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20th Century trends and budget implications of trihalomethanes and dihalomethanes inferred from North GRIP firn air

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Abstract

Four trihalomethane (THM; $CHCl_3$, $CHBrCl_2$, $CHBr_2Cl$ and $CHBr_3$) and two dihalomethane (DHM; CH_2BrCl and CH_2Br_2) trace gases have been measured in air extracted from polar firn collected at the North Greenland Icecore Project (NGRIP) site. $CHCl_3$ was also measured in firn air from Devon Island (DI), Canada, Dronning Maud Land (DML), Antarctica and Dome Concordia (Dome C), Antarctica. All of these species are believed to be almost entirely of natural origin except for $CHCl_3$ where anthropogenic sources have been reported to contribute ~10% to the global burden. A 2-D atmospheric model was run for $CHCl_3$ using reported emission estimates to produce historical atmospheric trends at the three firn sites, which were then input into a firn diffusion model to produce concentration depth profiles that were compared against the measurements. The anthropogenic emissions were modified in order to give the best model fit to the firn data at NGRIP, Dome C and DML. As a result, the contribution of $CHCl_3$ from anthropogenic sources, mainly from pulp and paper manufacture, to the total chloroform budget appears to have been considerably underestimated and was likely to have been close to ~40% at the maximum in atmospheric $CHCl_3$ concentrations around 1990, declining to ~19% at the beginning of the 21st Century. We also show that the atmospheric burden of the brominated THM's in the northern hemisphere have increased over the 20th Century while CH_2Br_2 has remained constant over time implying that it is entirely of natural origin.

1. Introduction

Halogens play an important role in the chemistry of both the troposphere and the stratosphere. In the polar troposphere, bromine chemistry has been implicated as the major cause of surface polar ozone depletion (Barrie et al., 1988; Berg et al., 1984; Cicerone et al., 1988) and bromine monoxide (BrO) as the major atmospheric oxidant driving mercury deposition (Ariya et al., 2004; Ebinghaus et al., 2002; Lindberg et al., 2002;

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Schroeder et al., 1998). The bromine resulting from the degradation of short lived bromocarbons has been implicated as a possible initiator for the autocatalytic activation and recycling of inorganic halogens from sea salt aerosols causing the observed "bromine explosion" events (Foster et al., 2001; Platt and Honninger, 2003; Sander et al., 2003; Vogt et al., 1999). It has been suggested that BrO may not be constrained to polar regions but could be widespread throughout the troposphere where it could influence the HO_x and NO_x cycles as well as providing a significant sink for dimethyl sulphide (von Glasow et al., 2004). If so, the short lived bromocarbons, in particular bromoform ($CHBr_3$), could constitute an important source of tropopsheric BrO especially in certain oceanic regions (e.g. tropics), where the acidity of sea salt aerosol is too low to maintain the autocatalytic cycles that release inorganic bromine species (Quack and Wallace, 2003).

In the stratosphere, bromine can deplete ozone with higher efficiency than chlorine, ~45 times (Daniel et al., 1999), and the dominant sources are understood to be from the photochemical degradation of methyl bromide (CH_3Br) and the long lived halon (bromoflurocarbon) compounds. However, recently there is increasing evidence to suggest that other short lived bromocarbon species ($CHBr_3$, CH_2Br_2, CH_2BrCl, $CHBr_2Cl$, $CHBrCl_2$, C_2H_5Br and $C_2H_4Br_2$) could be important source gases of stratospheric bromine. Simultaneous observations of several of these bromocarbons and BrO in the upper troposphere have been reported (Pfeilsticker et al., 2000), along with several aircraft (Schauffler et al., 1993, 1998, 1999) and balloon (Kourtidis et al., 1996; Pfeilsticker et al., 2000; Sturges et al., 2000) studies that have shown that these bromocarbons are present at concentrations in the part per trillion by volume (pptv) range and together are reported to contribute ~10–15% to the total organic bromine measured in the upper troposphere lower stratosphere (UTLS) region (Pfeilsticker et al., 2000; Sturges et al., 2000). It has further been suggested that a fraction of the inorganic bromine originating from the tropospheric breakdown of the same short lived precursors can reach the stratosphere at concentrations that can affect ozone levels (Dvortsov et al., 1999; Nielsen and Douglass, 2001; Pfeilsticker et al., 2000; Salawitch

et al., 2005).

Chloroform ($CHCl_3$) is the second most abundant organic source of natural chlorine to the atmosphere after methyl chloride and is an important source of tropospheric chlorine. As such it has been one of the subjects of the Reactive Chlorine Emissions Inventory (RCEI). $CHCl_3$ is only estimated to contribute ~2 Gg $CHCl_3$/yr or <10 pptv (Keene et al., 1999; McCulloch, 2003) to stratospheric chlorine as a result of its short tropospheric lifetime of 0.41 years (Ko et al., 2003) relative to other more persistent chlorine containing source gases. $CHCl_3$ is degraded in the troposphere, through oxidation by OH, to phosgene ($COCl_2$) a small percentage of which reaches the stratosphere where it can participate in ozone destruction (Kindler et al., 1995). Chlorine radicals derived from the atmospheric degradation of $CHCl_3$ can react with other organic gases, e.g., hydrocarbons and alkyl nitrates, in the troposphere similar to the OH radical. This can affect the tropospheric lifetimes of these species as well as influencing the local atmospheric composition, especially in the polar regions. In the case of hydrocarbons and alkyl nitrates the rates of reaction with chlorine radicals are greatly enhanced over those of OH oxidation (IUPAC, 2002; Muthuramu et al., 1994, and references therein).

The global tropospheric bromine loading has been reported to have peaked in 1998 and to have since declined by approximately 5% or ~0.8 ppt (Montzka et al., 2003). However, this decrease is based on the sum of methyl bromide and the halons only and is driven mainly by the reduction in atmospheric methyl bromide. The contributions of other organic bromine containing gases are considered to have remained constant as they are generally assumed to be almost entirely of natural origin.

Recently, Sturges et al. (2001) found no evidence for any significant temporal trends in the southern hemisphere concentrations of these gases. There are currently no published northern hemisphere trends of brominated trace gases as previous firn air studies of these species and CH_3Br at Devon Island, Canada (Sturges et al., 2001) and CH_3Br at Tunu, Greenland (Butler et al., 1999) resulted in the observation of anomalous profiles within the firn that were interpreted as having been affected by post depositional

effects.

In this work we present the first unperturbed firn profiles of four trihalomethanes ($CHBr_3$, $CHBr_2Cl$, $CHBrCl_2$ and $CHCl_3$) for the northern hemisphere from firn air collected at NGRIP (North GReenland Icecore Project), Greenland. The anthropogenic contribution to the $CHCl_3$ budget is assessed using a 2-D model and constrained using firn air measurements from NGRIP, Dome C and DML. The implications for the budgets of the other THM's are also considered based on the observed variations in the NGRIP firn air.

2. Sampling and analysis

2.1. Firn air measurements

Firn air samples were collected at NGRIP, Greenland (75.1° N, 42.4° W). Details of the NGRIP site (Reeves et al., 2005), sampling (Schwander et al., 1993; Sturges et al., 2001) and analytical methodologies (Fraser et al., 1999; Oram et al., 1995; Sturges et al., 2001) have been given elsewhere. In brief, aliquots of the firn air samples (~400 ml) were cryogenically concentrated using liquid argon, then desorbed and separated on a DB-5 capillary column (J&W, 60 m) prior to detection by single ion mode mass spectrometry (Micromass Autospec) with detection limits of ~0.001 pptv.

2.2. Firn modelling

A firn physical transport model that accounts for gravitational fractionation and gaseous diffusion (Rommelaere et al., 1997) was employed to interpolate atmospheric trends into firn concentration depth profiles. The required tortuosity profile was determined by inverse modelling of the CO_2 profile (Fabre et al., 2000). Diffusion coefficients of other molecules relative to CO_2 were estimated from Le Bas molecular volumes (Fuller et al., 1966). Thermal fractionation effects were not included in the model.

2.3. Atmospheric model

Temporal trends in atmospheric concentrations for the locations of the firn sites were generated using a 2-D atmospheric chemistry transport model. Details of the model are given in Reeves (2003). The model contains 18 equal area latitudinal bands and 6 vertical layers, each of 2.5 km. The ocean component of the 2-D model was removed as the lifetime of $CHCl_3$ with respect to loss to the ocean has been reported to be insignificant (Kindler et al., 1995; Yvon-Lewis and Butler, 2002) relative to the ~0.41 year lifetime resulting from the reaction with OH (Ko et al., 2003). Other sink terms including dry deposition and loss to soils were also removed as the reaction with OH was considered to be the dominant loss process (Keene et al., 1999; McCulloch, 2003). The stratospheric lifetime of $CHCl_3$ has been estimated at 3.18 years (Kindler et al., 1995) and this was used to determine the diffusive loss term out of the uppermost layer of the model.

