

# A record of atmospheric halocarbons during the twentieth century from polar firn air

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**Measurements of trace gases in air trapped in polar firn (unconsolidated snow) demonstrate that natural sources of chlorofluorocarbons, halons, persistent chlorocarbon solvents and sulphur hexafluoride to the atmosphere are minimal or non-existent. Atmospheric concentrations of these gases, reconstructed back to the late nineteenth century, are consistent with atmospheric histories derived from anthropogenic emission rates and known atmospheric lifetimes. The measurements confirm the predominance of human activity in the atmospheric budget of organic chlorine, and allow the estimation of atmospheric histories of halogenated gases of combined anthropogenic and natural origin. The pre-twentieth-century burden of methyl chloride was close to that at present, while the burden of methyl bromide was probably over half of today's value.**

Chlorofluorocarbons (CFCs) and other halocarbons have been used as refrigerants, propellants and solvents since the early to middle twentieth century. Both leakage and direct emission, in combination with long atmospheric lifetimes, have resulted in a steady accumulation of these gases in the atmosphere, allowing them to increase the burden of atmospheric chlorine (Cl) from  $\sim 0.5 \text{ nmol Cl mol}^{-1}$  (that is, 0.5 parts per billion, p.p.b.) to a peak of over  $3.5 \text{ nmol Cl mol}^{-1}$  by 1992–94<sup>1,2</sup>. Suggestions that a build-up of CFCs and long-lived halocarbons in the atmosphere could result in the depletion of stratospheric ozone prompted the need for systematic measurements<sup>3</sup>, but only in the mid-1970s were routine atmospheric monitoring programmes begun<sup>4,5</sup>. Industrial production and emission data, together with atmospheric lifetimes, have been used to estimate the atmospheric burden of CFCs before their detection and measurement<sup>6,7</sup>. Until now, however, no data have been available for testing these early estimates.

Natural sources have been suggested for many of the halocarbons involved in the depletion of stratospheric ozone<sup>8</sup>. Atmospheric methyl chloride ( $\text{CH}_3\text{Cl}$ ), for example, is believed to be predominantly of natural origin, although it does have a few anthropogenic sources and there appear to be unidentified sources of this gas<sup>9</sup>. The division of methyl bromide ( $\text{CH}_3\text{Br}$ ) emissions into natural and anthropogenic components has generated considerable scientific and regulatory controversy during recent years<sup>10,11</sup>. Some studies have suggested that natural sources may be significant for atmospheric  $\text{CCl}_4$  (ref. 12). Detection of CFCs in air sampled near volcanoes has led to the suggestion that volcanism might be a significant source of these gases in air<sup>13</sup>. The general absence of CFCs in the ocean's deep waters virtually precludes this possibility, but no reliable measurements in air taken before the onset of anthropogenic emissions have been made to date. Air samples from ice cores have been too small to obtain the precision necessary to address these questions for halocarbons. Previous collections of firn air

either were contaminated during sampling<sup>14</sup> or extended back no more than a few years<sup>15</sup>.

Here we use samples of air collected from firn (unconsolidated snow; Table 1) at the South Pole and Siple Dome in Antarctica and at Tunu in Greenland to obtain high-precision measurements spanning the full history of anthropogenic emission of most halocarbons (data reported here are available; see Supplementary Information). Samples of firn air from all three sites were analysed for  $\text{CCl}_3\text{F}$  (CFC-11),  $\text{CCl}_2\text{F}_2$  (CFC-12),  $\text{CH}_3\text{CCl}_3$ ,  $\text{CCl}_4$ ,  $\text{N}_2\text{O}$ ,  $\text{SF}_6$ ,  $\text{CBrF}_3$  (halon H-1301),  $\text{CBrClF}_2$  (halon H-1211),  $\text{CH}_3\text{Br}$  and  $\text{CH}_3\text{Cl}$ . Newly introduced hydrofluorocarbons (for example,  $\text{CF}_3\text{CH}_2\text{F}$  or HFC-134a), hydrochlorofluorocarbons (such as  $\text{CH}_3\text{CCl}_2\text{F}$  or HCFC-141b,  $\text{CH}_3\text{CClF}_2$  or HCFC-142), an additional CFC ( $\text{CCl}_2\text{FCClF}_2$  or CFC-113), and other partially halogenated methanes were measured in Tunu and Siple Dome samples only. ( $\text{CHClF}_2$ , or HCFC-22, showed significant signs of contamination in the upper samples, so have been omitted from this analysis.) Results for  $\text{N}_2\text{O}$ ,  $\text{CO}_2$ ,  $\text{CH}_4$ ,  $\text{O}_2/\text{N}_2$  and  $^{15}\text{N}$  at the South Pole already have been published<sup>16</sup>. Depth profiles from these sites have been presented in two NOAA/CMDL data reports<sup>17,18</sup>. Owing to physical

**Table 1 General properties of firn at sampling sites**

Site	South Pole, Antarctica	Siple Dome, Antarctica	Tunu, Greenland
Location	90° S	81° 40' S, 148° 49' W	78° 01' N, 33° 59' E
Elevation (m)	2,841	~600	~2,400
Sampling date	Jan. 1995	Dec. 1996	Apr. 1996
Lock-in zone depths (m)	114–122	48–56	58–68
Annual snow accumulation ( $\text{cm yr}^{-1}$ ice equivalent)	8	15	10
Annual mean temperature (°C)	−49.4	−25.4†	−29‡
'CO <sub>2</sub> age' at bottom*	1903	1953	1929†

\* CO<sub>2</sub> age is defined as the year the atmospheric CO<sub>2</sub> value<sup>33</sup> matched the CO<sub>2</sub> concentration in the deepest sample. This is a mean age for CO<sub>2</sub> in the bottom air, which has undergone considerable mixing. Mean ages of halocarbons are greater because of their lower diffusivities. Once in the lock-in zone, they then age at the same rate. This value is given to illustrate differences among the sampling sites; firn air at the South Pole records atmospheric history over longer time than the other two sites.

† This value is approximate owing to the unknown evolution of the interhemispheric CO<sub>2</sub> before 1972.

