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Trends of halon gases in polar firn air: implications for their emission distributions

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Abstract. Four halons (H-1301, H-1211, H-2402 and H-1202) have been measured in air samples collected from polar firn from Dome Concordia (Dome C), Antarctica, from Devon Island, Canada and the North Greenland Ice Core Project (NGRIP) site, Greenland. H-2402 and H-1202 are reported for the first time in firn air. The depth profiles show the concentrations of all four halons to be close to zero (i.e. below the detection limit of 0.001 ppt) at the base of the firn thus demonstrating their entirely anthropogenic origin. This is the first evidence of this for H-2402 and H-1202. A 2-D atmospheric model was run with emissions previously derived using archive air measurements from the southern hemisphere mid-latitudes to produce historical trends in atmospheric concentrations at the firn sites, which were then input into a firn diffusion model to produce concentration depth profiles for comparison with the firn measurements. This comparison provides an evaluation of the model-derived atmospheric concentration histories in both hemispheres and thus an indirect evaluation of the emission rates and distributions used in the atmospheric model. Atmospheric concentration trends produced using global emissions previously determined from measurements at Cape Grim are found to be consistent with the firn data from the southern hemisphere. Further emissions of H-1202 in recent years (late 1980s onwards) are likely to have come from latitudes mostly south of 40° N, but emissions prior to that may have come from further north. Emissions of H-1211 may also have shifted to latitudes south of 40° N during the late 1980s. Following comparison of the atmospheric model output with the firn data, modelled atmospheric trends of total organic bromine in the form of halons were derived for both polar regions.

1 Introduction

Halons have been used for many years (back to the early 1960s) as effective gaseous fire-extinguishing agents (McCulloch, 1992). Measurements of H-1301 ($CBrF_3$), H-1211 ($CBrClF_2$), H-2402 ($CBrF_2CBrF_2$) and H-1202 (CBr_2F_2) in atmospheric air samples collected since 1978 have shown that concentrations of all 4 of these halons have increased substantially during the latter part of the 20th Century (Fraser et al., 1999; Butler et al., 1998). Further measurements of H-1301 and H-1211 in air trapped in firn (partially consolidated snow) have demonstrated that natural sources of these compounds to the atmosphere are minimal or non-existent (Butler et al., 1999) and that atmospheric concentrations were zero up to about 1970 (Sturrock et al., 2002). Together the four halons made up 7.7 ppt of organic bromine (Br) in 2000, which was increasing at a rate of 0.2 ppt Br yr^{-1} (Montzka et al., 2003a), and Br in the most abundant halons (H-1301 and H-1211) continued to increase at a rate of 0.1 ppt Br yr^{-1} between mid-1999 and mid-2002 (Montzka et al., 2003b). Halons account for about 40% of the organic bromine that reaches the stratosphere (Schauffler et al., 1999; Pfeilsticker et al., 2000; Montzka et al., 2003a). Br is about 45 times more effective than chlorine (Cl) at destroying stratospheric ozone (O_3) (Daniel et al, 1999) and thus the halons constitute about 350 ppt of tropospheric equivalent Cl (ECL) (i.e. about 8%).

Due to the recognition of the importance of the halons for O_3 depletion, the production and consumption of H-1301, H-1211 and H-2402 have been regulated under the Montreal Protocol and subsequent Amendments, such that in non-Article 5 (developed) countries production and consumption should have ceased in 1994 and in Article 5 (developing) countries should have been frozen in 2002 at 1995–1997 levels and should be phased out by 2010 (HTOC, 2003). Despite

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this the concentrations of all four halons have grown considerably since 1994, although the rate of accumulation of Br from the halons is slowing (Butler et al., 1998; Fraser et al., 1999; Montzka et al., 2003a, b). This growth is due to release from existing equipment, which constitutes a substantial reservoir (commonly known as a "bank") of halons, and due to allowed continued production in developing countries (Butler et al., 1998; Fraser et al., 1999). It should be noted that H-1202 is not covered by the Montreal Protocol or its Amendments, since most of its production is not deliberate. It is produced from over-bromination during the production of H-1211 through bromination of $CHClF_2$ (HCFC-22) (HTOC, 1999; Fraser et al., 1999).

Measurements of air samples collected in the Southern Hemisphere (SH) at Cape Grim, Tasmania, Australia, since 1978 have been used to estimate the historical trends in global emissions of the four halons (Fraser et al, 1999). Measurements of air in polar firn from both the SH (Butler et al., 1999; Sturrock et al., 2002) and northern hemisphere (NH) (Butler et al., 1999) have been used to extend the records of atmospheric concentrations of H-1301 and H-1211 back to the early part of the 20th century. In this work, we present measurements of all four halons (H-1301, H-1211, H-2402 and H-1202) (Table 1) in samples of firn air from both hemispheres (Devon Island, Canada, North Greenland Ice Core Project (NGRIP), Greenland and Dome Concordia (Dome C), Antarctica). These therefore represent the longest historical records of H-2402 and H-1202 and the first opportunity to determine historical records of atmospheric concentrations of these species in the NH.