3. Results and discussion

3.1. Firn depth profiles

3.1.1. $CHCl_3$

Figure 1 shows the $CHCl_3$ measurements at four polar sites (NGRIP, DI, Dome C and DML) plotted versus CFC-12 instead of depth. This is in order to give an axis that is more linear with time and that allows comparisons between different sites (Sturges et al., 2001) because CFC-12 is long lived and has increased in both hemispheres at the same rate. 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 and 5 m for DI and DML, respectively). There is excellent agreement between the two arctic sites (NGRIP and DI) and between the two Antarctic sites (DML and

Dome C). The plot would suggest that in the northern hemisphere the atmospheric concentration of $CHCl_3$ has increased by almost a factor of 2, from 7 to 14 pptv, before declining in more recent times to around 10 pptv. $CHCl_3$ in the southern hemisphere would also appear to have increased but not to the same degree with an increase of ∼2 pptv. The maximum $CHCl_3$ concentrations occur at the 66.99 m sample depth, which as will be shown later (Sect. 3.2) corresponds to a date of ∼1990.

The major sink for atmospheric chloroform is from the reaction with OH (Keene et al., 1999; McCulloch, 2003) and the global average concentration of these radicals has been reported to have increased by ∼15±22% between 1979 and 1989 and to subsequently have decreased to levels in 2000 that were ∼10±24% lower than those in 1979 (Prinn et al., 2001). These findings are disputed due to reported continued emissions of methyl chloroform, used to determine the OH trend, from Europe that call into question the magnitude of the initial OH increase and the existence of a negative trend during the 1990's (Krol et al., 2003). These variations even if they are correct are not only unlikely to be significant enough to explain the magnitude of the observed variations but they are also in anti-phase to the observed changes in the $CHCl_3$ concentrations such that variations from OH driven changes in the atmospheric lifetime cannot be responsible. It is also unlikely that the observed variations recorded in the firn are due to changes in the natural fluxes from the oceans and soils as a result of the relatively short timescales involved. Although, the perturbation of the natural source fluxes by anthropogenic activities cannot be discounted, e.g., variations in soil based emissions as a result of changing agricultural practices or increased oceanic emissions resulting from human forced climatic changes.

3.1.2. Bromocarbons

Figure 2 shows the measured concentration depth profiles of $CHBr_3$, $CHBr_2Cl$, $CHBrCl_2$, CH_2BrCl and CH_2Br_2 derived from NGRIP firn air. The lines represent the firn model outputs corresponding to constant atmospheric burdens over time (the scenarios in all cases begin in 1900). As a result of their OH and photolysis sinks (Ko et

al., 2003) the concentrations in the shallow firn reflect the seasonal variations in atmospheric concentrations (Kaspers et al., 2004; Sturges et al., 2001). Essentially, the summer firn drilling takes place when OH and photolysis levels are close to the peak annual values and as a result the concentrations of these halocarbons species are at a minimum. The gradients between the surface and 15 m reflect the atmospheric concentrations from the previous 6 months or so and as such show the variation between the winter and summer concentrations. The scatter in the ambient (0 m) measurements are the result of variations in the local meteorological conditions between sample collections.

The modelled lines shown in Fig. 2 incorporate seasonal cycles for $CHBr_3$ and $CHBr_2Cl$, based on measurements from Alert, Canada (Yokouchi et al., 1996) and for CH_2Br_2 from measurements at Alert, Canada and Point Barrow, Alaska (Montzka, personal communication, 2005). As no seasonality for $CHBrCl_2$ in the polar regions was available in the literature the same seasonality as for $CHBr_2Cl$ was assumed based on similarities in their lifetimes (77 and 69 days, respectively) of these two species (Ko et al., 2003). Yokouchi et al. (1996) reported no seasonal variation for CH_2BrCl at Alert and the NGRIP firn measurements show very little evidence for a seasonal cycle, most likely reflecting its longer atmospheric lifetime (Ko et al., 2003). It appears from these firn profiles that the annual mean atmospheric concentration of the CH_2Br_2 and CH_2BrCl have been constant implying that non-natural sources are insignificant, although for CH_2BrCl the interpretation is complicated in the deepest firn by high concentrations that could be the result of post deposition effects. In contrast, it is evident that an increase in the atmospheric concentrations of $CHBr_3$, $CHBr_2Cl$ and $CHBrCl_2$ are necessary in order to explain the observed behaviour in the deepest firn. The similar nature of the observed changes in the deepest firn would implicate a similar source driving the increases in the brominated THM concentrations. The large magnitude change in the $CHCl_3$ concentrations at NGRIP relative to the brominated THM's (Sect. 3.1.2) implies a different source is likely to be responsible for the observed variations in atmospheric $CHCl_3$.

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Figure 3 shows the measurements of $CHBr_3$, $CHBr_2Cl$ and $CHBrCl_2$ versus CFC-12 at NGRIP. As a result of the seasonally influenced concentrations the samples collected in the shallow firn (<30 m) are not included in this plot and the remaining data have been corrected for gravitational settling. The depth where the concentrations "level off" can be dated at ~1992, based on the dates determined through the atmospheric $CHCl_3$ modelling (Sect. 3.2). It is important to note that the diffusion coefficients and hence the diffusion rates for the various trace gases within the firn are distinct such that the inferred age scale is only approximate.

3.2. Atmospheric modelling

The global $CHCl_3$ emissions were separated into 5 major source terms; oceans, soils, pulp and paper (P+P), water chlorination (WC) and other industrial processes (OI). Biomass burning is only considered to be a very minor component, <2 Gg $CHCl_3$/yr or <1% of the total annual emissions (Lobert et al., 1999), relative to the other natural emissions and thus was not included.

3.2.1. Natural emissions and distributions

Natural emissions are reported to be significantly larger than anthropogenic releases but are also far less constrained (Keene et al., 1999; McCulloch, 2003). The absolute values for both ocean and soil emissions are based on measurements made by Khalil et al. (1998, 1983) whose calibration scale for $CHCl_3$ has been shown, through an intercomparison of measurements at Cape Meares (Khalil; 45° N, 124° W) (Khalil and Rasmussen, 1999) and Trindad Head (AGAGE; 41° N, 124° W) (O'Doherty et al., 2001), to over estimate $CHCl_3$ concentrations by a factor of ~2 relative to the Atmospheric Lifetime Experiment/Global Atmospheric Gases Experiment/Advanced Global Atmospheric Gases Experiment (ALE/GAGE/AGAGE) network. This factor is also likely to be appropriate for comparisons to measurements made by the National Oceanic and Aeronautical Administration – Climate Monitoring and Diagnostic Laboratory (NOAA-

CMDL) flask sampling network, which have been shown to be in good agreement (<5%) with the ALE/GAGE/AGAGE measurements (Cox et al., 2003; O'Doherty et al., 2001). Hence, it follows that the quoted emission values are also likely to be overestimates by the same factor such that the values used here are 180±45 and 100 +100/−50 Gg $CHCl_3$/yr for oceans and soils, respectively, i.e., ∼50% lower than those values reported by Khalil et al. (1999).

As a result of the significant reported uncertainties in the natural emission magnitudes and a lack of information concerning the likely source distributions, the RCEI did not attempt to estimate the latitudinal distribution. Nevertheless as part of the RCEI's work (Khalil et al., 1999) the ocean and soil emissions were constrained into 4 latitudinal bands; 0–30°, 30–90° for each hemisphere. In order to incorporate the natural emissions into our model it was necessary to estimate the distribution of the natural sources on a finer scale (i.e., 18 latitudinal boxes). This was achieved by assuming that the flux rates per unit area within these bands are uniformly distributed. The latitudinal distribution of natural emissions from this very simple approach, from now on referred to as ND1, is shown in Fig. 4.

A second approach was aimed at developing this first approximation into a more smoothed distribution. This approach involved determining emission factors for the ocean and soils based on their fractional global coverage (Gross, 1972), which was used in conjunction with the assumption that the tropical oceans (≤30°) are more productive than the sub tropics (>30°) and that this relationship was linear with latitude, i.e., increasing linearly towards the equator. This assumption is supported in essence by the greater emissions reported at lower latitudes by Khalil et al. (1999), although the linearity of the relationship is based on speculation only. For the soils, they were assumed to cover all areas that were not classified as oceans by Gross (1972) and the emission factor was assumed to be independent of latitude and thus constant for the entire globe. This assumption is clearly limited since there are large differences in soil and landscape types. Soil emissions from the most southerly box were set to zero since the only land mass <60° S is Antarctica. However, due to the resolution of

the model, it was not possible to assume the same for the most northerly box because there is not a permanent icesheet covering all land masses >60° N.