‡ Temperatures from measurements made at the site at the time of sampling.

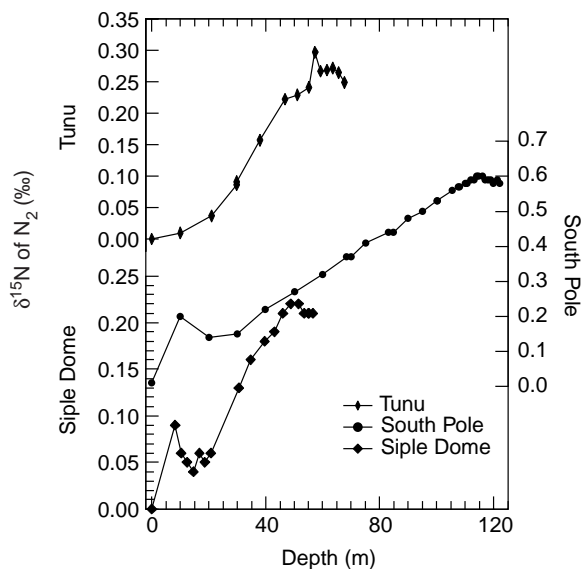
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effects, and in some instances chemical effects, the composition of firn air at any given depth does not correspond exactly to the atmospheric composition at some time in the past. Nevertheless, because the behaviour of each gas in the firn is governed primarily by its own diffusivity and molecular mass, we are able to estimate histories of both anthropogenic and naturally occurring halocarbons during a time of rapid population, agricultural and industrial growth.

**Concentration–depth profiles of trace gases**

Firn is a porous matrix in which constituent gases diffuse at rates governed by both the structure of the firn and the nature of the species in question. Profiles of  $\delta^{15}\text{N}$  values of  $\text{N}_2$  versus depth in the firn (Fig. 1) reflect the processes governing transport and storage of air<sup>19,20</sup>. Below the influence of seasonal temperature gradients and other surface-related effects (roughly 30 m),  $\delta^{15}\text{N}$  of  $\text{N}_2$  increases linearly with depth, owing to gravitational settling. The linearity indicates a porous column in which transport is governed predominantly by molecular diffusion<sup>21,22</sup>. The interval of constant  $\delta^{15}\text{N}$  of  $\text{N}_2$  at the base of the firn shows the lock-in zone<sup>23</sup>, where dense winter layers substantially impede vertical diffusion, while summer layers retain enough open porosity to allow sample collection. Gases within the porous column atop the lock-in zone communicate with the atmosphere through diffusion, creating a smoothed record of atmospheric changes. In contrast, vertical diffusion is considerably restricted within the lock-in zone, which tends to isolate this air from the diffusive column. Thus, air in the lock-in zone ages at approximately the same rate as the surrounding ice. At Siple Dome and Tunu, where the diffusive column is relatively short and smoothing is minimal, the composition of the overlying atmosphere is recorded in the lock-in zone without extensive diffusive mixing. At the South Pole, the deeper diffusive column significantly smooths the atmospheric history, but also allows for collection of very old samples<sup>16</sup>. By comparing results from these sites with different diffusive structures, we are able to reconstruct robust atmospheric histories.

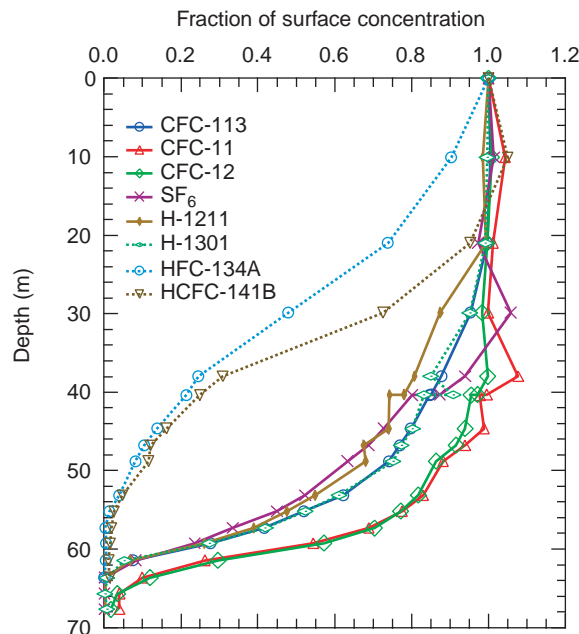
Variations in concentration with depth reflect both long-term trends and recent perturbations of trace gases in the atmosphere (Figs 2–4). Concentrations of compounds known to have sig-



**Figure 1** Measured depth profiles of  $\delta^{15}\text{N}$  of  $\text{N}_2$ . The results from the two boreholes at the South Pole are indistinguishable from one another. Enrichments of  $^{15}\text{N}$  at shallow depths reflect thermal fractionation associated with seasonal temperature changes at the surface.  $\delta^{15}\text{N}$  (in ‰) =  $\{[(^{15}\text{N}/^{14}\text{N})_{\text{sample}} / (^{15}\text{N}/^{14}\text{N})_{\text{standard}}] - 1\} \times 10^3$ ; the standard used here for all sites is contemporary tropospheric air.

nificant anthropogenic sources over the past few decades (for example, CFCs, solvents and halons) decrease considerably with depth, where the firn air is older. Concentrations of CFC-11, CFC-12, CFC-113, H-1301, H-1211 and  $\text{SF}_6$  all decreased to levels that did not differ significantly from zero by the bottom of the depth profiles (Fig. 2). This indicates that these gases were not present in the atmosphere during the early twentieth century and confirms their exclusively anthropogenic origin. Previously, the lowest values reported for CFC-11 and -12, also from firn air measurements, were 16 and 18  $\text{pmol mol}^{-1}$  (that is, parts per trillion or p.p.t.)<sup>14</sup>. The earliest direct measurements of atmospheric CFC-11 and -12 date from the early to mid-1970s, with values of roughly 50 and 200  $\text{pmol mol}^{-1}$  (refs 12, 24–26). CFC-113 has been measured in archived air from Cape Grim, Australia, as far back as 1978, for which a value of 13  $\text{pmol mol}^{-1}$  was reported<sup>27</sup>. Systematic  $\text{SF}_6$  measurements began in 1978 at levels of 0.6  $\text{pmol mol}^{-1}$ , or about 15% of the current atmospheric burden<sup>28</sup>, although the lowest reported value was for 1976, at 0.24  $\text{pmol mol}^{-1}$  (ref. 29). Early measurements of the halons are also available since 1976, with amounts of the order of 0.5  $\text{pmol mol}^{-1}$  (ref. 30).