A firn diffusion model was run with a number of prescribed atmospheric concentration time series to determine concentration depth profiles (direct mode) which have then been compared with the firn observations. These atmospheric time series were generated by a 2-D atmospheric chemical-transport model (Fraser et al., 1999) in which the global emission rates were adjusted to match atmospheric concentrations of all four halons from the Cape Grim record (Fraser et al., 1999; and updated using more recently measured concentrations). Using the measured data from the two hemispheres the latitudinal distribution of emissions was investigated.

2 Methods

2.1 Firn air measurements

Firn air was sampled at Dome C, Antarctica (75° S, 123° E) and from the Arctic, at Devon Island, Canada (75° N, 82° W) and NGRIP, Greenland (75° N, 42° W). Further site details and sampling dates are given in Table 2. Various depths were sampled from the surface to pore close off at each site. A range of electropolished, stainless steel and fused silica-lined flasks were used for sampling and these have previously been shown to exhibit excellent stability over several months to many years for a wide range of halocarbons (Fraser et al., 1999; Sturges et al., 2001a). The technique for extracting air from the firn has been described fully in Schwander et al. (1993) and Sturges et al. (2001a).

The whole air firn samples were cryogenically focused (400 mL aliquots) then desorbed and analyzed using a Micromass Autospec gas chromatograph combined with a trisector mass spectrometer (GC-MS) operated in single ion mode. The four halon gases and other halocarbons (including CFC-12) were separated on a KCl-passivated alumina (Al_2O_3/KCl) PLOT column. The complete analytical details with ion masses used for species detection are given elsewhere (Oram et al., 1995; Fraser et al., 1999). Detection limits were estimated at 0.001 ppt. Instrumental drift corrections and calibrations were made by reference to an air standard with mixing ratios assigned by static gas phase dilution detailed in Fraser et al. (1999).

To compare results from this current study with previous studies, all concentrations reported here are presented on the University of East Anglia (UEA) scale. The average UEA to National Oceanic and Atmospheric Administration Climate Monitoring and Diagnostics Laboratory (NOAA-CMDL) calibration scale ratios (UEA/NOAA-CMDL) are 1.16 (H-1211) and 0.92 (H-1301) and average UEA to Advanced Global Atmospheric Gases Experiment (AGAGE) calibration scale ratios (UEA/AGAGE) are 1.12 (H-1211) and 0.79 (H-1301) as derived from comparisons of data collected at Cape Grim (Fraser, personal communication, February, 2004). The appropriate factors are used for conversion of firn air results from Butler et al. (1999) and Sturrock et al. (2002) to the UEA scale.

2.2 Firn model

Reconstructed trends were derived for the halons at the Dome C and NGRIP sites using a firn physical transport model, run in direct mode, that accounts for gravitational fractionation and gaseous diffusivity (Rommelaere et al., 1997). The Devon Island firn unfortunately contained melt layers, which complicated the use of the firn diffusion model for this site. The firn model required physical parameters (including temperature profile, firn density) and a "diffusivity" profile that was calculated for Dome C and NGRIP by inverse modeling of the CO_2 and SF_6 profiles, respectively (Fabre et al., 2000). Diffusion coefficients for the halons in air relative to CO_2 were estimated from Le Bas molecular volumes (Fuller et al., 1966). The temporal trends in atmospheric concentrations used as input to the direct model were derived using an atmospheric model (see Sect. 2.3).

2.3 Atmospheric model

Temporal trends in atmospheric concentrations for the locations of the firn sites were generated using a 2-D atmospheric

Table 1. Halon species measured in firn air, their industrial and chemical nomenclature, lifetime and diffusion coefficients in air relative to carbon dioxide used in the firn modeling.

Name	Formula	Lifetime# (years)	Air Diffusion relative to CO_2
H-1211	$CBrClF_2$	17	0.590
H-1202	CBr_2F_2	2.9	0.565
H-1301	$CBrF_3$	65	0.637
H-2402	$CBrF_2CBrF_2$	20	0.490

Lifetime from Fraser et al. (1999)

Table 2. Sampling site details and firn air properties.

Site	Elevation (m)	Mean Annual Temp (°C)	Transition depth (m)	Snow accumulation rate (cm water yr^{-1})	Sampling date
Arctic					
Devon Island, Canada	1800	−23	59	30	April 1998
NGRIP, Greenland	2975	−31	78	20	July 2001
Antarctic					
Dome C	3240	−53	100	3	January 1999

chemistry-transport model. Details of the model and how it has been used previously to study halons are given in Fraser et al. (1999). The model contains 24 equal area latitudinal bands and 12 vertical levels, each of 2 km. Thus the latitude bands applicable to the firn air sites were the most northerly and most southerly (66.4°–90.0°). Further, since the altitudes of NGRIP and Dome C are about 3 km (Table 2), the concentrations for the second level (2–4 km) were used.