To obtain a distribution that fitted within the constraints of all these parameters it was necessary to use individual normalisation factors for both the oceans and the soils to correct the calculated figures within each of the 4 larger semi hemispheric bands to match those reported by Khalil et al. (1999). All of these applied normalisation factors were 1.0±0.1 giving good confidence for the calculated figures and for comparisons between the individual model boxes. It should be noted that the applied soil emission factors >33° S, i.e. in the most southerly semi-hemisphere, are higher by a factor of ~2.6 than for all other latitudes. This appears to be necessary in order to match the estimated emissions of Khalil et al. (1999) without requiring a large normalisation factor. Since land accounts for only 0.2 to 7.4% of the surface area in these boxes, this has a negligible effect on the overall budget. This distribution, from now referred to as ND2, is shown in Fig. 4.

3.2.2. Anthropogenic distributions and trends

The source strengths and distribution of $CHCl_3$ from anthropogenic emissions are reportedly smaller, but far better constrained, relative to the natural emissions. As part of the RCEI work a global 1°×1° grided inventory of anthropogenic $CHCl_3$ emissions was produced based on 1990 estimates (Aucott et al., 1999). The 3 Gg $CHCl_3$/yr emissions resulting from combustion sources, landfills and ruminants were not included in the grided inventory as they were considered to be too small to make a significant impact (Aucott et al., 1999). As emissions were given as mass emission per square metre it was necessary to multiply by the prescribed grid cell areas. These grid cell emissions were averaged into the latitudinal bands of the 2-D model to give a latitudinally dependent source distribution. The grided inventory suggests that ~93% of anthropogenic emissions are emitted in the northern hemisphere.

In 1990, 51% of the grided anthropogenic emissions (34 Gg $CHCl_3$/yr) were estimated to originate from the manufacture of pulp and paper, 32% from the chlorination

of drinking waters and the chlorination of cooling waters used in power plants (21 Gg $CHCl_3$/yr) and 17% from other industrial uses (11 Gg $CHCl_3$/yr) (Aucott et al., 1999).

3.2.3. Anthropogenic trends

By assuming that all three anthropogenic source terms have identical global distributions allows us to separate them and consider their temporal evolutions independently. As there are not any long term trends which describe the evolution of these source emissions it was necessary to use surrogates in order to extrapolate their values to the beginning of the 20th Century.

In the case of the pulp and paper industry the surrogate chosen was the global trend in paper production and/or consumption (Fig. 5) determined from a 3rd order polynomial fit to reported global figures for the period 1910–2002 (FAO, 2004; Paperloop, 2004; Robins and Roberts, 1996), with the greatest frequency of data occurring post 1960. The more recent higher frequency datasets of the FAO (2004) and Paperloop (2004) are for paper production, whereas the longer trend of Robins and Roberts (1996) is for paper consumption. There is good overlap between the three datasets, which suggests that the differences between production and consumption are negligible in the interests of this approximation. Now by assuming that in 1990 the amount of paper produced released the reported emissions of $CHCl_3$ facilitates the determination of an emission factor (145 g $CHCl_3$ / ton of paper) that allows the extrapolation of $CHCl_3$ emissions from the pulp and paper industry as a function of paper production. This emission factor lies within the range of previous estimates (Aucott, 1997, and references therein) and as such is consistent with previous calculations. In 1990, ~95% of the global bleached chemical pulp used molecular chlorine (AET, 2001) and therefore the relationship between $CHCl_3$ emissions and paper production ought to be close to 1:1 and in the pursuit of simplicity was assumed as such.

This surrogate was used to determine only the pre-1990 trend for the P+P industry due to significant changes in the industry during the 1990's (AET, 2001). The changing trends within the global industry are illustrated in Fig. 6, which shows that the

percentage of global bleached chemical pulp production using elemental chlorine has decreased by slightly more than a factor of 5, from ∼95% in 1990 to ∼17% in 2002, and that the elemental chlorine free (ECF) and totally chlorine free (TCF) bleaching methods have both increased over the same time frame, from 5% to 68% and 0.2% to 6.5%, respectively (AET, 2001). These changing trends are reflected, for the United States of America (USA) at least, by significant reductions (∼86%) in the air emissions of $CHCl_3$ from the P+P industry (USEPA, 2004). This declining trend was well approximated (R^2=0.98) by a 2nd order polynomial function, which was used in all further calculations. The decline in the USA's use of elemental chlorine in pulp production is shown (Fig. 7) to be well correlated (R^2=+0.74) with the global decrease (AET, 2001). This correlation suggests that it is reasonable to assume that the observed decrease in $CHCl_3$ emissions from the USA P+P industry (USEPA, 2004) also reflects what has been occurring on a global scale. This is a reasonably quantitative assumption since the USA's P+P production has accounted for ≥30–60% of world production over the last 40 years (Paperloop, 2004). These approximations were used to determine the declining trend in $CHCl_3$ emissions from the global P+P industry for the period 1990–2002 and combined with the surrogate trend based on paper production and consumption figures to give an estimation of the 20th Century emission history.

The global population was used as a surrogate for WC and OI processes and was based on the assumption that with an increasing population comes an increasing demand and use of chlorinated drinking water and an increasing demand for electricity and hence a likely increase in the amount of cooling water chlorinated for use in power stations. The increasing global population is also likely to reflect the additional demands of an industrialising society that are considered as part of the other industrial processes by the RCEI. The global population has been used previously as a surrogate for anthropogenic $CHCl_3$ emissions (Trudinger et al., 2004) and this trend was determined from population figures above the 1920 population, hence fixing a timeframe for zero emissions. The chlorination of water began at the turn of the century and became widespread by 1920 (AWWA, 2004) suggesting this was a reasonable approximation

for zero emissions.

The global population trend was determined from data published by the United Nations (UN, 2004) and the Population Reference Bureau (Ashford et al., 2004) with the higher frequency data occurring post 1950. It was necessary to assume a linear growth rate between 1900 and 1950 due to a lack of data. A surrogate global population trend was devised by correcting to population figures above that of 1920. Now by assuming that in 1990 the reported releases of $CHCl_3$ for the water chlorination and other industrial processes categories were associated with the surrogate population at that time allows the determination of emission factors, 6.28 and 3.34 Gg $CHCl_3$/billion people for water chlorination and other industrial processes, respectively. These emission factors allow the determination of $CHCl_3$ emissions from these industries as a function of the global population.

The temporal variations, over a 100 year period, for all source terms are shown in Fig. 8, including the natural source emissions from oceans and soils which are predicted to have remained constant over this time frame. Also shown in Fig. 8 are dashed lines relating to alternative temporal variations that will be described later in this section. An inherent assumption with this approach is that the latitudinal distributions of all source terms have remained constant with time.

3.2.4. Varying the soil source as function of population

To reconcile their modelling results, Trudinger et al. (2004) hypothesise that the soil source may have increased with time as a result of agricultural interference. This is supported by a recent report that suggests that the amount of land being cultivated has increased substantially in recent times and that since 1940 the amount of land turned over to agriculture was larger than in the two previous centuries combined (UN, 2005). However, the notion that cultivated soil emits more $CHCl_3$ than uncultivated soils is one of speculation and there is no supporting evidence for this at the current time.

To investigate the suggestion of an increasing soil source, the soil emissions were

fixed at 100 Gg $CHCl_3$ for 1990 and extrapolated back to the beginning of the century as a function of the global population in the same way as was performed for the WC and OI temporal variations. This trend is referred to from now on as the changing soil source (ΔSS). The effect of constant soil and changing soil emissions are discussed later.

It is apparent that a much smaller variation in the natural emissions (e.g., soils) would be needed relative to any changes in the anthropogenic emissions to affect the same magnitude change in the concentrations observed at the Antarctic sites, as a result of the northern mid latitude bias of the anthropogenic distribution.

3.2.5. Varying the magnitude of anthropogenic emissions

The level of uncertainty associated with each of the anthropogenic source terms suggest that these values could be up to a factor of 2 different for P+P emissions or up to a factor of 5 different for WC and OI emissions (Aucott, 1997). Therefore, all the anthropogenic emissions were doubled, which resulted in a better approximation to the NGRIP data (Fig. 9).

By using increasing population as a surrogate for anthropogenic emissions Trudinger et al. (2004) had difficulties modelling the recent declining trend in atmospheric levels at Cape Grim, Tasmania as observed from ALE/GAGE/AGAGE measurements such that they suggested that the anthropogenic emissions were most likely to have increased with population until 1990 before decreasing slightly contrary to the continued population growth. Following this the WC, OI and ΔSS trends, which are all based on the same global population trend, were also modelled fixed at 1990 levels for all subsequent years. These alternative temporal variations are all shown in Fig. 8 as dashed lines. The effect of this change is clearly illustrated in Fig. 9 where the observed declining trend resulting from the reduced emissions of the P+P industry are no longer offset by the increasing emissions from the WC, OI and soil processes. In the case of WC, this condition is supported, for the USA at least, by a USA Geological Survey report that would suggest that as much as the population has increased in the last 15 years

the amount of water withdrawn from the distribution system has remained relatively constant over the same period (USGS, 2004) due to water conservation measures. There was no information on the likely recent changes in soil and OI emissions.