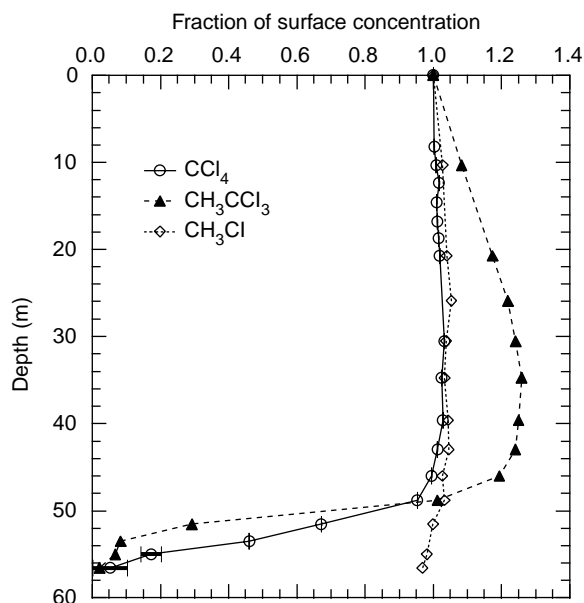
The concentrations of two abundant chlorocarbons,  $\text{CH}_2\text{Cl}_2$  and  $\text{CCl}_4$ , also decreased rapidly with depth (Fig. 3). Both of these gases reached concentrations near the bottom of the profiles that were at or near detection limits, suggesting that natural sources are insignificant and that both gases were essentially absent in the pre-twentieth-century atmosphere. The detection limit for  $\text{CH}_2\text{Cl}_2$  was  $\sim 1.5 \text{ pmol mol}^{-1}$ , although for  $\text{CCl}_4$  it was  $\sim 5 \text{ pmol mol}^{-1}$  because of a co-eluting peak on the gas chromatography/electron-capture detection (GC/ECD) system (see Supplementary Information). Thus natural sources, if they are significant at all, could not be responsible for more than 5  $\text{pmol mol}^{-1}$  of  $\text{CCl}_4$  in the atmosphere. Of course, this requires that  $\text{CCl}_4$  is stable in firn air, a question that is raised in our attempts to reconcile an atmospheric history of  $\text{CCl}_4$



**Figure 2** Measured depth profiles of anthropogenic gases with ‘known’ emissions (Tunu, Greenland). These profiles are similar to those obtained at South Pole and Siple Dome. Depth profiles at all sites show the CFCs, halons and  $\text{SF}_6$  penetrating deeply into the firn and dropping to zero or near-zero at the bottom, which implies no significant sources before the introduction and use of these gases by humans in the middle to late twentieth century. In general, gases emitted for longer periods and with higher diffusivities penetrate most deeply. The atmospheric increases of HCFC-141b and HFC-134a (defined in the text) are recorded only in the diffusive zone of the firn, as these gases have not been present long enough in the atmosphere to become locked in at depth.

from both Siple Dome and South Pole profiles. Although absolute calibration was a concern for some of the early real-time measurements of these two gases<sup>12,24</sup>, values from the late 1970s were reported at around 60 pmol mol<sup>-1</sup> for CH<sub>3</sub>CCl<sub>3</sub> and 90 pmol mol<sup>-1</sup> for CCl<sub>4</sub>, after normalizing to recent calibration scales<sup>2,31</sup>. Also apparent in the data from Siple Dome (Fig. 3) and Tunu is the 1991–93 turnaround of CH<sub>3</sub>CCl<sub>3</sub> in the atmosphere that resulted from decreased anthropogenic emissions<sup>1,31</sup>. Those HCFCs and HFCs that have been used only recently appear exclusively in the upper layers of the firn, as they have not been present in the atmosphere long enough to have been isolated in the lock-in zone<sup>1</sup> at concentrations above our detection limits (Fig. 2).

Concentrations of CH<sub>3</sub>Cl are significant in the deepest samples, and increase gradually toward the surface of the firn (Fig. 3). This is evidence that this gas has both natural and anthropogenic sources or at least sources that existed before the twentieth century. The concentrations of CH<sub>3</sub>Cl in samples collected between 20 m and 45 m depth are similar to the mean annual concentrations at Cape Grim, Tasmania, in recent years<sup>18</sup>. The decrease of 15–20 pmol mol<sup>-1</sup> observed in the upper 10–12 m of the firn is consistent with the seasonal variability observed for CH<sub>3</sub>Cl in the Southern Hemisphere, as lower mixing ratios are observed in summer when atmospheric loss processes outweigh sources. Concentrations between 20 and 45 m depth are about 10% higher than at the bottom of the profile. If we assume that CH<sub>3</sub>Cl is not being degraded slowly over time in the firn, these results indicate that the