Fraser et al. (1999) used the model to derive global emissions for the four halons consistent with the concentrations observed at Cape Grim (41°) up until March 1998. This was done by adjusting the emission strengths until the concentrations for the surface box of the band 35.7°–41.8° agreed with observations. For the current study the temporal trend in global emissions has now been updated using more recent observed concentrations from Cape Grim to the end of 2001, such that it covers the firn air sampling times (Table 2). The latitudinal distribution used for the derivation of global emissions was that for industrial activity (Rodhe and Isaksen, 1980; Hough, 1989) with 6% release in the SH and, as in Fraser et al. (1999), this distribution was not varied with time. The run using this latitudinal distribution is referred to as Run A. The sensitivity of the concentrations at the firn sites to the latitudinal distribution of emissions used was tested, the results of which are presented and discussed below.

To determine the latitudinal emission distribution of the halons, it is important to understand the accuracy with which the model's transport scheme (Hough et al., 1989) reproduces observed concentrations, particularly in polar regions, of species that are predominantly emitted in northern mid-latitudes. The model was therefore run for CFC-11, CFC-12 and methyl chloroform. The CFCs were chosen because they have negligible sinks within the model domain and have well characterized emission strengths (Fisher et al., 1994; McCulloch et al., 2003) and emission distributions (Global Emissions Inventory Activity (GEIA), based on McCulloch et al., 1994). Methyl chloroform was used since its lifetime of about 5 years (Montzka et al., 2003a) is much closer to that of H-1202 (Table 1) than are those of the CFCs. It too has well characterized emission strengths (McCulloch and Midgley, 2001), emission distributions (Global Emissions Inventory Activity (GEIA) distribution for 1990, based on Midgley and McCulloch, 1995) and atmospheric lifetime (Montzka et al., 2000, 2003a; Prinn et al., 2001). The model output was compared to observed concentrations at Mace Head, Ireland (53° N), Cape Meares, Oregon (45° N), Barbados (13° N), Samoa (14° S) and Cape Grim, Tasmania (41° S) from the ALE/GAGE (Atmospheric Lifetime Experiment/Global Atmospheric Gases Experiment) (Prinn et al., 2000) and at Alert (82° N), Barrow (71° N) and South Pole (90° S) from NOAA-CMDL. It was found that for the CFCs, whereas the modelled concentrations agreed well with the northern hemispheric ALE/GAGE sites, the southern hemispheric ALE/GAGE sites were under-predicted by about 5%. The model agreed with the data from NOAA-CMDL for CFC-11 and CFC-12 mostly to within 5% and, when normalized to the Antarctic site, gave values 2–3% higher than those from the Arctic sites. For methyl chloroform the model derived concentrations agreed well with the mid to high

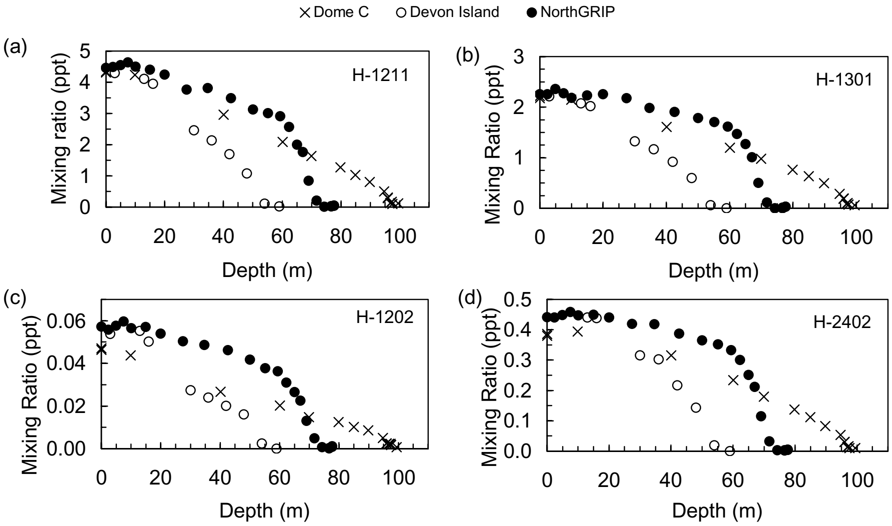

Fig. 1. Depth profiles of four halons in firn air at the three sampling locations: Dome C (crosses), Devon Island (open circles) and NGRIP (filled circles).

southern latitude ALE/GAGE sites whilst over-predicting the northern hemisphere ALE/GAGE concentrations by up to 20%. For the NOAA-CMDL data up to 1996, when GAGE data stopped and the MCF emissions had reduced substantially, the model over-predicted South Pole by 0–5%, and Alert by 6–13%. This suggests that in this study, where the model derived halon concentrations have been constrained to observed concentrations at a southern hemispheric site, errors in the transport scheme may give rise to concentrations 5–10% higher, but probably no more than 15% higher, than those observed at an Arctic site.