It is also evident from Fig. 9 that the magnitude of the anthropogenic emissions required to fully capture the maximum values observed in the NGRIP firn air measurements still needs to be larger than double the reported values. The strong declining trend in atmospheric $CHCl_3$ observed at NGRIP coupled with the proposed source trends would suggest that only by further increasing the emissions from the P+P industry would it be possible to both model the maximum values observed in the firn while still maintaining a good approximation to the observed decline in the firn between 60 m and the surface. Several runs were preformed to evaluate the sensitivity of the model to increases in emissions from the P+P industry. During these model runs the natural emissions were constrained at a constant value of 280 Gg $CHCl_3$/yr throughout. The WC and OI emissions were constrained with the same population dependent time trends and incorporating either constant values post 1990 or increasing values based on the link to the global population, which allowed the two different trends to be compared. The magnitude of the WC and OI emissions were fixed at either the reported values (Aucott et al., 1999) or at double these values dependent on the particular run. The P+P emissions were varied between 3–5 times the value reported by Aucott et al. (1999).

The various model outputs are shown in Fig. 10 where it is clear that too effectively model the near surface concentrations the emissions from the WC and OI industries need to be double those reported in the literature effectively. P+P emissions between ~3–4 times the reported values would appear to be necessary to simulate the maximum $CHCl_3$ concentrations observed in the firn with the bias being towards the upper end of this range. We are not alone in believing that the anthropogenic emissions fluxes have been underestimated, Trudinger et al. (2004) also invoked an increase in emissions from anthropogenic sources to model their firn air measurements although our magnitude is smaller by comparison.

The conclusions regarding the magnitude of the anthropogenic emissions are based on the assumption that the magnitude of the natural emissions are correct. It should be noted that although the uncertainties in the natural source terms are fairly large the fact that the concentrations observed at the bottom of the firn at NGRIP where natural emissions account for >90% of the total emissions coupled with the modelled concentrations for Dome C and DML together suggest that the emission magnitudes are reasonable. The values corresponding to the model outputs corresponding to the increased anthropogenic emissions are shown as latitudinal variations for 1990 levels compared against the natural emissions in order to illustrate the importance of the anthropogenic contribution to the total budget. The largest contribution is in the northern hemisphere mid latitudes where this modelling would suggest that the anthropogenic emissions strongly dominant over the natural emissions (Fig. 11).

3.2.6. Latitudinal variation of peak anthropogenic emissions

In order to model the sensitivity of the location of the latitudinal maximum peak in the anthropogenic emissions the peak of the emissions was moved north and south while keeping the total emissions constant. The result is four different latitudinal distributions shown in Fig. 12. The base case scenario used to test these latitudinal distributions was with constant natural emissions, double the reported WC and OI emissions (Aucott et al., 1999) with constant values between 1990–2002 and treble the reported P+P emissions (Aucott et al., 1999). As might be expected the location of the maximum peak in the anthropogenic distribution has less effect on the modelled trends at sites that are far removed from the northern mid latitudes, i.e., DML and Dome C. At NGRIP (Fig. 13) the dependency is the largest and the concentrations vary by $\leq$+7.6/–7.1 % between peak emissions in box 2 and boxes 1 and 4, respectively. This approach also simulates a difference in transport rates, e.g., moving the maximum peak north simulates a more northerly bias in the transport and vice versa, that perhaps is not captured as a result of the parameterisation of the transport scheme within the 2-D model.

It is likely that the anthropogenic distribution used in this work is reasonably accurate since, for the majority of the anthropogenic emissions, the RCEI used the reported addresses of $CHCl_3$ emitting facilities to create their grided inventory. The largest uncertainty associated with the conversion of the RCEI grided inventory into the 2-D model is from the pulp and paper emissions from China and Russia. The location of their pulp and paper plants are not known accurately since they are not listed in the International Phillips' 1997 Paper Directory (Miller Freeman Information Services 1996), which was used by Aucott et al. (1999) to locate facilities in other parts of the world. Instead, the emissions for China and Russia were re-distributed based on population density (Aucott et al., 1999). In the case of China, this issue is complicated because its geographical location straddles two of the model boxes. However, the effects are likely to be small as China is responsible for <10% of global pulp and paper production (Johnston, 1996).

3.2.7. Varying anthropogenic emissions

The closest fitting model trends are shown for NGRIP, Dome C and DML in Fig. 14. There are four best fit trends that correspond to slightly different emission scenarios, as defined in the figure legends. At 1990 levels, the emissions for all four scenarios equate to oceanic emissions of 180 Gg $CHCl_3$, soil emissions of 100 Gg $CHCl_3$ and total anthropogenic emissions of ~160–190 Gg $CHCl_3$. These anthropogenic emissions are significantly larger than the estimated 66 Gg $CHCl_3$ reported by the RCEI (Aucott et al., 1999) and arise as a result of doubling the emissions from WC and OI and tripling or quadrupling those from the P+P industry. These increases were necessary in order to capture the magnitude of the variation observed within the firn air at NGRIP. Invoking more northerly transport would slightly reduce the estimated magnitude of the these emissions.

The modelling strongly suggests that the reported anthropogenic emission estimates are underestimated, especially for the P+P industry. The incorporated values for the WC and OI industries are within the described uncertainties of between a factor of 2

and 5 (Aucott, 1997). However, the emission values used for the pulp and paper industry are outside the described uncertainties of a factor of 2 (Aucott, 1997). This would suggest that the defined emission factors used to extrapolate the global emissions are inaccurate and need to be re-evaluated.

The four determined best fit trends model the maximum measured values at NGRIP reasonably well within the uncertainties associated with both the measurements and the model, although the values at the bottom of the firn are slightly over predicted in all but one of the modelled scenarios (Fig. 14). The same three trends which over predict the deepest firn at NGRIP also slightly over predict the absolute values observed from the Dome C and DML firn data, although the general trends are well simulated. An anthropogenic perturbation of the soil source cannot be ruled out and through the modification of the soil source, referred to as ΔSS, an improved fit to the southern hemisphere firn air could be obtained. In the absence of a varying soil source the over predicted values for the southern hemisphere firn air suggest that the estimations of the reported oceanic and soil based emissions could be slight over estimated.

The contribution of anthropogenic sources to the total global $CHCl_3$ emissions at the peak in 1990 was likely to have been ∼40% (Table 1) and is strongly dependent on exactly which values are chosen for the natural and anthropogenic emissions. What is clear is that this value is significantly larger than the ∼10–12% previously reported by Khalil et al. (1999) and McCulloch (2003) and slightly lower than the ∼60% estimated by Trudinger et al. (2004). This contribution declines between 1990 and 2001 as a result of the reduced emissions from the P+P industry but is still predicted to be ∼19% in 2001 (Table 1).

However, it is likely that the anthropogenic contribution is actually slightly higher than these values since to improve the model fits at all three firn sites would involve slightly lowering the natural and slightly increasing the anthropogenic emissions. The atmospheric lifetime for $CHCl_3$ determined from the model was 0.4±0.01 years, which is consistent with that recently reported by Ko et al. (2003). The total $CHCl_3$ emissions associated with the best fit scenarios discussed above were ∼440–480 Gg $CHCl_3$/yr at

the maximum peak in atmospheric levels around 1990, declining to ∼340 Gg $CHCl_3$/yr by 2001, which are both within 20% of the reported modelled OH sink of 410 Gg Cl/yr for 1990 (Keene et al., 1999; McCulloch, 2003).

The absolute values for the global and hemispheric averages, corresponding to the scenario incorporating a ΔSS and P+P emissions 3 times those reported by Aucott et al. (1999), suggest a global background of ∼5.4 pptv around the turn of the century (Fig. 15). This is higher than the ∼4 pptv southern hemisphere background predicted by Trudinger et al. (2004), although it is important to take into account the much lower resolution of their model and that their value is more likely to be representative of southern polar latitudes. The average global concentration between 1994–1998 is 10.2 pptv, which is higher than the 8.9±0.1 pptv reported by O'Doherty et al. (2001). The rate of decline, −0.29 pptv/yr, during this period is slightly outside the errors of the estimated decrease during the same period reported by O'Doherty et al. (2001). These would suggest that there are still some uncertainties with the results and budget implications of this modelling. The over estimates in the southern hemisphere that result by assuming constant natural emissions over the time frame of the modelling suggest that the absolute magnitude of the natural emissions could be slightly lower than those incorporated within the model.