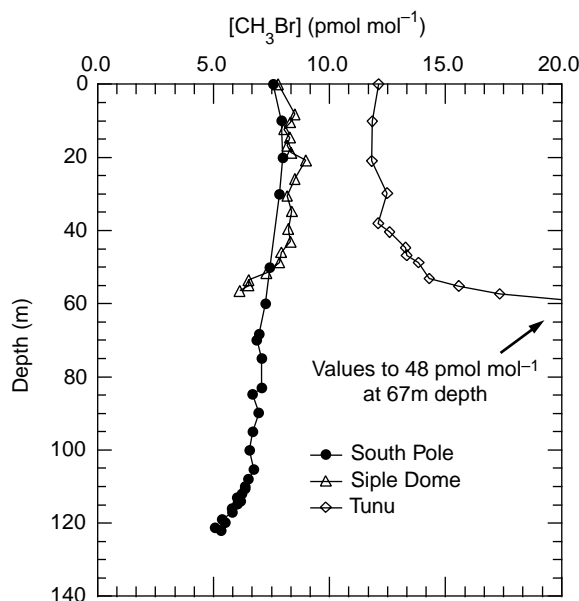
**Figure 3** Measured depth profiles of chlorocarbons (Siple Dome, Antarctica). Profiles at Tunu and the South Pole were similar. Atmospheric histories of these gases are poorly known. Natural sources have been suggested for each of these species, but these profiles show that natural or pre-twentieth-century sources are large only for CH<sub>3</sub>Cl. CCl<sub>4</sub> concentrations are significant at the bottom of this profile, which nominally represents the early 1950s. At Tunu, where the mean age of the bottom samples is in the early 1930s, and at South Pole, where the mean age dates from the early 1900s, the CCl<sub>4</sub> concentration near the bottom was essentially zero. The detection limit for CCl<sub>4</sub>, however, was ~5 pmol mol<sup>-1</sup>, owing to an interfering peak in the GC/ECD system. Traces of CH<sub>3</sub>CCl<sub>3</sub> were found in some of the deepest samples at all sites, but these may be artefacts associated with filling high-pressure steel flasks at the bottom of the hole or storage in the glass flasks. The detection limit for CH<sub>3</sub>CCl<sub>3</sub> was ~1.5 pmol mol<sup>-1</sup>. Note also that the 1993 peak in atmospheric CH<sub>3</sub>CCl<sub>3</sub> in the Southern Hemisphere<sup>1,31</sup> appears in the firn near 40 m depth at this site; this peak (1991–92 in the Northern Hemisphere) also appeared in the Tunu depth profiles (see Supplementary Information).

atmospheric mole fraction of CH<sub>3</sub>Cl has increased by about 40 pmol mol<sup>-1</sup> over the past century.

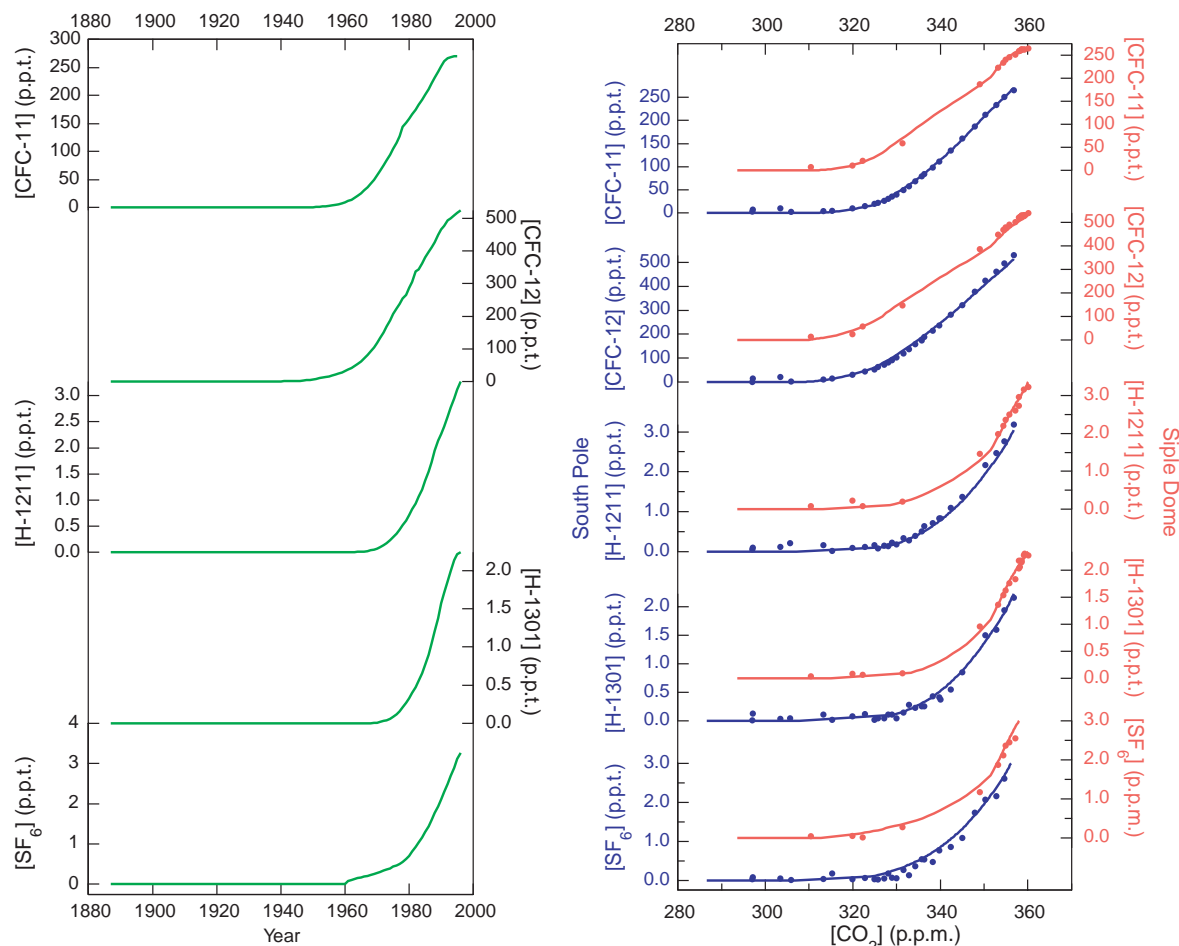
The firm data for CH<sub>3</sub>Br are more difficult to interpret. At the two Antarctic sites, CH<sub>3</sub>Br concentrations at the top of the firn air profiles are 20–25% higher than at the bottom, implying a significant pre-twentieth-century source and an increase in the atmospheric burden of this gas over the past 50–100 years (Fig. 4). Unlike CH<sub>3</sub>Cl, however, the observed difference of 5–10% between the surface samples and those below 10 m is not explained by seasonally varying mixing ratios; no significant seasonality is observed in the atmosphere at sites in the Southern Hemisphere<sup>32</sup>. This anomaly remains a mystery, as it was present at both Antarctic sampling sites and appears not to be a sampling or analytical artefact. More disturbing, however, are the samples from Tunu. At this seasonally warm and coastally influenced Greenland site, the concentration of CH<sub>3</sub>Br was very high near the bottom of the profile, reaching mixing ratios of nearly 50 pmol mol<sup>-1</sup> at the firn–ice transition (Fig. 4). We are confident that this increase in concentration at depth is not an artefact of sample collection, storage or analysis. CH<sub>3</sub>Br–depth curves were essentially identical in our two Tunu firn-air profiles, although the second profile did not extend as deeply as the first. Tests of the sampling equipment showed no evidence whatsoever of contamination by CH<sub>3</sub>Br (CFCs were present in our equipment, but our sampling design and procedure still allowed for concentrations of zero or nearly zero in deep samples.) Samples in steel and glass flasks yielded similar profiles for CH<sub>3</sub>Br and CH<sub>3</sub>Cl, and chromatographic results, obtained by both electron-capture or mass spectrometry, were independent of analytical technique. This leads us to believe that the observed high values (up to 48 pmol mol<sup>-1</sup>) for CH<sub>3</sub>Br in the firn at Tunu are real, although not necessarily of atmospheric origin. Concentrations of other marine, biogenic gases (such as CH<sub>2</sub>Br<sub>2</sub> and CH<sub>3</sub>I) also increased at depth in the Tunu firn, although the anomalies were smaller than for CH<sub>3</sub>Br.

