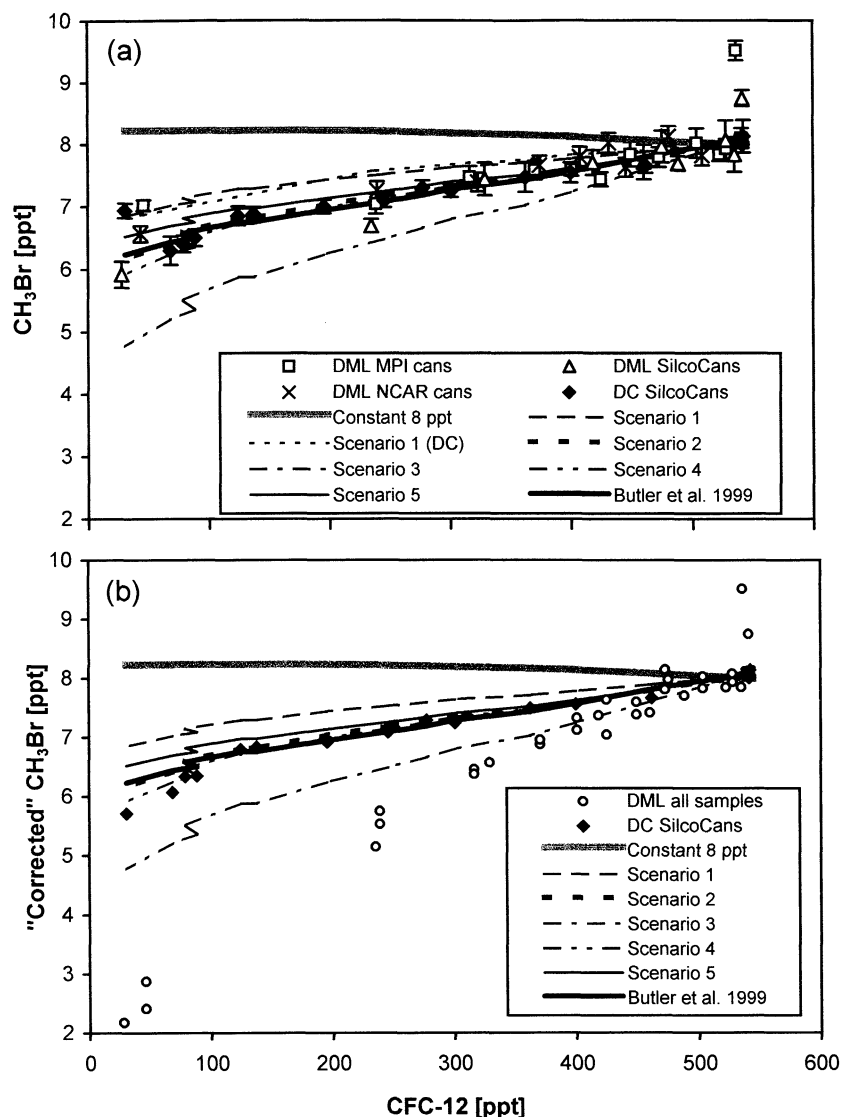
Figure 4. (a) Profiles of CH₃Br versus CFC-12 for the two Antarctic locations. Measurements are shown as symbols, with error bars being the accumulated 1-sigma analytical error limits. The lines are the firn diffusion model-predicted profiles based on a number of assumed atmospheric scenarios shown in Figure 5 and described in the text. (b) Same as Figure 4a, except that an attempt has been made to correct the CH₃Br concentrations for an hypothetical in situ production artefact based on CH₃I measurements (see text). In the latter panel all of the samples shown in Figure 4a have for simplicity been divided into DML and Dome C samples.

0.992. This clearly indicates a common origin of these compounds in the firn. The other brominated compounds showed much weaker correlations, but all displayed generally increased levels with depth. It is not clear whether the growth of these compounds is directly related to the apparent CH₃Br and CH₃I production.

Increased CH₃Br has been noted at other firn sampling sites by other workers and also by ourselves. At Tunu, Greenland (2400 m above sea level (asl), -29°C annual mean temperature), CH₃Br reached 48 ppt near close-off [*Butler et al.*, 1999]. We have measured (unpublished data, 1996) maximum CH₃Br levels of 103 ppt at 45 m in firn at Col du Dome, France (Mont Blanc; 4300 m asl, -11°C annual mean temperature). We furthermore noted a linear correlation between CH₃Br and CH₃I at Col du Dome.

CH₃Br at Devon Island was also strongly correlated with CH₃Cl, C₂H₅Br, CH₂ClI, CH₃ONO₂, C₂H₅ONO₂, CH₃CHO (acetaldehyde), CH₃COCH₃ (acetone), and C₂H₅COCH₃ (2-butanone), amongst other species (unpublished data, 1998). We speculate that these might arise from biological processes. Halocarbon production by microalgae has been observed in both Arctic and Antarctic sea ice [e.g., *Sturges et al.*, 1992; 1993]. We would not, however, expect any significant biological activity at such depths in the firn. Perhaps more salient is an observation of abiotic production of partially oxidized volatile organic carbons, including acetone, from degradation of organic matter [*Warneke et al.*, 1999]. It is noted that the Arctic is surrounded by, and partly encompasses, vegetated continental areas that must provide a strong source of organic particulate matter to the Arctic ice caps. In contrast, the Antarctic is very remote from any vegetated areas. It

would be instructive to compare dissolved and particulate organic matter in firn cores from the different locations.