3.3. Pulp and paper production versus water chlorination

The difference between $CHCl_3$ and the other brominated THM modelled trends (Sect. 3.1) would suggest that the major cause of the observed variation in the $CHCl_3$ concentrations at NGRIP does not result in significant brominated THM production. During both the processing of pulp and paper and through water chlorination, the added chlorine reacts with organic material through classic haloform reactions (Ballschmiter, 2003) to form principally $CHCl_3$, but in the presence of bromide the other brominated THM are also observed to be produced (Cooper et al., 1985; Rook, 1974; Rook et al., 1978). The major differences between these two industrial processes are the availability of bromide, which has been shown to directly effect the speciation of THM by-

products (Cooper et al., 1985; Richardson et al., 2003; Rook, 1974; Rook et al., 1978) and the amount of organic material that is present in the reaction system.

It is possible to make an estimation of the available pools of organic bromine that are present during pulp and paper production and water chlorination processes. The total water chlorinated globally has been estimated to be $\sim 3.8 \times 10^{15}$ litres/yr of which ~40% was inland source water, i.e., river water, and the remainder was coastal in origin, i.e., seawater (Quack and Wallace, 2003, and references therein). The reported concentrations of bromide in non-seawaters are shown in Table 2, which give a range of upper limit values for the potential formation of brominated organics assuming that all the bromide present reacts with the organic material. An estimate of the average chloride content in surface and ground waters is also shown in Table 2 for comparison. The concentration of bromide in average composition seawater has been estimated to be 67.4 mg/l (Libes, 1992). Using these figures the total organic bromine that could result from the chlorination of drinking and cooling waters is $\sim 1.5 \times 10^{14}$ grams/yr dependent on the concentration of bromide in the inland source water.

In 1990, around the time of the observed maximum peak in reconstructed atmospheric $CHCl_3$, it has been estimated that, globally, 6.27×10^{10} kg of bleached chemical pulp was produced through the use of elemental chlorine (AET, 2001). The average bromide content of a variety of tropical and temperate woods are shown in Table 3. An estimate of the average chloride content in tropical and temperate woods is also shown in Table 3 for comparison. Using these figures the total organic bromine that could result from the production of pulp and paper is between 4.1×10^6–6.2×10^8 grams/yr, depending on the whether the wood being processed is temperate or tropical in origin.

These are only approximate figures and assume that all available bromide reacts with the available organic matter. However, they suggest that water chlorination has a much larger pool (6–8 orders of magnitude) of bromide and hence a greater potential to produce brominated organics, such as the brominated THM's, relative to the production of pulp and paper.

The much lower availability of bromine during the processing of pulp and paper rela-

tive to water chlorination would imply that THM by-production from this process is significantly biased towards $CHCl_3$ formation. The difference in available bromide provides an explanation for the observed differences in the firn air measurements at NGRIP between $CHCl_3$ and the other brominated THM species, which are most likely formed as by-products in water chlorination. Following the higher bromide concentrations in seawater it is also logical to conclude that when the source water to be chlorinated is marine derived the speciation of THM are likely to be more biased towards the bromine containing species. This suggestion is supported by larger estimates of $CHBr_3$ production from coastal power plants relative to inland ones (Quack and Wallace, 2003) and with observations of high concentrations of $CHBr_2Cl$, $CHBrCl_2$ and $CHBr_3$ around seawater cooled power plants (Allonier et al., 1999; Jenner et al., 1997).

3.4. Implications for the THM budgets

The concentration depth profiles of the brominated THM, as shown earlier (Figs. 2 and 3), would imply that their atmospheric burdens have increased during the 20th Century. As has been described for $CHCl_3$ (Sect. 3.1.1) the reported variations in OH cannot account for the observed concentration variations in the firn. It also seems unlikely that natural variations in solar radiation would have declined significantly over the last 50 years or so to account for the increases in these species considering the timescale involved.

As part of work reported by the WMO in the 2002 report the atmospheric removal rates were estimated for the brominated THM's (Table 4) by dividing the global average burden by the global average lifetime (Ko et al., 2003). The global average burden was determined by deriving an expression based on the median boundary layer mixing ratios determined during the TRACE-P, PEM tropics A and B campaigns coupled with the estimated altitudinal profiles (Ko et al., 2003). This expression assumed that removal in the stratosphere was negligible and that the atmospheric lifetime was uniform throughout the troposphere. In order to estimate the emission fluxes in the northern hemisphere only, the species were assumed to be in steady state such that the annual

emission flux was equivalent to the annual removal rate and the value was halved. The uncertainty, shown in Table 4, reflects both the range in the estimated removal rates resulting from the different median mixing ratios and the ranges in these mixing ratios used to determine the atmospheric burdens (Ko et al., 2003). It does not include any uncertainty in the average global atmospheric lifetime.

It was possible to estimate the increase in fluxes for the three brominated THM's as a function of the observed increases from the NGRIP firn air measurements. This assumes that the concentrations at NGRIP are representative of the northern hemisphere such that the observed increases in the firn can be directly related to corresponding increases in the annual northern hemispheric fluxes. Between the bottom of the firn and the depth (~60 m) where the concentrations are observed to "level off" the concentrations of $CHBr_3$, $CHBr_2Cl$ and $CHBrCl_2$ are observed to increase by ~20% (Table 5), which would suggest similar percentage increases in the annual fluxes reflecting the contribution from anthropogenic sources (Table 5). This depth interval in the NGRIP firn represents approximately 40 years of history (~1950–1990) according to dating based on the modelled and measured atmospheric evolution of CFC-12 (Sturges et al., 2001). The estimated uncertainty, shown in Table 5, reflects the likely errors in determining the observed increases in the firn between the close off and 60 m.

$CHBr_3$ has been reported to contribute ~95% (Allonier et al., 1999; Jenner et al., 1997) to the total THM's measured in coastal power plant effluent such that this is reported to be the dominant source of anthropogenic $CHBr_3$ (Quack and Wallace, 2003). As a result the contribution of the other brominated THM's ($CHBr_2Cl$ and $CHBrCl_2$) are much smaller and this difference may account for the much smaller estimated fluxes of these species relative to $CHBr_3$ (Table 5). This is in agreement with the observations of $CHBr_2Cl$ and $CHBrCl_2$ being present at concentrations approximately 4–7% of $CHBr_3$ in a variety of coastal power plant effluents (Allonier et al., 1999; Jenner et al., 1997). Interestingly, the estimated fluxes of $CHBr_2Cl$ and $CHBrCl_2$ (Table 5) are ~4% of the $CHBr_3$ flux, which would support the source of these species being the result of seawater chlorination.

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The total global emission of bromoform from both fresh and sea water chlorination has been estimated to be ~28 Gg Br yr^{-1} (Quack and Wallace, 2003) with the majority (~90%) being from sea water chlorination used in coastal power stations. Estimates of the hemispheric distribution of electricity production (WRI, 2004) would suggest that >90% of these emissions (~25 Gg Br yr^{-1}) are likely to be located in the northern hemisphere, which considering the associated uncertainties results in good agreement to the 20 Gg Br yr^{-1} estimated from this work (Table 5). Gschwend et al. (1985) reported the total organobromines estimated to result from water chlorination to be 4.6 Gg Br yr^{-1}, which was considerably lower especially considering that it also includes emissions of other bromine containing gases. The most significant difference between the estimates of Quack and Wallace (2003) and Gschwend et al. (1985) is that Quack and Wallace (2003) report that the chlorination of seawater is by far the larger source of $CHBr_3$ (~90%) whereas Gschwend et al. (1985) estimated that freshwater chlorination produces an order of magnitude more organobromines than seawater chlorination. Our results show that, in the case of bromoform at least, seawater chlorination far outweighs freshwater as an anthropogenic source of bromoform, and the small apparent atmospheric fluxes of the bromochloromethanes, which are believed to exceed emissions of bromoform in freshwater chlorination (Lepine and Archambault, 1992), also argues against a significant impact of freshwater chlorination on observed atmospheric THM concentrations.

Another consideration is that, due to its location (~75° N) and the modelled transport pathways (Kahl et al., 1997), the concentration increase observed at NGRIP could be more representative of only the northern most semi hemisphere (30–90° N) as opposed to the whole of the northern hemisphere. This suggests that the concentration increase in $CHBr_3$ in the firn would be representative of only emissions that are emitted into these latitudinal bands where they are likely to be subjected to a longer lifetime than tropical emissions (<30° N) but that are also effectively emitted into a smaller volume. The increased lifetime and the reduced dilution factor act in opposing directions such that they could arguably cancel each other out, which would suggest that the estimated

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anthropogenic flux from this work could still be a good approximation. Interestingly, the absolute magnitude of $CHBr_3$ and $CHBr_2Cl$ concentrations at NGRIP are reasonably comparable to the concentrations detected during the TRACE-P and the PEM tropics A and B campaigns (Blake et al., 1999a, b, 2001, 2003) that were used to determine the global burden (Ko et al., 2003).