### Interpreting concentration–depth data

Obtaining a representative atmospheric history of any gas from a diffusion model and measurements of firn air requires some knowledge of the diffusivity of gases in the firn. This can be derived from



**Figure 4** Measured depth profiles of CH<sub>3</sub>Br at all three sites. Whereas the profiles from South Pole and Siple Dome imply a similar atmospheric history involving both natural and anthropogenic sources, the data from Tunu are in direct contrast to the Antarctic observations and indicate that atmospheric CH<sub>3</sub>Br signals are not necessarily conserved in firn air.



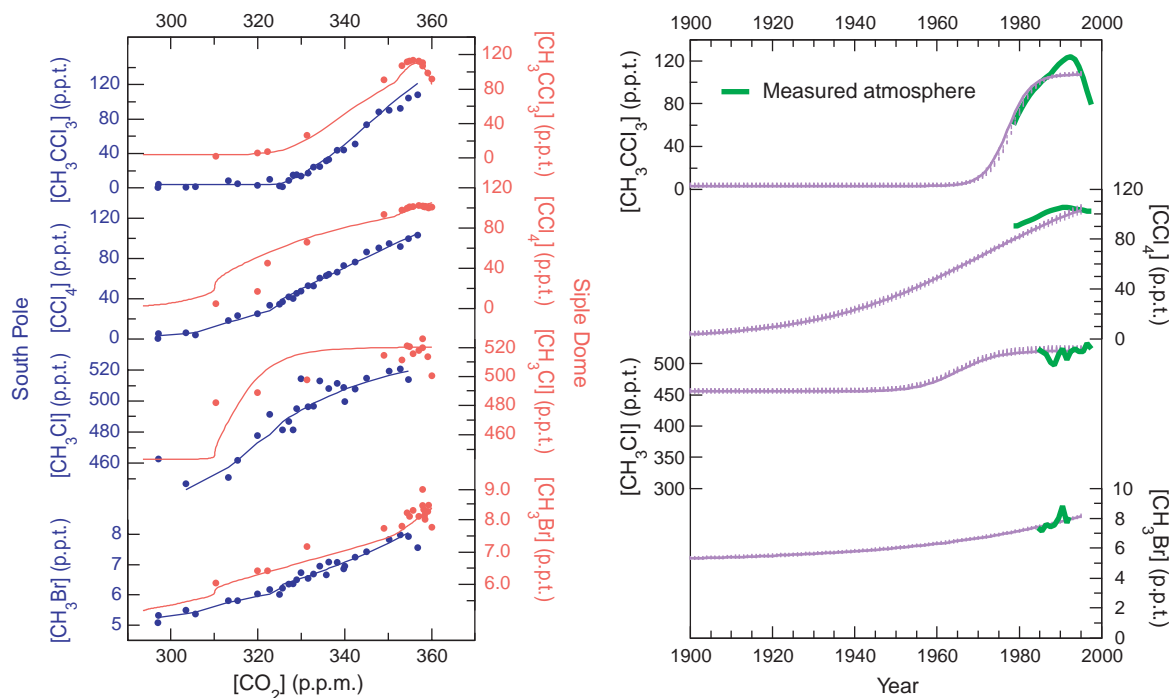
**Figure 5** Histories of CFCs, halons and SF<sub>6</sub> in the Southern Hemisphere. Data are for Antarctic firn air only. Modelled values are shown as lines and measured mole fractions are shown as points (p.p.t., pmol mol<sup>-1</sup>). Assumed Southern Hemispheric histories (green lines) for each of these gases are obtained from combinations of industrial emission models and real-time measurements<sup>1,35-37</sup> (left panel). These histories are incorporated into the firn at both sites with the one-dimensional firn diffusion model. Model results are then plotted as a function of CO<sub>2</sub> in firn air (right panel) for the South Pole (blue) and Siple Dome (red). (Note offset scales for each site.) Diffusivities used in these models are calculated from Wilke and Lee<sup>49</sup>, except for CFC-11 which was lowered by 10%, but still remains

within uncertainties. Lifetimes used for the gases are those given in the 1994 Scientific Assessment of Ozone Depletion<sup>38</sup>, except for H-1211, which was lowered to 11 years to assure concordance with current atmospheric measurements<sup>37</sup>. The good agreement between model results and measurements at these two sites, which have different firn depths and diffusion profiles, indicates that the assumed histories are consistent with concentrations observed in the firn. The detection limit for SF<sub>6</sub> in the South Pole samples was 0.3 pmol mol<sup>-1</sup>, a value that was much improved for analysis of samples from the other two sites.