3.2. Antarctic Firn Air Results

3.2.1. CFC-12.
CFC-12 profiles for the Antarctic sites are shown in Figure 2 for comparison with the Devon Island profile. The difference in depth profiles is due to different mean temperatures, accumulation rates, and tortuosity profiles between sites. Minimum CFC-12 concentrations were similar at all locations, indicating that the atmospheric records from all three sites cover approximately the same time period. An effort was made at Dome C to collect firn air samples at closely spaced depths (every 1 to 2 m) near the bottom of the hole, to provide better time resolution over the earlier part of the record than had been possible at DML.

3.2.2. Methyl Bromide.
Results of methyl bromide analyses in firn air at both Antarctic sampling locations are shown in Figure 4a. In this figure, CFC-12 has been used as the abscissa instead of depth. This is because the change in mean age of the firn air becomes increasingly compressed approaching pore close-off [*Schwander et al.*, 1993]. CFC-12 can be used to set an x axis that is more nearly linear with time.

At both sites the concentration of CH_3Br declined from about 8 ppt at the surface to between 6 and 7 ppt at the greatest depths (i.e., lowest CFC-12). At DML the measurements were rather more scattered, and the trend less well defined below CFC-12 concentrations of 240 ppt due to the sparcity of samples covering this concentration range. Concentrations of CH_3Br in the two ambient air samples at DML (8.8 and 9.5 ppt, respectively) were significantly higher than in the firn. It should be noted, however, that these were "grab" samples reflecting instantaneous concentrations, whereas the firn samples represent time-integrated averages [*Schwander et al.*, 1993]. Furthermore the same effect was not observed at Dome C. At the very bottom of the borehole an upturn in concentration was noted at both Dome C and DML. A number of other compounds, such as HCFC-141b also showed marked increases, but less so CFC-12 which argues against a leak

of contemporary air past the firn seal. It is noted, however, that backpressure in the sampling train was very high in these samples as the open porosity in the firn declined to almost zero. These higher concentrations may therefore arise from some desorption effect from the pumping system itself. For the remainder of the samples there was a very high level of agreement both between the two sampling sites, and between different sample containers.

Also shown in Figure 4a are lines representing firn diffusion modeling of various hypothetical atmospheric scenarios. These scenarios are shown in Figure 5. In Figure 5 the only published long-term time trend of CH_3Br in the SH has also been plotted (from Cape Grim, Tasmania [*Khalil et al.*, 1993]). This forms an additional constraint on the trend between 1983 and 1992. For the hypothetical trends the year 1940 has been taken as a benchmark; this marks the first known commercial organobromine usage (1,2-dibromoethane as a lead scavenger in leaded petrol additives [*Thomas et al.*, 1997]). The first three scenarios (scenarios 1 to 3) bracket the *Khalil et al.* [1993] trend with linear increases to a 1998 concentration of 8 ppt starting at 1940 baselines of 3, 5, and 6 ppt, respectively. Two variations on these tends are shown as sensitivity studies. Scenario 4 is the same as scenario 2 from 1940 but starts at a lower value of 3 ppt in 1900. Scenario 5 is the same as scenario 2 from 1960 but remains constant at 6 ppt before this date. Finally, a published "best fit" time trend to CH_3Br firn air data from two other Antarctic locations (Siple Dome and South Pole) is shown [*Butler et al.*, 1999; M. Battle, personal communication, 2000]. This trend was extrapolated from 1996 to 1999 using a linear fit to the preceding 5 years. This resulted in a small mismatch with our mean near-surface firn concentrations in 1998 and 1999 (8.4 ppt to our measured 8.1 ppt). For consistency with our data, we have reduced the *Butler et al.* [1999] trend by this ratio. No seasonality of CH_3Br, consistent with *Wingenter et al.* [1998], was assumed in the firn modeling.

The resulting model-predicted depth profiles were scaled to CFC-12 and plotted in Figure 4a. For clarity, the full suite of model runs have only been shown for conditions representative of
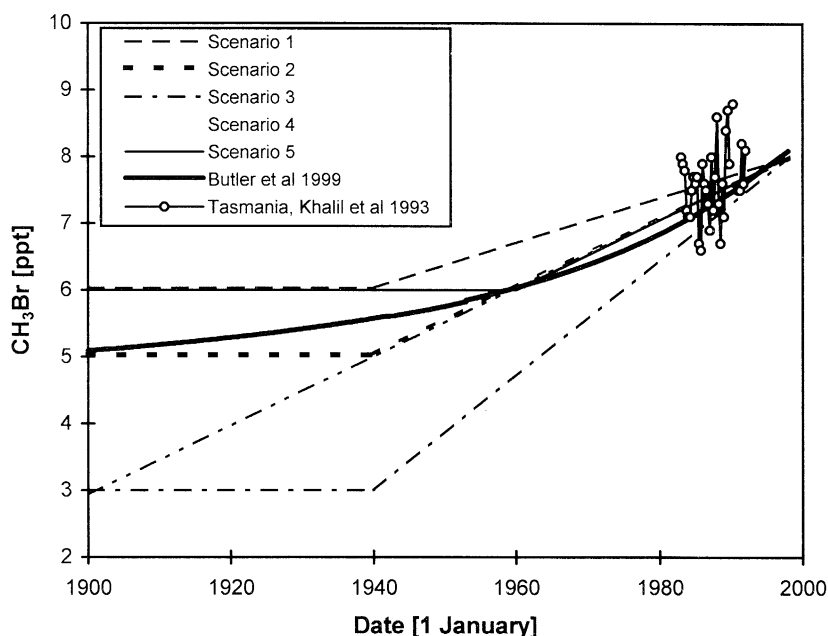