The estimated anthropogenic fluxes for the brominated THM's suggest, assuming they are entirely the result of seawater chlorination, that seawater chlorination is a significant atmospheric source of these species accounting for ~10% of the estimated global fluxes (Ko et al., 2003). However, these anthropogenic fluxes are less significant when compared to the estimated natural flux of ~800 Gg Br yr^{-1} reported by Quack and Wallace (2003). Since there appears to be a measurable rise in concentrations at NGRIP this suggests that if the global flux were to be much larger than that estimated in the WMO 2002 report, then the estimated anthropogenic flux might also be proportionately larger. Conversely, if much of the global flux were located in the tropics then it might be, as a result of the shorter lifetime of $CHBr_3$ within the tropics, that the observations at NGRIP are relatively insensitive to the magnitude of such a flux.

4. Summary

We have presented polar firn air data for $CHCl_3$ from both hemispheres that shows excellent agreement between sites in the same hemisphere and also evidence for changes in the $CHCl_3$ burden over the last century, with the greatest variations occurring in the northern hemisphere. With the aid of 2-D atmospheric chemistry model we have shown that the contribution of anthropogenic emissions to the total global $CHCl_3$ budget was previously been underestimated and was likely to have been as high as ~40% at the maximum peak in atmospheric $CHCl_3$ concentrations in 1990. Our results also suggest that the soil source may not have been constant over time and could have been increasing over the 20th Century possibly as a result of agricultural interference. The 2-D model results indicate that anthropogenic sources dominate over

natural emissions >20° N and suggest that the global $CHCl_3$ concentration has doubled over the last century. From NGRIP firn air we have shown measurements of 5 brominated species ($CHBr_3$, $CHBr_2Cl$, $CHBrCl_2$, CH_2Br_2 and CH_2BrCl) and with the aid of firn diffusion model have shown that while CH_2Br_2 is entirely of natural origin the brominated THM's show evidence for increases in their atmospheric burdens over the 20th Century, which would appear to be predominantly the result of the chlorination of seawater used as cooling water in coastal power stations contributing ~10% to the global budgets.

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Table 1. Comparison of anthropogenic and total estimated $CHCl_3$ emissions for 1950, 1990 and 2002.

Year	Emissions Gg yr^{-1}		Anthropogenic
	Anthropogenic	Total	Contribution (%)
1950	37–46	260–270	14–17
1990	160–190	440–470	36–41
2001	65	340	19

Table 2. Mean halide contents of ground and surface source waters for disinfection treatment.

Water Type	[Cl^-] mg/l	[Br^-] mg/l	References
Ground	25	0.12	Luong et al. (1983)
Surface	35	0.15	
Non-Seawater	–	<2	Richardson et al. (2003)

Table 3. Mean halide contents of tropical and temperate wood.

Wood Type	$[Cl^-]$ mg kg^{-1} Dry Wt.[a]	$[Br^-]$ mg kg^{-1} Dry Wt.[b]
Tropical	254	3.7, <10[c]
Temperate	109	0.07

[a] Watling and Harper (1998).
[b] Lee-Taylor and Holland (2000).
[c] Harper (personal communication, 2005).

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Table 4. Estimated lifetimes, removal rates/emission fluxes and associated uncertainties for the three brominated THM in the northern hemisphere only (adapted from Ko et al., 2003).

Species	Lifetime (years)	Estimated Removal Rate/Emission Flux Average, [Range] (Gg Br yr^{-1})	Uncertainty in Estimated Removal Rate/Emission Flux (%)
$CHBr_3$	0.07	100, [75–125]	55
$CHBr_2Cl$	0.19	4.1, [2.1–6.0]	66
$CHBrCl_2$	0.21	3.3, [3.1–3.5]	35

Table 5. Average observed increases in the brominated THM's from NGRIP firn air measurements, the associated uncertainties and the estimated anthropogenic fluxes based on the observed increases.

Species	Average Observed Increase (%)	Estimated Anthropogenic Flux (Gg Br yr^{-1})
$CHBr_3$	20	20±6
$CHBr_2Cl$	19	0.78±0.17
$CHBrCl_2$	22	0.71±0.10

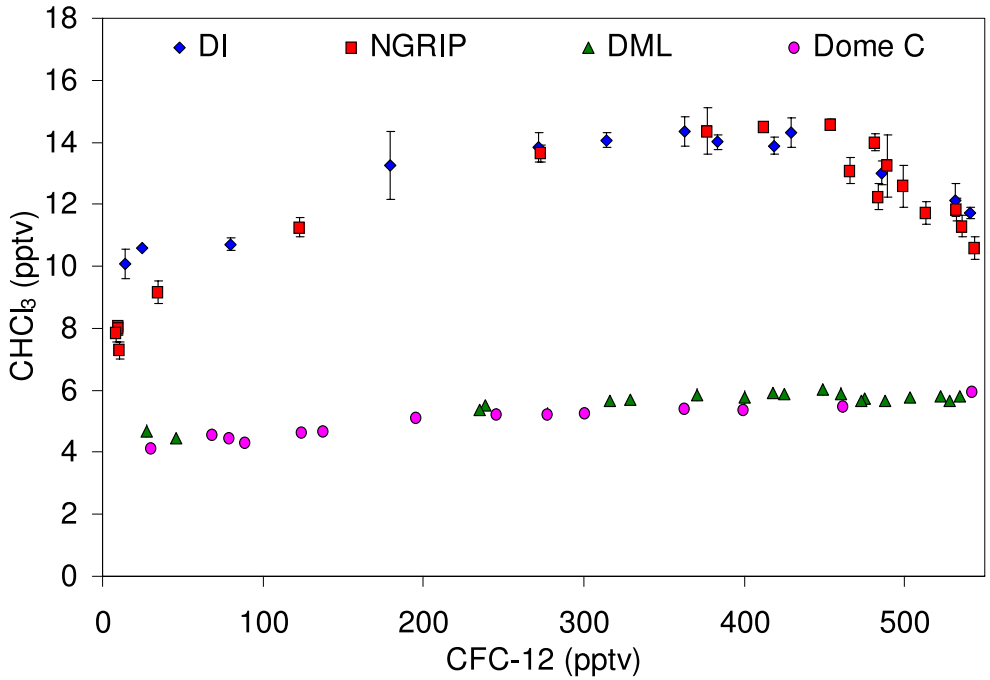

Fig. 1. Firn air measurements of $CHCl_3$ versus CFC-12 at NGRIP and DI in the Arctic and DML and Dome C in the Antarctic.

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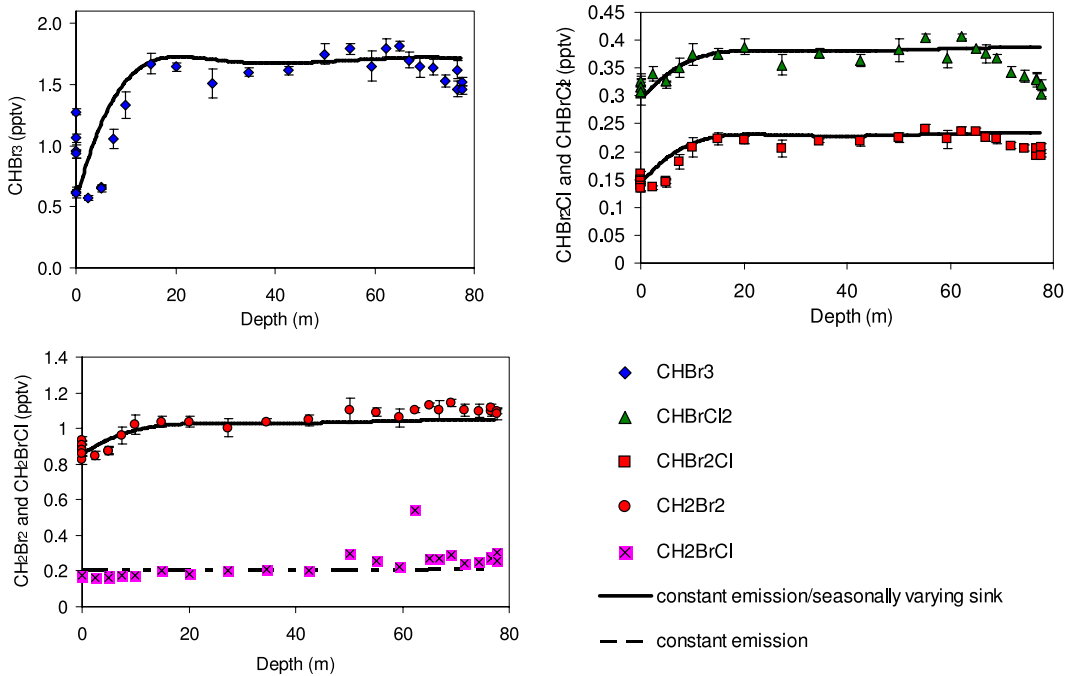

Fig. 2. Depth profiles of the brominated THM and DHM in firn air from NGRIP (symbols). Model lines corresponding to constant atmospheric burdens incorporating seasonal cycles, where appropriate, are also shown.