density–porosity–diffusivity relationships<sup>19</sup>. These relationships, however, are poorly constrained, so we prefer to calibrate diffusivity with the measured atmospheric history of CO<sub>2</sub> deduced from real-time flask samples and the Law Dome ice core<sup>33</sup>. We refrain from modelling the Tunu profile because of the extensive convective zone and the possibility that the firn-air CO<sub>2</sub> profile at that site is erroneously offset by covariance between seasonal convective mixing and seasonal variations in atmospheric CO<sub>2</sub> (‘rectifier’ effects). To account for the effects of diffusion in the firn on each species at the South Pole and Siple Dome, we use the simple one-dimensional firn diffusion model described in detail by Battle *et al.*<sup>16</sup>. As in that investigation, we infer a site-specific diffusivity–depth relationship by adjusting diffusivity until the model reproduces the observed CO<sub>2</sub> firn-air profile when driven by the atmospheric CO<sub>2</sub> history. We then calculate halocarbon–depth profiles using this adjusted diffusivity–depth profile in the diffusion model. However, we examine these as halocarbon–CO<sub>2</sub> rather than halocarbon–depth profiles; the former are much less sensitive to errors in the inferred profiles of diffusivity versus depth. Our results remain sensitive to errors in the diffusivities of halocarbons relative to the diffusivity of CO<sub>2</sub>.

We apply the firn diffusion model with one of two goals, depending on the halocarbon: (1) to test an independently derived atmospheric history, or (2) to infer an atmospheric record for species with uncertain or unknown histories. The first approach is suitable for gases such as the CFCs, halons and SF<sub>6</sub>, for which atmospheric histories have been derived from emission estimates and real-time measurements. We use these histories and the firn-air diffusion model to predict concentration–CO<sub>2</sub> profiles for these gases and to compare the predictions with observations in the Antarctic firn. The second approach is used for those chlorocarbons and methyl halides for which there is insufficient information to estimate or calculate complete atmospheric histories. In this approach we choose one or more suitably general mathematical descriptions of concentration as a function of time, with consideration given to recent direct atmospheric measurements as well as firn-air data. The free parameters of the mathematical expressions are then adjusted using inverse methods to optimize agreement between measured and modelled concentration–CO<sub>2</sub> profiles at one or both sites.

We cannot eliminate the possibility that these gases are very slowly produced or degraded in the firn. However, we have strong



**Figure 6** Histories in the Southern Hemisphere of halocarbons with uncertain emission records. Modelled (lines) and measured (points) mole fractions of  $\text{CCl}_4$ ,  $\text{CH}_3\text{CCl}_3$ ,  $\text{CH}_2\text{Cl}$  and  $\text{CH}_3\text{Br}$  are shown plotted against  $\text{CO}_2$  in firn air (left panel) for the South Pole (blue) and Siple Dome (red) (note offset scales for each site). The model results represent gas mole fractions (p.p.t.,  $\text{pmol mol}^{-1}$ ) predicted in the firn based on the atmospheric histories shown in the right panel (purple). These histories are inferred by optimizing the data–model agreement for the South Pole (blue lines) and then checking this for agreement with data from Siple Dome (red lines). Also shown are real-time atmospheric measurements (in green) from the

ALE/GAGE/AGAGE network<sup>25,51</sup> and from Khalil *et al.*<sup>9,52</sup>, normalized to NOAA/CMDL South Pole measurements<sup>1</sup>. In the inversion model, real-time atmospheric measurements have been used only to adjust the diffusivities<sup>49</sup> of  $\text{CH}_3\text{Br}$  (–20%) and  $\text{CH}_3\text{CCl}_3$  (–20%). The shapes of the inversion results are independent of these measurements. Atmospheric concentration histories shown here follow sigmoid curves, with parameters determined by the firn data. The use of other functional forms for the atmospheric histories yields indistinguishable results. Errors (shown as purple bars) correspond to a 68% confidence envelope.

evidence that such production or degradation is not significant for most of them. Agreement of emission records with the firn model for those gases with available data provides one level of assurance. Consistent histories inferred from measurements at Siple Dome and the South Pole provide additional assurance; Siple Dome and the South Pole are sites sufficiently different in firn properties that any physical, biological or chemical effects on the gas concentrations should be expressed differently at these two sites.

**Tests of independently derived atmospheric histories**

Concentration– $\text{CO}_2$  profiles predicted for CFCs, halons and  $\text{SF}_6$  based on emission histories<sup>6,34</sup>, real-time measurements<sup>1,35–37</sup> and firn-air diffusion modelling are in good agreement with firn-air data (Fig. 5). This agreement, together with zero or near-zero concentrations in the oldest samples, is consistent with solely anthropogenic sources of these gases. It also suggests that the emission models used<sup>7,36</sup> yield reasonably accurate estimates of the early atmospheric histories.

The one significantly inconsistent species is halon H-1211. Both modern measurements and firn results suggest either a shorter lifetime than that given solely by atmospheric chemistry models (11 compared to 20 years) or lower emissions<sup>37,38</sup>. The atmospheric curve and model output in Fig. 5 incorporate the 11-year lifetime. For the CFCs, for which significant emissions began in the 1940s, analyses of firn air provide data for long periods where few or no real-time measurements are available<sup>36</sup>. For the halons, with significant emissions beginning in the 1960s, real-time measurements span a larger fraction of their atmospheric history, although calibrations of earlier measurements are less certain<sup>30,37</sup>. For  $\text{SF}_6$ , with significant emissions beginning in the 1970s, the concentration history is derived almost entirely from direct atmospheric

measurements<sup>28,35</sup>, and thus is insensitive to errors in estimates of emissions or lifetimes.