Figure 5. Various Southern Hemispheric (SH) time trend scenarios (lines) assumed for CH_3Br in the firn model (including the previously reported reconstruction of *Butler et al.* [1999]), compared with the SH measurements of *Khalil et al.* [1993] (symbols).
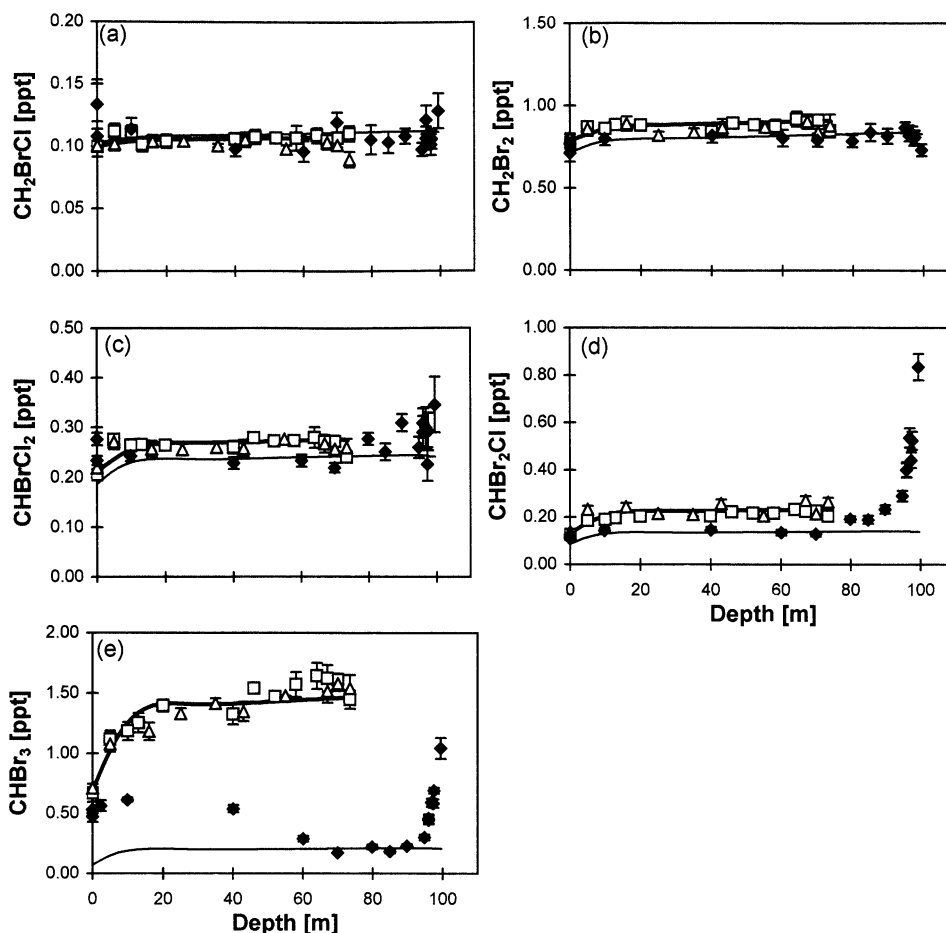
Figure 6. Depth profiles of short-lived bromomethanes (other than CH_3Br) at DML and Dome C. Symbols are the same as in the legend to Figure 4a. The lines depict the firn diffusion model results (thick line for DML, thin line for Dome C) based on hypothetical time series comprising constant annual average values from 1930 to the present, modulated by a seasonal cycle (see text for explanation). The error bars on the symbols are the 1-sigma accumulated analytical error limits.

the Dome C site. The model run of scenario 1 for DML conditions has, however, also been plotted, and illustrates that the model runs were almost identical between the two sites when normalized to CFC-12. In addition to the above scenarios, a model run in which CH_3Br was held constant at 8 ppt has also been plotted. This latter line shows the increase in concentration expected with depth arising solely from gravitational fractionation of gases according to their molecular weights.

Of the various scenarios modeled, scenarios 1 and 3 appeared to significantly over and under predict the observed concentrations, respectively. All of the other scenarios gave very similar depth profiles, and all fitted the observations quite well. They cannot confidently be distinguished, and this includes the previously published reconstructed trend of *Butler et al.* [1999]. It is notable that scenarios 2 and 4 gave almost identical modeled profiles, from which it can be deduced that the modeling is relatively insensitive to the trend before 1940, effectively establishing a limit to the time period represented by the firn data for CH_3Br. Clearly, any number of different scenarios could be constructed that would more-or-less well fit the observations. Given the constraints of the ambient air trend [*Khalil et al.*, 1993], however, we can at least conclude that CH_3Br has risen by about 2 ppt, at a relatively steady rate, since about the 1940's.