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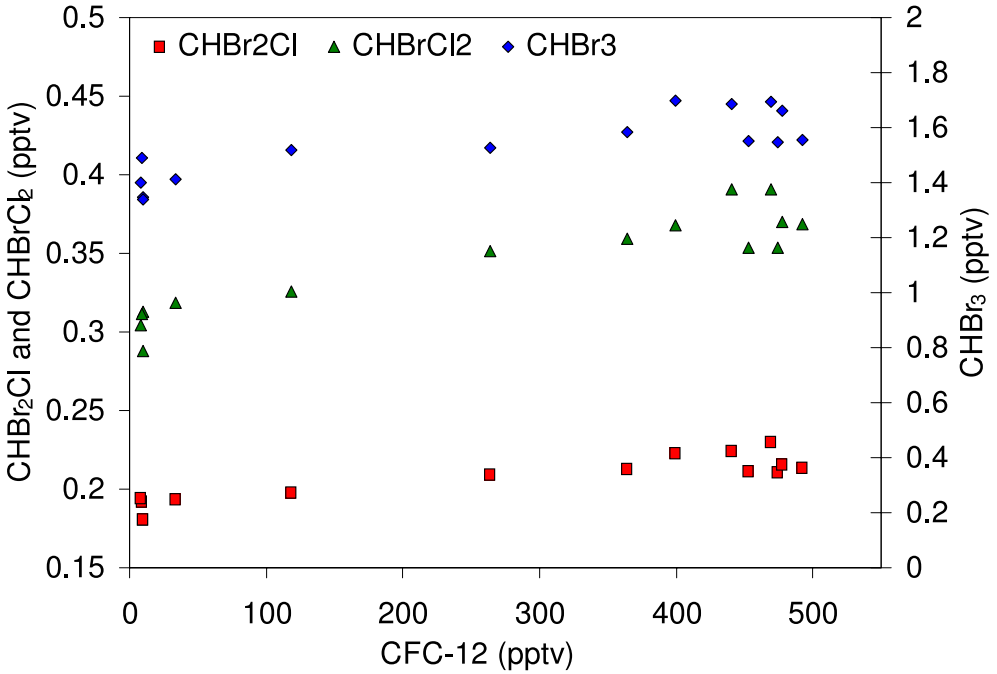

Fig. 3. Gravity corrected firn air measurements of $CHBr_3$, $CHBr_2Cl$ and $CHBrCl_2$ versus CFC-12 at NGRIP.

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Trends of THM and DHM trace gases from NGRIP firn air

D. R. Worton et al.

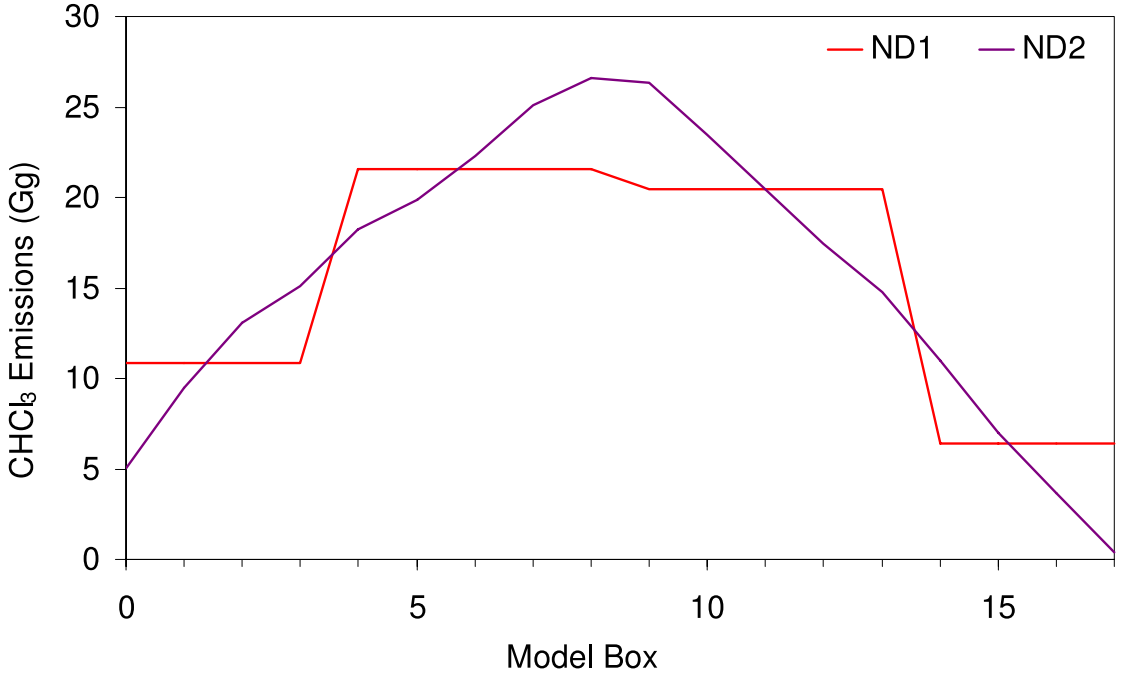

Fig. 4. The two estimated natural distributions used within this 2-D modelling work.

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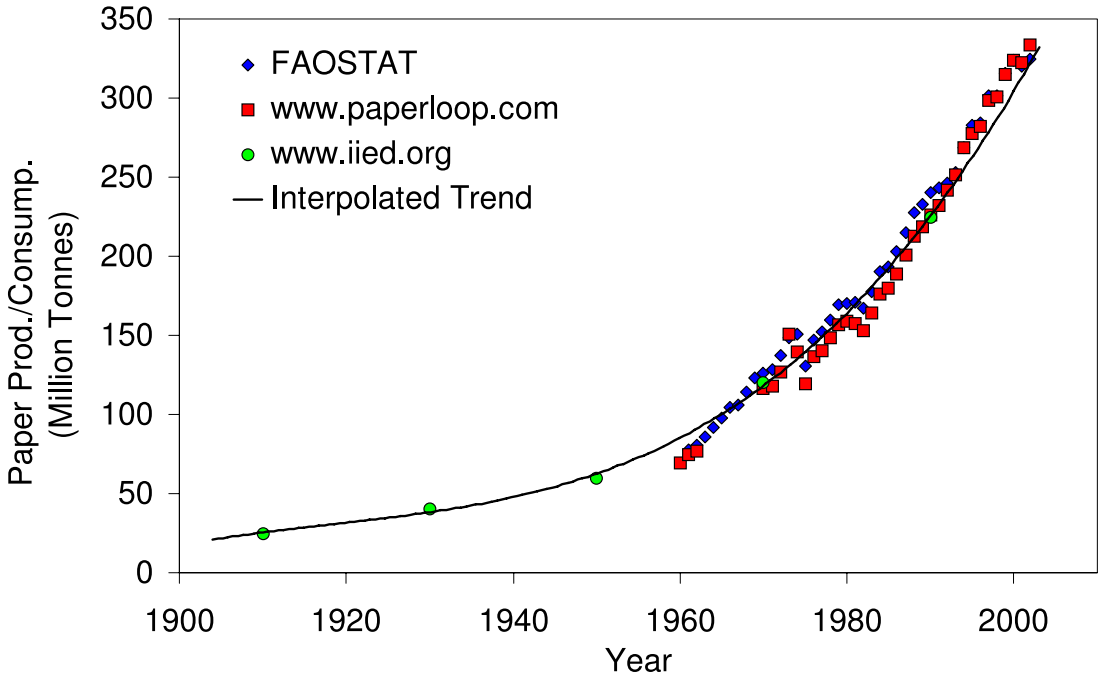

Fig. 5. The reported global trend in paper production/consumption during the 20th Century and the interpolated trend used to construct a time history of the pulp and paper industry.