3 Results and discussion

3.1 Firn depth profiles

Depth profiles at Dome C, Devon Island and NGRIP show the concentrations of the four halons falling to below detection limit (<0.001 ppt) at the base of the firn (Fig. 1), which represents 2% of the modern day atmospheric abundance of H-1202 and much less for the other halons. This agrees with previous findings for H-1301 and H-1211 (Butler et al., 1999; Sturrock et al., 2002) that demonstrated their entirely anthropogenic origin. The results also demonstrate, for the first time, that H-2402 and H-1202 are also entirely anthropogenic in origin. Comparison for H-1211 and H-1301 with measurements in the firn from Butler et al. (1999) (South Pole and Siple Dome, Antarctica and Tunu, Greenland) and Sturrock et al. (2002) (Law Dome, Antarctica) are shown in Fig. 2. In preference to CO_2, CFC-12 is used here as a pseudo-age normalizer due to it having no seasonal cycle and broadly similar diffusivity and temporal trend to the halons. Its use as an age tracer to allow the comparison of various sample sites and other datasets, however, is becoming limited in the more recent years, as its atmospheric growth rate is approximately zero. The samples collected in the convective zones (i.e. effectively surface air) are not included in the comparison plots (above 10 m for NGRIP and Dome C, and above 3 m for Devon Island). Measurements in the firn for H-1211 and H-1301 reported here are found to be broadly consistent with these previous studies.

Mean ages derived from the CFC-12 concentration in the deepest firn samples collected at Dome C, Devon Island and NGRIP equate to approximately 1961, 1954 and 1951, respectively. The spread of ages within each individual sample, however, particularly at the bottom of the firn, is very large (Sturges et al., 2001b). This age spectrum for CFC-12 is given to provide an indication of the spread of ages at depth in the firn. The mean ages for the halons will differ slightly from that of CFC-12 since (with the exception of H-1301) they have free air diffusivities less than that of CFC-12 (e.g. 21% less in the case of H-2402), and so will likely have slightly older mean ages than CFC-12 at the same depth. The firn model is required to obtain more accurate representations of the temporal trends of the molecules of interest. From Devon Island, the oldest air has an age range of 1930 to 1977 based on CFC-12 concentrations (Sturges et al., 2001a). Although the presence of melt layers at Devon Island complicated the use of the firn diffusion model for this site, the data essentially confirm the more recent profile obtained at NGRIP.

Depth profiles generated by the firn diffusion model using the atmospheric model output from Run A, which was adjusted to the Cape Grim observations, as input, give excellent agreement with the concentration profiles for all four halons at Dome C (Fig. 3a). For NGRIP, however, the depth profiles