The issue remains as to whether some in situ production of CH_3Br might have occurred even in the Antarctic firn profiles. We will return to this in the Discussion section.

3.2.3. Other Bromomethanes. Depth profiles of the bromomethanes other than methyl bromide are shown in Figures 6a-6e for the two Antarctic sites. For these compounds a simple depth scale has been used, instead of plotting the concentrations against those of CFC-12 as was done in the case of CH_3Br above. This is, as will become evident, because effects within the firn such as seasonality and in situ production close to the close-off zone are important, whereas no long-term trend was detected for any of these gases.

All of the bromomethanes plotted in Figure 6 are relatively short-lived in the troposphere, and indeed are shorter-lived than the "best estimate" of the methyl bromide lifetime (see Table 2) given by *Kurylo et al.* [1999]. From the same table it is seen that loss by reaction with hydroxyl radical (OH) is important for all of these compounds, with photolysis also important for $CHBr_2Cl$ and $CHBr_3$. These gases are therefore expected to exhibit some degree of seasonality in the atmosphere due to the higher solar flux and greater OH abundance in the summer.

There are, unfortunately, no year-round ambient air measurements of such compounds in the Antarctic, and almost no

Table 2. Approximate Globally and Seasonally Averaged Tropospheric Lifetimes (Adapted From *Kurylo et al.* [1999]) in Days

Compound	τ_{OH}	$\tau_{h\upsilon}$	τ_{atmos}
CH_3Br			117–475[a]
CH_2BrCl	150[b]	15000[c]	149[d]
CH_2Br_2	130[b]	5000[c]	127[d]
$CHBrCl_2$	120[b,e]	222[c]	78[d]
$CHBr_2Cl$	120[b,e]	161[c]	69[d]
$CHBr_3$	100[b]	36[c]	26[d]
CH_3I		4[f]	4[d]

[a]Range of estimates; "best" estimate given as 256 days.
[b]Calculated for $T = 275$ K and $[OH] = 1 \times 10^6$ molecules cm^{-3}.
[c]Globally and seasonally averaged J value estimated for 5 km.
[d]From $1/\tau_{atmos} = 1/\tau_{OH} + 1/\tau_{h\upsilon}$.
[e]Estimated T dependence of [OH] rate [*Kurylo et al.*, 1999].
[f]Surface value; 1.5 days at 10 km.

measurements at all of these species in the Antarctic interior, from which we might judge the likely nature of this seasonality. Clear seasonal cycles have, however, been reported from the Arctic at Alert, Canada [*Yokouchi et al.*, 1996] for a range of short-lived halocarbons, including three of the bromomethanes reported here: CH_2BrCl, $CHBr_2Cl$, and $CHBr_3$. All of the gases studied showed a summer minimum and winter maximum, with the amplitude increasing according to their relative OH-lifetimes. Ratios between the means of the 3 winter months to the means of the 3 summer months ranged from just 1.1 for CH_2BrCl to 59 for trichloroethylene (C_2HCl_3). Although not directly analogous to the halocarbons, strong seasonal cycles of nonmethane hydrocarbons have been reported for the Antarctic. Ethane and propane both showed pronounced seasonal cycles (summer minimum, winter maximum) over 6 years of observations at Scott Base, Antarctica [*Clarkson et al.*, 1997], with July:January ratios of 1.8 for ethane (global average OH-lifetime of about 2 months), and 2.4 for propane (global average OH-lifetime of about 2 weeks). Similar seasonalities in ethane and propane measurements were also observed at Neuymayer; another Antarctic coastal location [*Rudolph et al.*, 1992]. In the latter study, an even larger seasonal cycle was observed for acetylene (amplitude of 4.7), although the OH-lifetime of this molecule is intermediate between ethane and propane. Although the sources of NMHCs are likely to be different to those of the halocarbons, there is, overall, ample reason from the above to also expect a seasonality in the short-lived halocarbons.

We have used the firn diffusion model here to test the hypothesis that there have been both no long-term trends of these gases in the atmosphere over the last several decades and, further, that there have been no in situ effects either producing or removing halocarbons in the firn column. To do this, we have input into the direct model a constant annual average concentration from 1930 up to the date of sampling, and this has been modulated by a sinusoidal seasonal cycle with a winter (July) maximum and summer (January) minimum. In practice, we modulated the annual mean only for dates from 1970 to the present since annual variations are rapidly smoothed out with depth in the firn [*Schwander et al.*, 1993] and an oscillating time series causes spurious effects in the model output close to firn close-off. A 1 month time step was used for the input time series.