**Inferred atmospheric records of chlorocarbons**

$\text{CCl}_4$  appears to be derived solely from anthropogenic sources, but this conclusion must be tempered by the analytical uncertainty of  $\pm 5 \text{ pmol mol}^{-1}$  for the lowest-concentration samples, owing to an interfering peak in the GC/ECD system. This inference is based primarily upon the longer South Pole firn-air record (Fig. 6), although the concentration of  $\text{CCl}_4$  also does not differ from zero at the bottom of the Tunu profile. The firn data do show that  $\text{CCl}_4$  has been present in the atmosphere for a longer time than the CFCs, owing to its earlier industrial use. This earlier use also appears in the deep ocean record where  $\text{CCl}_4$  is present in the relative absence of CFCs<sup>39</sup>. Although our data from Siple Dome suggest that, before 1960,  $\text{CCl}_4$  was substantially lower in concentration than predicted from estimated production and emissions<sup>40</sup>, the data from the South Pole agree quite well with the emission prediction. Emission estimates for  $\text{CCl}_4$ , however, are much less certain than for the CFCs or halons. The lowest value at Siple Dome, corresponding to the late 1940s or early 1950s, was 4–7  $\text{pmol mol}^{-1}$ , but the South Pole data suggest a value of about 35  $\text{pmol mol}^{-1}$  for 1950. In an early analysis of  $\text{CCl}_4$  emissions, Galbally<sup>41</sup> used a lifetime of 38 years to derive an expected atmospheric mixing ratio of 40  $\text{pmol mol}^{-1}$ . More recently, and using a lifetime of 35 years, Walker *et al.*<sup>40</sup> suggest a value of about 33  $\text{pmol mol}^{-1}$  for  $\text{CCl}_4$  in the Southern Hemisphere in 1950. Though uncertainties are large, both of these estimates from emission records are reasonably consistent with our South Pole data since the 1950s, yet are lower for earlier years. Unfortunately, the inconsistency between Siple Dome and South Pole data suggests that  $\text{CCl}_4$  is, to some extent, either consumed or absorbed in the

firn; thus, we cannot make an unambiguous reconstruction of its concentration history.

Although the derived atmospheric record of  $\text{CH}_3\text{CCl}_3$  is consistent at the two Antarctic sites, which suggests that this gas is stable in firn air, two data points in the lower part of the South Pole record do show measurable amounts of  $\text{CH}_3\text{CCl}_3$ . These, however, are most probably caused by contamination. The lowest value at each of the three sites, representing years from the 1890s to the 1940s, was  $<2 \text{ pmol mol}^{-1}$  ( $<2\%$  of maximum atmospheric levels). Such concentrations are very near or below our limit of detection ( $3\text{--}5\sigma$ ; see Supplementary Information) and probably result from low-level contamination in the sampling apparatus. Note also that, although the turnaround in atmospheric  $\text{CH}_3\text{CCl}_3$  was recorded in the firn at Tunu (Fig. 3), this was not the case at South Pole (Fig. 6). This is because the South Pole was sampled only shortly after the turnaround. There is a time lag of about one year in transporting signals from the Northern Hemisphere to the Southern Hemisphere and wind pumping causes some mixing in the uppermost part of the firn, so the signal would be suppressed or absent in the South Pole firn in early 1995.

Because the inferred temporal change in  $\text{CH}_3\text{Cl}$  is small relative to its variability in the firn air, a detailed history cannot be estimated reliably from these data (Fig. 6). Nevertheless, the difference of  $5\text{--}10\%$  between bottom and mid-hole samples remains significant and suggests that the atmospheric burden of  $\text{CH}_3\text{Cl}$  has increased by about this amount during the past century.  $\text{CH}_3\text{Cl}$  is the most abundant chlorine-containing gas in the atmosphere and is emitted from the ocean<sup>42</sup>, from biomass burning<sup>43</sup>, and by fungi<sup>44</sup>. Its current atmospheric budget remains uncertain. Real-time measurements of atmospheric  $\text{CH}_3\text{Cl}$  extend back only to 1980<sup>9</sup> and show wide seasonal oscillations. The firn data represent a much longer time span, and are compatible with the real-time measurements.

### Methyl bromide

Methyl bromide measurements from the South Pole and Siple Dome suggest a simple atmospheric history, with a rate of growth increasing from  $0.01 \text{ pmol mol}^{-1} \text{ yr}^{-1}$  in the early 1900s to  $0.05\text{--}0.06$  ( $\pm 0.01$ )  $\text{pmol mol}^{-1} \text{ yr}^{-1}$  (90% confidence limits) during the 1970s and 1980s. These two sites differ in snow accumulation rate, firn depth and temperature (Table 1). Thus the similarity of the two  $\text{CH}_3\text{Br}\text{--CO}_2$  profiles suggests that the record in the firn is atmospheric in origin. Taken at face value, such a record implies that the concentration of  $\text{CH}_3\text{Br}$  was increasing slowly in the atmosphere through the first half of the century, perhaps as a function of increased biomass burning or some other global change. The upturn in the mid-1960s coincides with the onset of  $\text{CH}_3\text{Br}$  use as an agricultural fumigant, which suggests that the increase since the 1960s could indicate the expected reduction, about  $15\text{--}25\%$ , from the international ban on the use of this gas as a fumigant<sup>45</sup>. However, the response of  $\text{CH}_3\text{Br}$  in the atmosphere to a ban on agricultural use is also dependent upon how other sources have changed since 1960. The budget of  $\text{CH}_3\text{Br}$  for the modern atmosphere, calculated from what is known of sources and sinks, is grossly out of balance. Based upon current understanding<sup>46,47</sup>, there is a large source of this gas that has not been identified. From the atmospheric concentrations implied by the deepest samples at the South Pole, it appears that this 'missing' source was also present at the turn of the century. These results suggest that the unidentified source is separate from modern fumigation practices, or that the overall sink, calculated for  $\text{CH}_3\text{Br}$  from atmospheric reactions and loss to the oceans and soils, is currently overestimated.