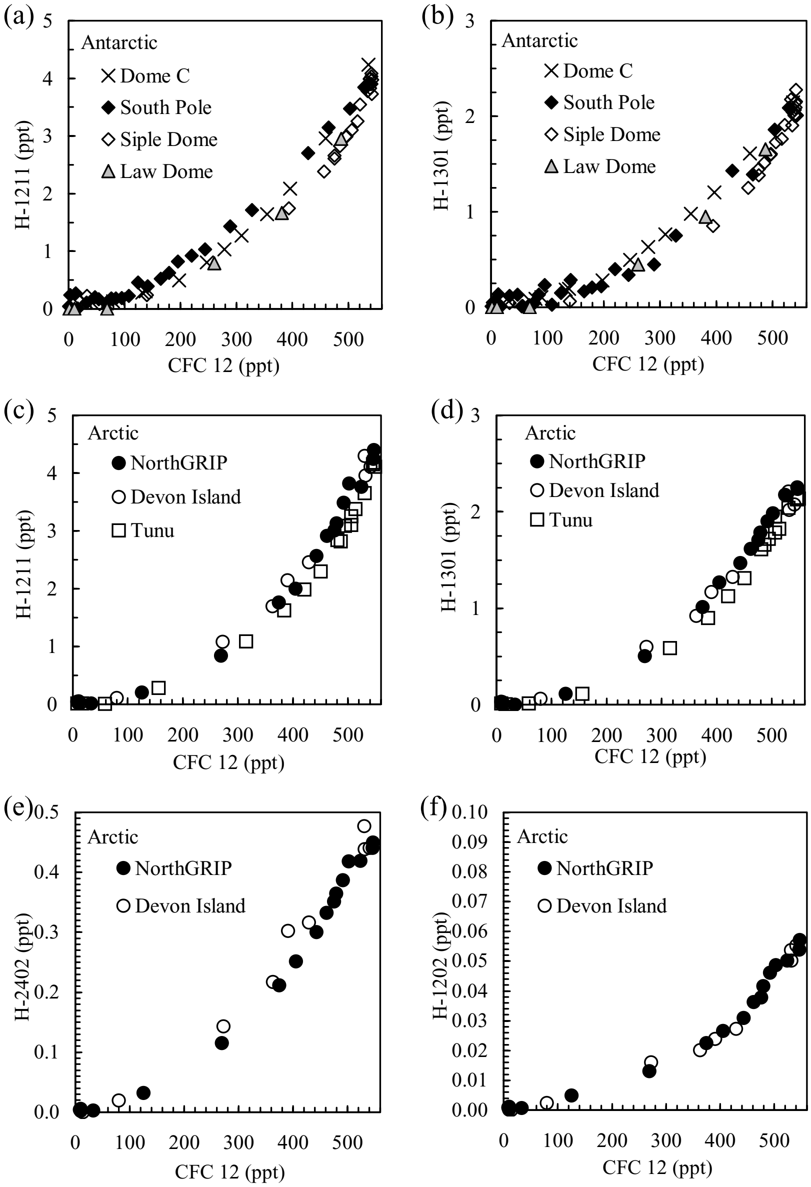

Fig. 2. Profiles of halons against CFC-12 for a number of firn sites in **(a)** the Antarctic for H-1211, **(b)** the Antarctic for H-1301, **(c)** the Arctic for H-1211, **(d)** the Arctic for H-1301, **(e)** the Arctic for H-2402, **(f)** the Arctic for H-1202. The Antarctic studies include data from UEA at Dome C (crosses), data from Butler et al. (1999) South Pole (filled diamonds) in December 1996 and at Siple Dome (open diamonds) in January 1995, and from Sturrock et al. (2002) at Law Dome (grey triangles) in January 1998. The Arctic studies include data from UEA at NGRIP (filled circles) and Devon Island (open circles) and data from Butler et al. (1999) at Tunu (squares) in April 1996.

generated for Run A do not agree as well with the observations, in general over-predicting the concentrations of all four halons, in particular for H-1202 and to a lesser extent H-1211 (Fig. 3b). The over-prediction for H-1301 and H-2402 is around 5–10%. For H-1211 it is around 10–20% whilst for H-1202 it is around 30–50%. Comparison of model-derived atmospheric concentrations with concentrations of H-1301 and H-1211 observed between 1989 and 1997 by NOAA-CMDL (Butler et al., 1998), adjusted to the UEA calibration scale, at the South Pole (Antarctic), Alert (Arctic) and Barrow (Arctic) show a similar pattern. Whilst the agreement for both halons at the South Pole is within 3%, and those for H-1311 at Alert and Barrow are within 2%, the model-derived concentrations for H-1211 at Alert and Barrow are about 10% too high.