A "best estimate" of the annual average concentration was taken as the mean of the firn air measurements over a certain

depth range in the firn profile. The range taken was below the uppermost layers, where convection and seasonal effects can be significant, but above the deeper layers where gravitational fractionation of the gases becomes more significant, and also where evidence for in situ production of gases was noted in some cases. At DML the depth range used was 13 to 46 m, which encompassed eight samples. The smaller number of samples in the upper firn at Dome C meant that a larger depth range of 10 to 70 m was taken to include four samples. With one notable exception, the concentrations of the gases were almost constant over these depth ranges at each site, giving us confidence that they were relatively free of in situ effects, and therefore representative of the long-term mean average ambient air concentrations. Owing to the diffusive nature of the transport of gases through the firn, each sample measurement itself represents an integrated concentration over several years [*Schwander et al.*, 1993]. The one aforementioned exception to the observed consistency of concentrations in the upper half of the firn was seen in the $CHBr_3$ measurements at Dome C. This showed a marked increase toward the surface. In this case we instead took the mean of the measured concentrations between 70 and 90 m (four samples).

As will be demonstrated below, plausible evidence for a seasonal concentration cycle was discerned in the upper 20 m of firn at DML, most notably for $CHBr_3$ and (as discussed in the next section) CH_3I. We therefore estimated the seasonal cycles at DML from the difference between the surface air measurements (taken as representative of minimum summertime concentrations) and the above long-term annual mean concentrations. The July:January ratio was taken as twice this value. A similar seasonality was not always evident in the upper firn at Dome C. For consistency and for comparison purposes, however, we have included the same relative seasonal amplitude in modeling the Dome C profiles. The lines plotted in Figure 6 are thus the output from the firn model for the two drilling sites using the above time series, the parameters for which are summarized in Table 3. These will now be discussed individually by compound.

Bromochloromethane (CH_2BrCl) is the most long-lived of the organobromines reported in this section (see Table 2). The results, plotted in Figure 6a, showed little evidence for a seasonal cycle, nor of any significant difference between the two sampling sites. This lack of apparent seasonality is consistent with the findings of *Yokouchi et al.* [1996] (see above) for this compound at Alert. The data agree well with the firn diffusion model results for seasonally modulated but constant annual mean concentrations (thick and thin lines for DML and Dome C, respectively), from which we can assert that there has been no significant long-term change in CH_2BrCl concentrations in the Antarctic atmosphere since the first half of the twentieth century. This molecule appears

Table 3. Mean Annual Concentrations and Seasonal Amplitudes (Ratio of July to January at DML) Used as Input Scenarios for the Firn Model Runs Shown in Figures 6 and 7

Compound (X)	$[X]_{DML}$, ppt	$[X]_{Dome\ C}$, ppt	$[X]_{Jul}/[X]_{Jan}$ (DML)
CH_2BrCl	0.10	0.11	1.1
CH_2Br_2	0.86	0.80	1.2
$CHBrCl_2$	0.26	0.23	1.5
$CHBr_2Cl$	0.20	0.14	2.3
$CHBr_3$	1.35	0.20	2.9
CH_3I	0.63	0.02	8.6

therefore to be of entirely natural origin, at least in the SH. Given the relatively long lifetime of this molecule (about 6 months), it might be assumed that there has been no large change in NH concentrations either, and again that the sources are therefore predominantly natural.

Dibromomethane (CH_2Br_2) is believed to have a somewhat shorter tropospheric lifetime than CH_2BrCl (Table 2). This is apparently confirmed here by the lower concentrations observed at the higher altitude and more inland Dome C site than at DML (Figure 6b). There is some evidence for a downturn in concentrations at the surface at both sites that may be related to lower summertime concentrations. We conclude that, like CH_2BrCl, CH_2Br_2 has exhibited essentially invariant concentrations in the SH since the 1930s and is also therefore of entirely natural origin in the SH. The reason for the low concentration in the deepest sample at Dome C is unknown, but it is unlikely to be due to any actual change in atmospheric levels since this would require a relatively sudden step change in emission or loss rates and, furthermore, no such change was seen at DML.

Figure 6c shows the profiles of bromodichloromethane ($CHBrCl_2$) in Antarctic firn. The difference between the average levels at the two sites is more evident again than in the case of CH_2Br_2 (above), consistent with its shorter atmospheric lifetime (Table 2). We therefore might expect it to have a larger seasonal amplitude. This seems to be supported by a low surface concentration at DML, but the same is not true at Dome C, where the results are quite scattered. In general, the scatter of data at Dome C appears larger than at DML, suggesting some possible degree of random contamination in the former.

The difference in mean $CHBr_2Cl$ concentrations between sampling sites was larger again (Figure 6d) than for the above gases; again continuing the trend with expected atmospheric lifetime. Measurements at both sites are seen to be consistent with the modeled seasonal modulation in the uppermost firn. The seasonal amplitude used in the firn model (2.3 from Table 3) is remarkably similar to the winter:summer ratio of 2.1 quoted by *Yokouchi et al.* [1996] for the same compound measured at Alert. It is also comparable with the seasonal amplitude of ethane (July:January ratio of 1.8) measured at Scott Base, Antarctica [*Clarkson et al.*, 1997], as discussed above. Ethane has a similar atmospheric lifetime to $CHBr_2Cl$. A surprising finding was the rapidly increasing concentration of $CHBr_2Cl$ below 80 m at Dome C. The same effect was not observed at DML. Furthermore, the concentrations below 90 m at Dome C exceeded those observed at DML, whereas the reverse is true in the upper firn. Clearly, this upturn at Dome C cannot be related to actual changes in ambient atmospheric concentrations, but rather to some process within the firn itself.