The main problem in interpreting the  $\text{CH}_3\text{Br}$  data comes from the Tunu site, where concentrations of  $\text{CH}_3\text{Br}$  increased with depth (Fig. 4). The Tunu record does not appear to reflect past atmospheric changes, and it casts some doubt upon the utility of the Antarctic data. The simultaneous occurrence of  $\text{CH}_3\text{Br}$  at  $50 \text{ pmol mol}^{-1}$  in the Northern Hemisphere and  $5 \text{ pmol mol}^{-1}$  in

the Southern Hemisphere is highly improbable, as it would require an atmospheric lifetime of 0.1 year or less for  $\text{CH}_3\text{Br}$ . All evidence today points to a lifetime of 0.5–1.2 years (ref. 47). Locally increased atmospheric concentrations are possible, but unlikely at these levels in remote areas. The most logical explanation is that  $\text{CH}_3\text{Br}$  has been injected into the firn air at Tunu, perhaps by desorption or *in situ* production. Tests with our firn diffusion model indicate that one can account for the anomalous enrichments only by invoking net injection of  $\text{CH}_3\text{Br}$  at or near the firn–ice transition (see Supplementary Information). We know of no physical, chemical or biological mechanism that could easily explain this injection. Simple adsorption followed by subsequent release during densification would have injected  $\text{CH}_3\text{Br}$  into the firn air at all three sites. Abiotic chemical transformation at such cold temperatures ( $-45^\circ\text{C}$ ) cannot be ruled out, although attempts to identify possible source materials are speculative. Tunu has significant marine influence and is located in an area affected by arctic haze, which is known to contain significant amounts of bromine<sup>48</sup>. There is no evidence to date suggesting that organisms grow at the low temperature of the firn, but it is possible that loosely bound material could be slowly released from enzymes or cell surfaces. Whatever the source of the anomalous  $\text{CH}_3\text{Br}$ , we cannot prove it to be absent in Antarctica. However, if the process is driven at the firn–ice transition zone, as it most probably was at Tunu, then it could not have been significant at the South Pole or at Siple Dome, which yield observed profiles of concentration decreasing monotonically with depth to the bottom of the holes. Even a very low net production at the lock-in zone would have changed the shape of the profiles noticeably, and also would have elevated the bottom concentrations substantially. Competing, unknown production and degradation processes throughout the firn might have altered the firn-air concentrations of  $\text{CH}_3\text{Br}$ , but the probability is low that these processes would produce similar profiles at the two physically dissimilar Antarctic sites.

### Summary

Antarctic and Greenland firn can provide reliable archives of many atmospheric halocarbons dating back to the late 1800s, extending records of gases that have been measured in real time only during the past two decades. Robust records of CFCs, halons and  $\text{SF}_6$  extracted from the measurements of firn air agree with real-time estimates in the later parts of the profiles, corroborate emission models for some species and are useful in evaluating lifetimes and emission estimates for others. Although there are still important uncertainties, our data refine halocarbon histories and give experimental evidence about their pre-anthropogenic concentrations. It appears that for many species the cold, dry air in the firn preserves the gases. Except for  $\text{CH}_3\text{Cl}$  and  $\text{CH}_3\text{Br}$ , which have significant natural sources, all of the halocarbons studied appear to have been derived entirely from emissions during the twentieth century.  $\text{CH}_3\text{Br}$  and perhaps  $\text{CCl}_4$  are, for unknown reasons, not always conserved in firn air, and other reactive halocarbons could conceivably behave similarly. □

### Methods

Two holes were drilled at each site. At the South Pole, both boreholes reached the firn–ice transition; at Tunu and Siple Dome the second holes ended in the diffusive zone. We only consider data from the first hole at Siple Dome for our model because of inconsistencies in the sampling protocol. Low-pressure samples ( $\sim 120 \text{ kPa}$ ) were collected into duplicate, 2.5-litre glass flasks at all three sites. Higher-pressure samples ( $\sim 380 \text{ kPa}$ ) were also collected into single or duplicate 2.4-litre stainless-steel flasks at Tunu and Siple Dome. Details on drilling and flask filling can be found in Battle *et al.*<sup>16</sup>. Glass flasks were filled at all three sites with a pump (MB-158, Metal Bellows, Senior Flexonics, Sharon, Massachusetts) attached to nylon or Dekabon tubing, and analysed by GC/ECD for 11 trace gases.  $\text{CO}_2$  and  $\delta^{15}\text{N}$  of  $\text{N}_2$  also were measured in air from the glass flasks. Surface air was excluded from the borehole by inflating a

natural rubber bladder with stainless-steel end-caps. After the bladder was inflated, ~500–1,500 litres of firm air was extracted and pumped to waste, followed by flushing of the sample flasks with 10 volumes of firm air. Stainless-steel flasks filled with a pump (KNF Neuberger, Princeton, New Jersey) at Tunu and Siple Dome were analysed for over 20 halocarbons by GC/ECD and by gas chromatography with mass spectrometric detection (GC/MS). Measurements were calibrated with gravimetrically prepared standard gases, typically spanning a range of 20–150% of current atmospheric values. GC/MS calibration curves were linear in all cases and no zero-corrections were required; those for GC/ECD were predominantly linear. Zero air, a 20/80 mixture of purified, synthetic O<sub>2</sub> and N<sub>2</sub>, was analysed to confirm values obtained at the bottom of the profiles and to establish detection limits for both instruments. Detection limits for the CFCs typically were within 1 or 2 pmol mol<sup>-1</sup> of zero and, for SF<sub>6</sub> and the halons, within 0.1 and 0.2 pmol mol<sup>-1</sup> of zero.

Received 18 December 1998; accepted 28 April 1999.

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**Supplementary information** is available on Nature's World-Wide Web site (<http://www.nature.com>) or as paper copy from the London editorial office of Nature.

**Acknowledgements.** We thank those responsible for drilling at South Pole (D. Giles and J. Kyne), Tunu (J. Kyne and B. Bergeron) and Siple Dome (E. Ramsey, J. Brown, and S. Root). We also thank R. Myers for preparation of standards used in this work. This research was supported by the NSF Office of Polar Programs, the National Institute of Global Environmental Change (NIGEC), the Atmospheric Chemistry Project of NOAA's Climate and Global Change Program, and the Methyl Bromide Global Coalition.

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