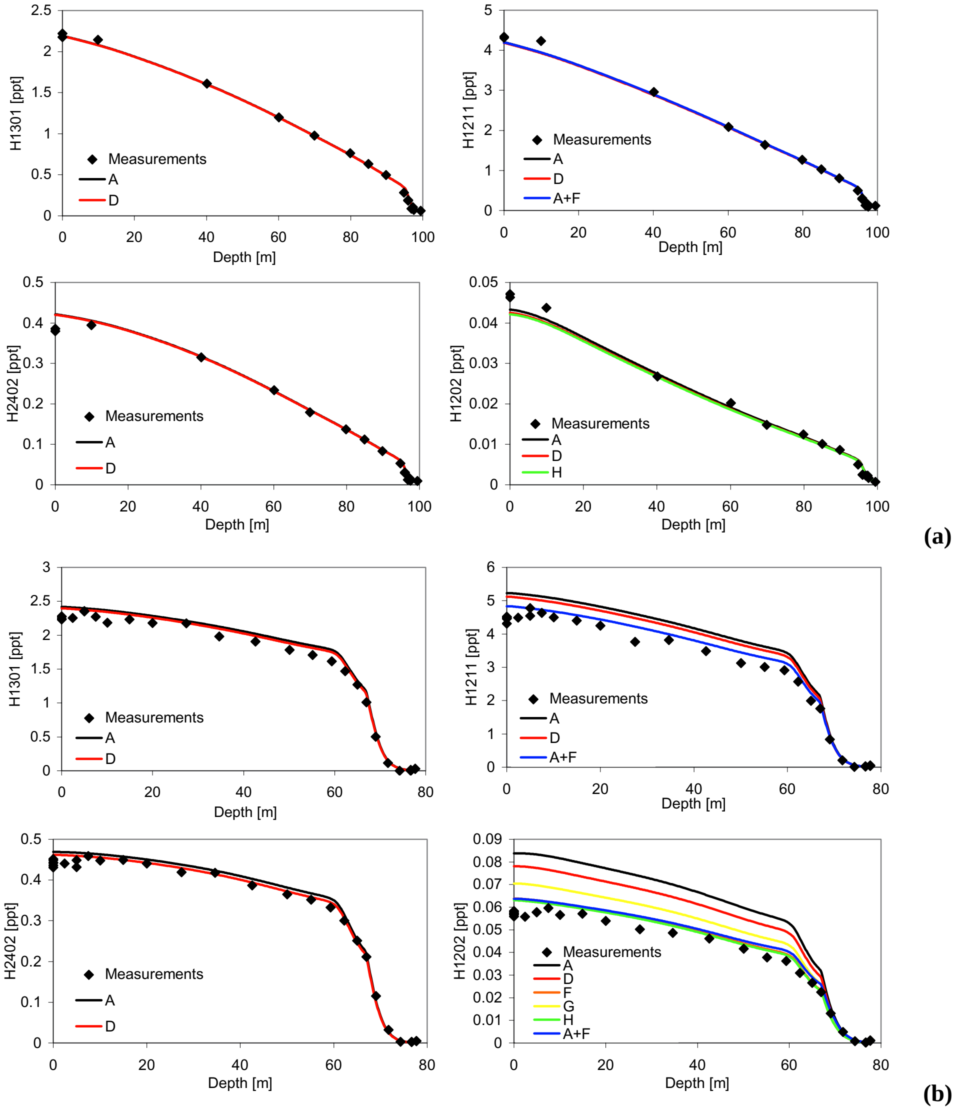

Fig. 3. Measured and model derived depth profiles of the four halons at **(a)** Dome C, **(b)** NGRIP. The model runs are defined in the text.

3.2 Latitudinal emission distributions

The data from the two polar firn sites (Dome C and NGRIP), one in each hemisphere, provide a constraint on the interhemispheric gradient (IHG) in atmospheric concentration for all four halons, including how this might have changed with time. Halons, like most other anthropogenically-produced species, are predominantly emitted to the atmosphere in the NH (HTOC, 2003) and once they have been transported to the SH they are reasonably well mixed. Therefore, the good agreement between the depth profiles created from the atmospheric model and those observed at Dome C, Antarctica is not surprising given that the atmospheric model runs were adjusted to observations made at another southern hemispheric site, Cape Grim. However, the discrepancy between the model trends and the firn measurements at NGRIP suggests that the atmospheric model is not reproducing the IHG correctly. This may be due to a number of factors: the atmospheric model transport scheme; model derived atmospheric lifetimes; and the latitudinal distribution of emissions.

This tendency to over-predict northern hemispheric concentrations whilst agreeing with observed southern hemispheric concentrations can be partly explained by the errors in the transport scheme (see Sect. 2.3). The magnitude of the over-prediction for H-1301 and H-2402 for NGRIP is similar to that expected from the transport scheme based on the runs for the CFCs and methyl chloroform. The over-prediction for H-1211 is more than that for the CFCs for the Artic sites and towards the upper end of the discrepancy for methyl chloroform, whilst that for H-1202 is far greater than that expected due to errors in the transport scheme.

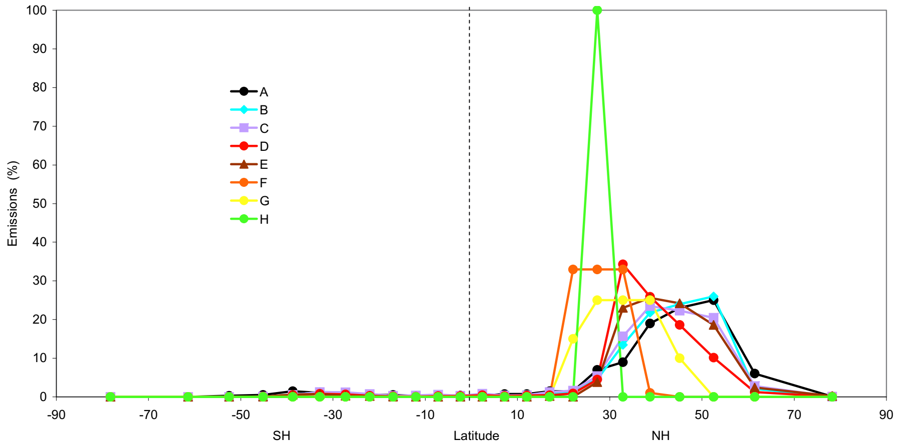

Fig. 4. The latitudinal emissions distributions for model runs A to H. The percentage of the total emissions is plotted as a function of the central latitude of the model boxes. The vertical dashed line indicates the equator.

The model derived lifetimes (Table 1) agree well with current best estimates (Montzka et al., 2003a). There is some uncertainty regarding the lifetime of H-1211 (Montzka et al., 2003a), but a shorter lifetime as suggested by Butler et al. (1998) would increase the IHG rather than lessen it. Increasing the lifetime of H-1202 would decrease the IHG towards that implied by the firn data. Although this would increase the concentrations of H-1202, the global emission rates could be reduced since they were originally derived using the assumed lifetime. For example, decreasing the photolysis rates and increasing the emissions rates both by 20% reduces concentrations in 2001 at NGRIP by 9%, whilst only reducing those at Dome C by 1%. However, this change at NGRIP is still far less than the 30–50% required.