Bromoform (tribromomethane, $CHBr_3$) in firn presents a yet more complicated picture (Figure 6e). The DML profile displayed an apparent clear seasonal influence in the upper 20 m of the firn, which was closely tracked by the firn model output. The seasonal amplitude derived from the DML results and used in the firn model was 2.9. This, again, is quite consistent with the observations by *Yokouchi et al.* [1996] at Alert, Canada, who reported a winter:summer ratio of 3.6 for the same compound, and is also consistent with long-term measurements of $CHBr_3$ at Barrow, Alaska [*Cicerone et al.*, 1988], which showed a factor of about 3 between winter and summer concentrations. It is slightly higher than the measured seasonal amplitude of propane at Antarctic coastal locations of 2.4 for Scott Base [*Clarkson et al.*, 1997], and 1.6 for Neumayer [*Rudolph et al.*, 1992], but is smaller than the

seasonal amplitude of 4.7 measured for acetylene in the latter study.

In general, the firn model described the $CHBr_3$ profile at DML well, although the measured concentrations were slightly higher below 60 m than predicted. It cannot be determined whether this reflects some genuine change in atmospheric concentrations or is due to an in situ effect.

The $CHBr_3$ profile at Dome C was, in contrast, entirely in disagreement with the predicted profile from the firn model. As with $CHBr_2Cl$, there was a sharp upturn in $CHBr_3$ below 90 m at Dome C, and again this was not in evidence at DML. Unlike $CHBr_2Cl$, however, the levels of $CHBr_3$ in firn at Dome C did not at any point exceed those observed at DML. Nevertheless, the strong correlation between $CHBr_2Cl$ and $CHBr_3$ at depth at Dome C leads us to suspect that this is due to some common in situ process. Concentrations in the upper 40 m were also much higher than predicted. The reason for this is unknown. It might have been that the months preceding the firn sampling had been characterized by larger-than-average ambient concentrations of $CHBr_3$, but this was not apparent for any of the other "natural" halocarbons examined here, which would be anticipated to have related sources. Given the short lifetime of this molecule, and the progressively widening discrepancy between concentrations at Dome C and DML with increasing reactivity, then the rather similar near-surface concentrations of $CHBr_3$ observed at the two sites is unexpected. We can advance no adequate explanation for these findings at present, but instead suggest they may relate to either contamination, in situ production, or the recent incursion of unusually bromoform-enriched air masses.

3.2.4. Methyl iodide. Methyl iodide (CH_3I) is the shortest lived of the compounds reported here, and is removed predominantly by photolysis (Table 2). This short lifetime is evident both from the strong apparent seasonal signal observed in the upper firn layers at DML (Figure 7), and also in the very large difference in concentrations between the two sampling sites (note the separate concentration scales for the two sites in Figure 7). A 2-year segment of the time series used as input to the firn model is shown as an inset to Figure 7. This allows the amplitude of the seasonal cycle estimated from the DML results (July:January ratio of 8.6 from Table 3) to be appreciated, and likewise the large difference in mean concentrations between the two drilling sites. The estimated seasonal amplitude is considerably smaller than the winter:summer ratio of 59 determined for C_2HCl_3 at Alert, Canada [*Yokouchi et al.*, 1996], although this large value may partly relate to transport factors and distance of sources for this pollution-derived compound. The same authors also quote a winter:summer ratio of >7 for CH_2ClI (summertime concentrations were below detection limit) which is shorter-lived again than CH_3I. A large annual cycle in CH_3I in the Antarctic is therefore not unexpected.

At DML the observed concentrations followed the model line in the upper 20 m. No depletion relative to the model line was observed over this depth range despite the short photolytic lifetime of CH_3I. This demonstrates the effective attenuation of short wavelength solar radiation by the overlying firn. No downturn of concentrations near the surface was observed at Dome C. As with the case of $CHBr_3$ and $CHBrCl_2$, we are unsure of the reasons for this behavior.