The sensitivity of the model derived concentrations to the latitudinal distribution of the emissions was examined. Four runs of the atmospheric model were performed using the latitudinal emission distributions estimated for other halocarbons since they might be more typical of the emission distribution of the halons than one for general industrial activity. These were (Run B) CFC-11 from GEIA (McCulloch et al., 1994), (Run C) CFC-12 from GEIA (McCulloch et al., 1994), (Run D) methyl chloroform from GEIA (Midgley and McCulloch, 1995), and (Run E) HFC-23 from fire-extinguishers from the Emission Database for Global Atmospheric Research (EDGAR) (Olivier and Berdowski, 2001; Olivier, 2002) (Fig. 4). These made very little difference to the concentrations calculated for both Dome C and NGRIP, such that when plotted the curves for Runs B, C and E were virtually indistinguishable from that of Run A. Therefore only the results from Run D (emission distribution for methyl chloroform) are plotted in Fig. 3. Even then the only difference of note is reduced concentrations of H-1202 for NGRIP, but these are still significantly greater than those measured (Fig. 3b).

In an attempt to reproduce the measured H-1202 concentrations at NGRIP a number of runs of the atmospheric model were performed in which the emissions of H-1202 were allocated, in various ways, to the 5 model bands between 19° N and 49° N and, to illustrate the impact, the results from 3 of these runs (F, G and H) (Fig. 4) are presented (Fig. 3). Again the concentrations at Dome C were affected only slightly and run H, which made the largest difference, is shown in Fig. 3a. The concentrations for NGRIP were significantly reduced (Fig. 3b), with the runs in which the emissions were mostly located in the bands between 19° N and 36° N (F and H) agreeing best with the measured data. It should be remembered that the error in the atmospheric model transport scheme is likely to cause an over-prediction of the concentrations at NGRIP, such that Run G also agrees reasonably well with the measured data given this uncertainty.

In general, the location of halon production does not equate to the point of emissions. However, in the case of H-1202, a by-product of the inefficient production of H-1211, H-1202 emissions will be co-located with the sites of H-1211 production. Production of H-1211 in Article 5 countries (mostly China) increased substantially in 1987, whilst total H-1211 production from N. America, W. Europe and Japan peaked in 1988 before declining to zero in 1994 (HTOC, 2003) (Fig. 5). Certainly, since 1987, with the bulk of H-1211 production occurring in China, the more southerly emission distributions of runs F, G and H are likely to be more realistic for H-1202 than those of runs A-E and this is clearly in agreement with the results from NGRIP. The emission distributions of H-1202 that appear to fit best with the NGRIP data are those located at the latitudes of southern and central China. This is consistent with the location of the Chinese H-1211 plants (E. Pederson, personal communication). A large number of small H-1211 plants existed in the Zheijiang Province (28–31° N), which recovered H-1202 in

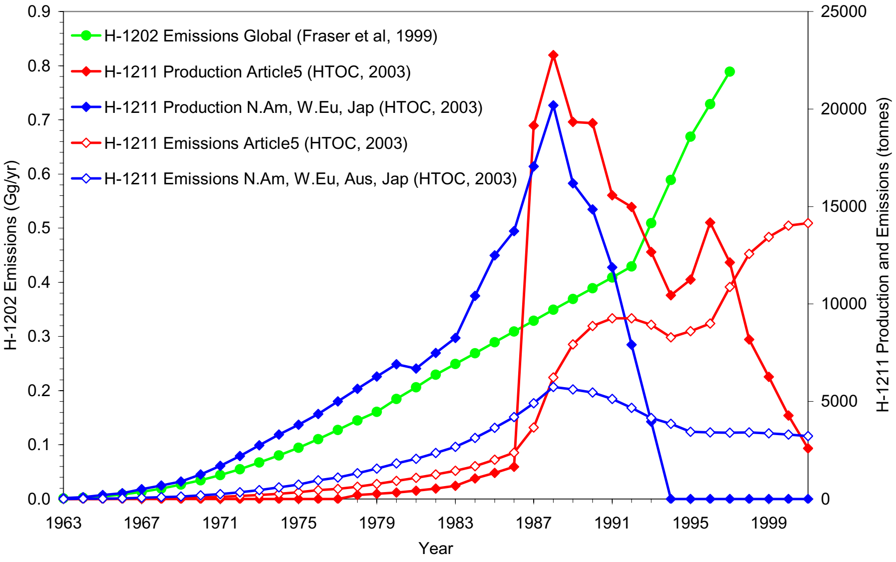

Fig. 5. Historical trends in the production and emissions of H-1211 and H-1202. Green circles are global emissions of H-1202 from Fraser et al. (1999), solid red diamonds are production of H-1211 from Article 5 countries (HTOC, 2003), solid blue are production of H-1211 from N. America, Western Europe and Japan (HTOC, 2003), open red diamonds are emissions of H-1211 from Article 5 countries (HTOC, 2003), open blue diamonds are emissions of H-1211 from N. America, Western Europe, Australia and Japan (HTOC, 2003).

tanks. These have been closed as part of the halon phase out program and there remain three large plants (one in Zheijiang Province; one in Guandong Province (20–25° N); and one in Shandong Province (35–38° N)) which recover and feedback H-1202 through closed systems.