At both locations there was a dramatic increase in CH_3I toward the close-off zone. This is the only compound reported here for which an unambiguous increase at depth was observed at the DML site. A small increase in CH_2ClI was also observed (not shown here) in the bottom few meters of the DML profile, but this
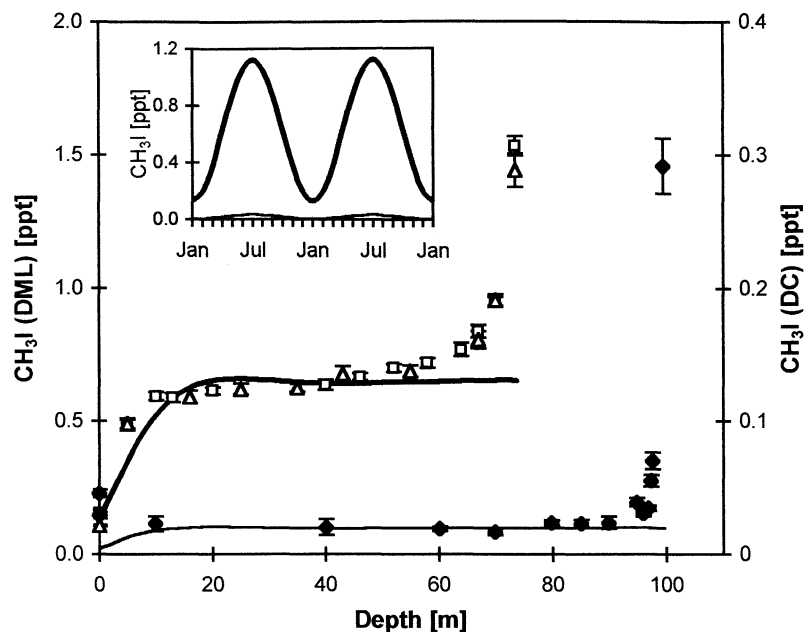
Figure 7. Depth profiles of CH$_3$I at DML and Dome C. Symbols are the same as in the legend to Figure 4a. The lines depict the firn diffusion model results (thick line for DML, thin line for Dome C) based on hypothetical time series comprising constant annual average values from 1930 to the present, modulated by a seasonal cycle (see text for explanation). A 2-year portion of the time series is shown in the inset. Error bars on the symbols are the 1-sigma accumulated analytical error limits.

gas was undetectable at Dome C. The relative increase in CH$_3$I with depth was larger at Dome C than at DML, but the absolute concentration at the lowermost depth was still 5 times less than that observed at the base of the firn profile at DML. At Dome C the occurrence of concentrations elevated above the firn model line was restricted to just the bottom 3-4 m, whereas the lowest 15 m or more of the profile was affected at DML. This may relate to differences in diffusion rates between the two sites. In both cases we think it is implausible that these deviations from the modeled scenario of constant annual average concentrations could be attributed to any genuine change in ambient atmospheric abundance, but rather that they are due to some in situ process.

4. Discussion

4.1. Production of CH$_3$Br in the Firn

Increased concentrations of certain halocarbons with depth appear to be a feature of all three firn profiles, although there were distinct differences between sites, and the effects were much lower in the Antarctic. There are curious inconsistencies such as a pronounced growth of CHBr$_3$ and CHBr$_2$Cl near pore close-off at Dome C but not at the other Antarctic site. A strong growth of CH$_3$I was observed in all of the firn profiles, but elevated CH$_3$Br, CH$_2$Br$_2$, and CHBrCl$_2$ concentrations were only observed at the Arctic site. Since "anomalous" profiles are observed in the Antarctic, we have to question whether this may have influenced our interpretation of the apparent long-term trend of CH$_3$Br. We will argue that this is not the case.

At Devon Island, CH$_3$I was one of the gases most strongly correlated to CH$_3$Br (Figure 3), and we might therefore use this as an indicator of the potential in situ CH$_3$Br production. From the linear correlation between CH$_3$I on CH$_3$Br at Devon Island we predict an increase of 4.5 ppt CH$_3$Br in firn for every 1 ppt in-

crease in CH$_3$I. (At Col du Dome the corresponding increment was only about 0.6 ppt of CH$_3$Br per ppt of CH$_3$I.) Using the Devon Island relationship, CH$_3$Br concentrations below 40 m at DML and Dome C were "corrected" by an amount equal to 4.5 times the CH$_3$I excess above the apparent annual mean for each site (determined from the firn model). The results are shown in Figure 4b. There was very little discernible change to the Dome C profile in which the absolute levels of CH$_3$I were extremely low, and the match to the scenarios was essentially unchanged. At DML, however, there was a dramatic reduction in CH$_3$Br levels. The corrected values fell well below even those predicted by scenario 3, which itself underestimates the 1983–1992 SH ambient air measurements of *Khalil et al.* [1993] (see Figure 5). Furthermore, the corrected values give entirely different apparent atmospheric trends between the two Antarctic sites, which is entirely unrealistic for a relatively long-lived and well mixed gas.

Our measurements of other compounds that were strongly perturbed at Devon Island, such as CH$_3$Cl and short-chain alkyl nitrates (unpublished data, 1998), showed no evidence of increased concentrations close to close-off at either DML or Dome C. Any biological or abiological decomposition processes would be expected to be much reduced at the lower temperatures of DML and Dome C, and the presence of organic matter should be very much lower at the Antarctic sites due to the enormous distance from vegetated landmasses. We therefore suspect that the processes producing elevated organic gases at Devon Island are quite different to those producing elevated methyl iodide and some other gases at the cold Antarctic sites, and that these latter processes do not significantly impinge on the CH$_3$Br measured in Antarctic firn.

Most importantly, we now have evidence from four entirely separate firn profiles (the two from this work, and the two of *Butler et al.* [1999]) of a consistent reconstructed temporal trend,
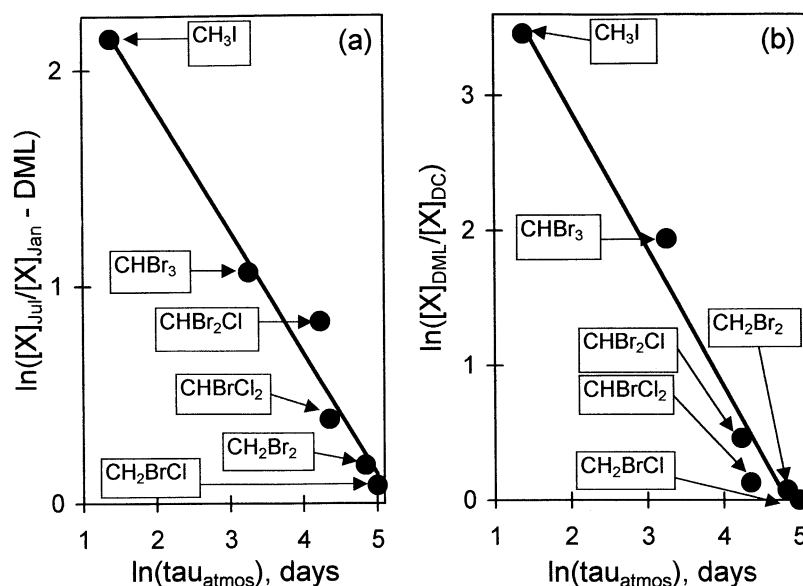
Figure 8. Log-log plots of (a) seasonal amplitude of the halocarbon concentrations at DML versus global average tropospheric lifetimes (see Table 2), and (b) the ratio between long-term annual average concentrations of the halocarbons at DML and Dome C versus tropospheric lifetimes. The lines are linear fits through the data.

despite widely varying conditions of firn temperature, accumulation rate, and physical structure. This gives us considerable confidence that there has indeed been a sustained upward trend in CH_3Br in the SH over the past several decades from preindustrial levels that were likely to have been around 5 ppt [this work; Butler et al., 1999]. What we have yet to ascertain is the long-term trend in the NH, but this might not be possible from firn analyses because of the effects of in situ production seen at both Devon Island and Col du Dome.

4.2. Differences in Firn Air Composition Between DML and Dome C

Two reasons can be advanced to explain the difference in concentrations of the short-lived halocarbons between DML and Dome C. First, the two sites could be affected by air from different source regions with different emission characteristics. Second, the air masses could be of different photochemical "age," and therefore have been subject to different degrees of chemical processing. In the first instance, there is evidence that precipitation at the two sites has different origins. Delaygue et al. [2000] used a general circulation model (GCM) to show the dominant source of precipitation at Dome C to be the Indian Ocean sector, while at DML the Atlantic and Pacific sectors jointly accounted for most precipitation.

Some effect arising from the short lifetimes of these gases is, however, also to be expected given the higher altitude and more inland situation of Dome C relative to DML. Figure 8 shows some evidence to support this assertion. In Figure 8a we have plotted the log-transformed estimated seasonal amplitudes of the various halocarbons measured at DML against their theoretical global average tropospheric lifetimes (the combination of photolysis and OH lifetimes shown in Table 2). This shows a high degree of correlation and confirms at least the relative lifetimes of these gases in the Antarctic. In Figure 8b we have then plotted the log-transformed ratios between the long-term annual average concentrations at DML to the corresponding average values at

Dome C (see Table 2) against the same tropospheric lifetimes. Again, there is a reasonable correlation between the two quantities, suggesting that at least part of the difference between the two firn sampling locations may indeed be accounted for by their relative distance from oceanic sources. There are uncertainties in this approach, not least because the assumed atmospheric lifetimes are global averages and have not been adjusted for differences in latitude, temperature, altitude, and season, etc. Nevertheless, it is encouraging that the compounds at least plot in the order expected based on their assumed reactivities. There is a pressing need to conduct year-round measurements of these compounds in the Antarctic, particularly at inland locations representative of the drilling sites.

5. Conclusions

The two Antarctic firn profiles show a consistent modeled time trend of CH_3Br since at least the midtwentieth century, rising from levels of about 6 ppt to about 8 ppt today. There is now good closure between our measurements of this trend and that of Butler et al. [1999]. Although some of the other halocarbons measured showed apparent in situ production in the lower firn layers, there is no evidence for a similar significant production mechanism for CH_3Br at these sites. In contrast, extraordinarily high levels of CH_3Br and numerous other organic gases were found in firn at Devon Island, Canada, which we believe may be linked to the presence of more organic matter in NH firn.

The profiles of the other bromocarbons suggest that there has been no significant change in their concentrations over the same time period, and therefore none of them have significant anthropogenic sources, in the SH at least. The notable differences in concentrations between the two sites suggest that the air masses affecting the two sampling sites have different origins and that transport times of the gases to the two sites may differ. From this it is evident that due account must be taken of location and general circulation patterns when interpreting the past history of short-

lived organic species in the SH based on Antarctic firn (or indeed ice core) measurements.

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E. Atlas and V. Stroud, Atmospheric Chemistry Division, NCAR, Boulder, CO 80307-3000.

J.-M. Barnola and J. Chappellaz, Laboratoire de Glaciologie et Geophysique de l'Environnement, CNRS, 38402 Saint Martin d'Heres Cedex, France.

H.P. McIntyre, S.A. Penkett and W.T. Sturges (corresponding author), School of Environmental Sciences, University of East Anglia, Norwich NR4 7TJ, England, UK.

R. Mulvaney, British Antarctic Survey, Natural Environment Research Council, Cambridge CB3 0ET, England, UK.