Emissions of H-1202 have been calculated to have gradually increased almost linearly up until 1992, after which there was an increase in the rate of growth (Fraser et al., 1999) (Fig. 5). No step change in global emissions was calculated for 1987 when production of H-1211 rose substantially in China. This might suggest that emissions of H-1202 prior to 1987 came from somewhere other than China. Alternatively the increase in production of H-1211 in China may have been associated with an increase in the efficiency of H-1211 production and/or H-1202 recycling. A model run was performed in which emission distribution A was used up until 1986, after which emission distribution F was used. Given the tendency of the atmospheric model transport to slightly over-predict the concentrations at Artic sites, there is some suggestion that run F may under-estimate the concentrations of H-1202 at NGRIP at depths below 67 m (Fig. 3b), whilst the combined run A+F gives a better fit. Although the results of this study clearly show that emissions of H-1202 in recent years are likely to have come from latitudes mostly south of 40° N, it is possible that emissions in earlier years may have come from further north.

The run A+F was also performed for H-1211 leading to an improved fit at NGRIP (Fig. 3b), suggesting that emissions of H-1211 in the 1990s are from latitudes closer to 30° N than 50° N. This is consistent with the estimated shift in emissions from N. America, W. Europe and Japan to Article 5 countries during the late 1980s (HTOC, 2003).

3.3 Total organic bromine

Figure 6 shows the polar atmospheric trends in total organic bromine in the form of halons as derived from model runs that give reasonable fits to the firn air data (Run A for H-1301 and H-2402, and Run A+F for H-1211 and H-1202). Essentially the global trend in emissions has been constrained by the measurements at Cape Grim whilst the latitudinal distributions of emissions have been refined by the firn air data.

4 Summary

- Depth profiles at Dome C, Devon Island and NGRIP show the concentrations of four halons to be zero at the base of the firn thus demonstrating their entirely anthropogenic origin. This agrees with previous findings for H-1301 and H-1211, but is the first evidence of this for H-2402 and H-1202.
- Global emission trends previously determined from measurements at Cape Grim are consistent with the firn data from both the Antarctic and Artic.
- Polar firn data from both hemispheres demonstrates that emissions of H-1202 in recent years (late 1980s onwards) are likely to have come from latitudes mostly south of 40° N, but that emissions prior to that may have come from further north.

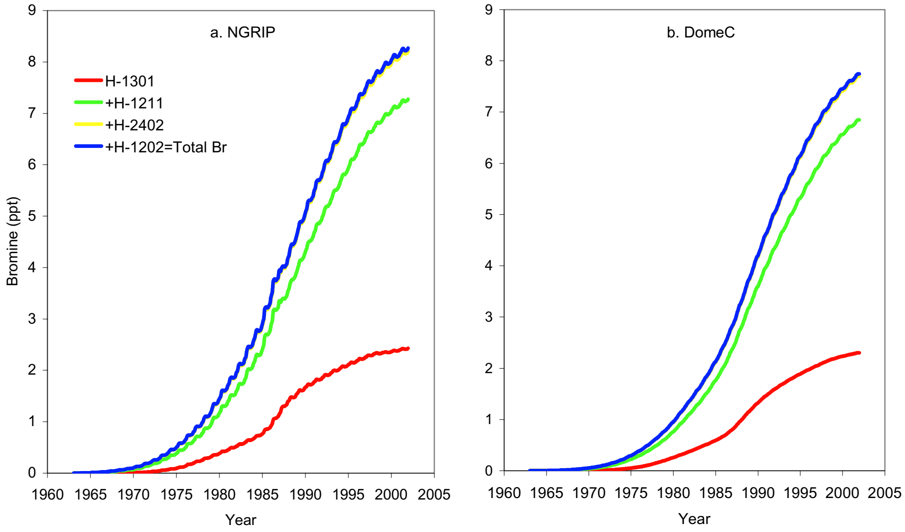

Fig. 6. Historical trends in atmospheric concentrations of total organic bromine from halons at **(a)** NGRIP, **(b)** Dome C (plotted as the sum of Br from the halons). Red line is Br from H-1301 from Run A, green line is plus Br from H-1211 from run A+F, yellow line is plus Br from H-2402 from run A and blue line is plus Br from H-1202 from run A+F.

- The firn data also suggests that emissions of H-1211 may also now be mostly from latitudes south of 40° N and are consistent with a shift from more northerly latitudes during the late 1980s.

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