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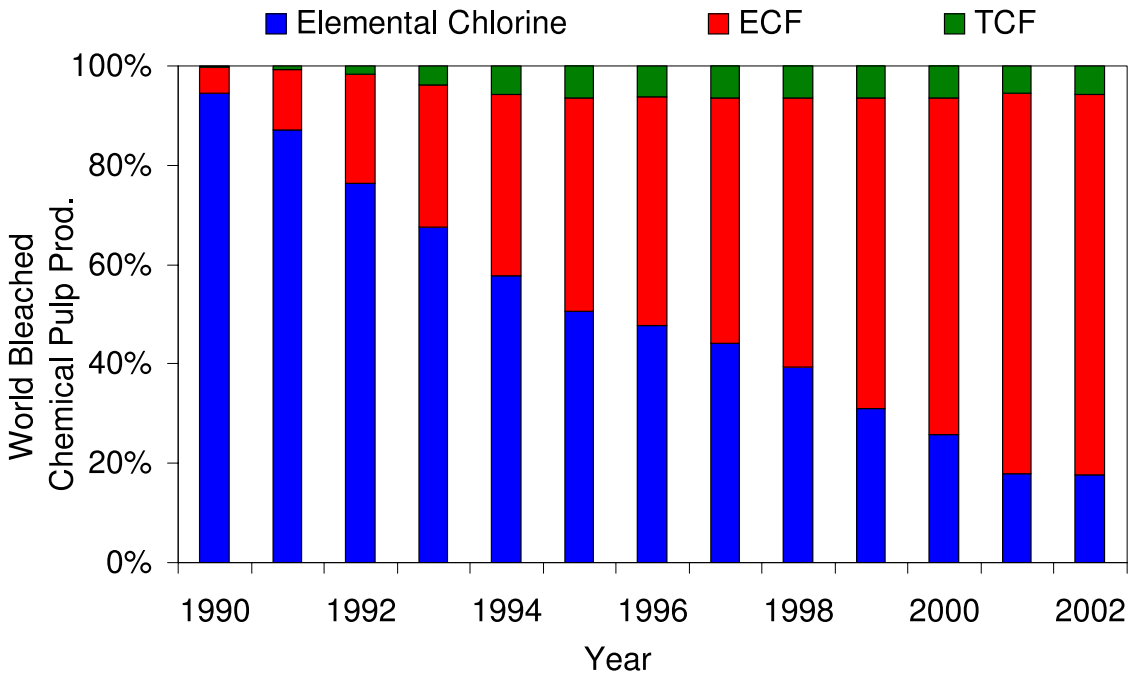

Fig. 6. The changing trend in the bleaching methods used in the pulp and paper industry during the 1990's (AET, 2001).

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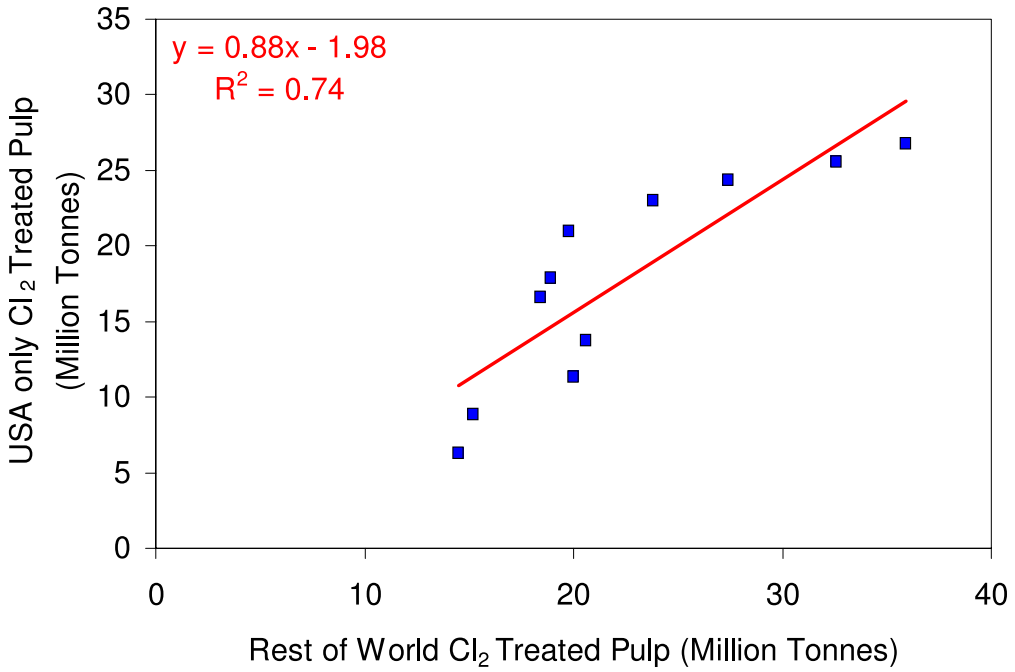

Fig. 7. The relationship between the use of elemental chlorine during the bleaching of paper pulp in the United States of America and the rest of the world.

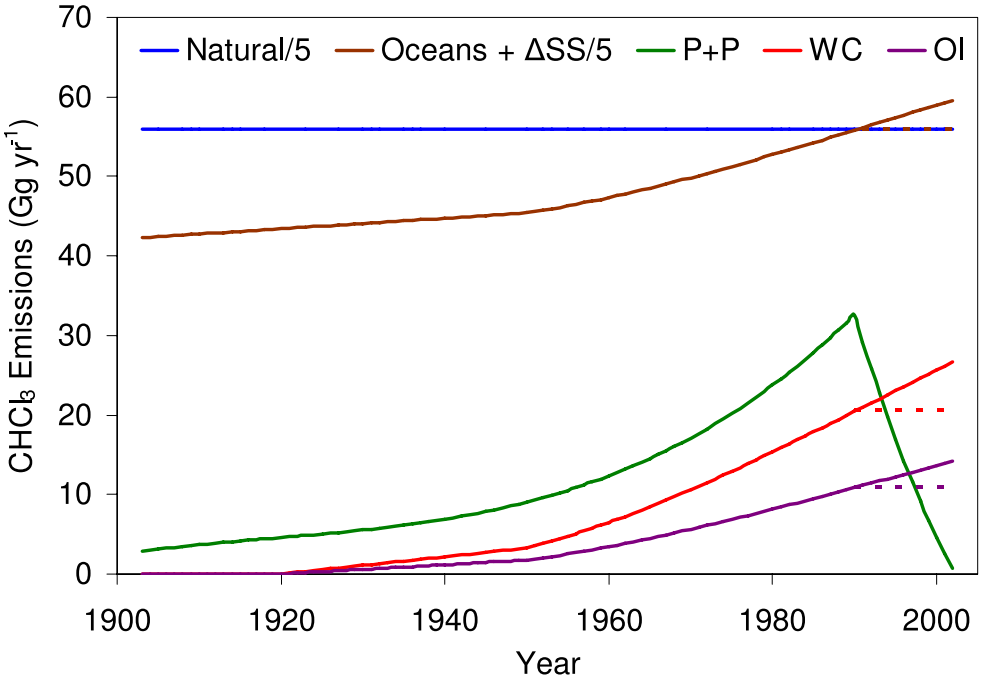

Fig. 8. The time trends over the 20th Century for all the natural and anthropogenic source components incorporated in the modelling.

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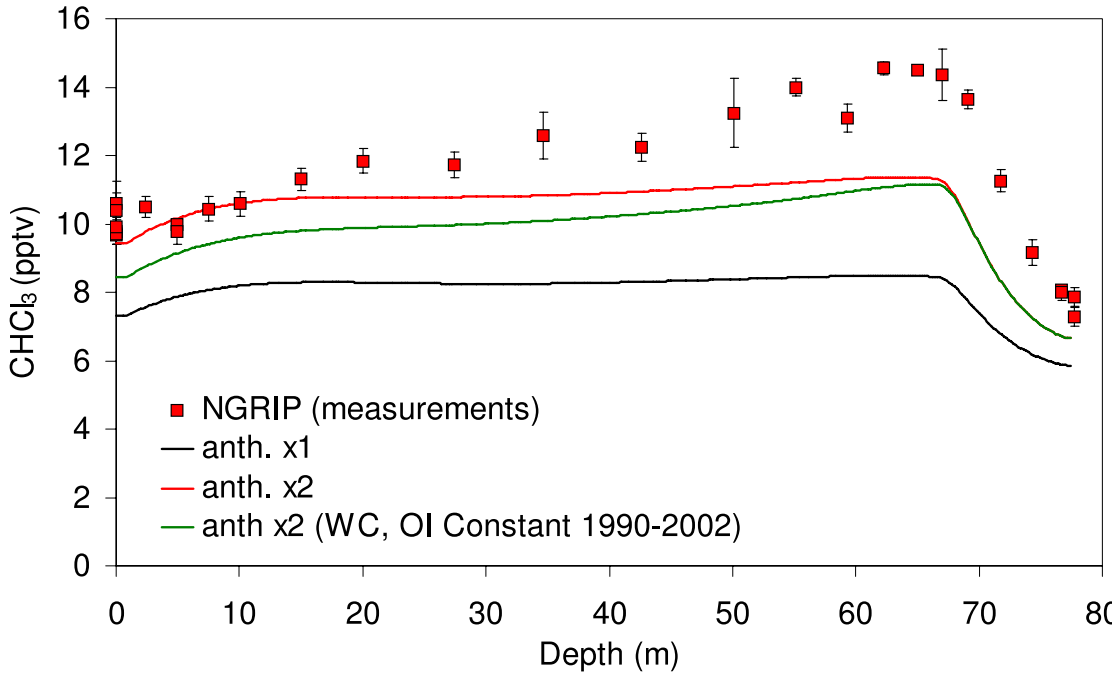

Fig. 9. A comparison of the effect of varying the magnitude of all anthropogenic sources with the NGRIP firn air measurements of $CHCl_3$.

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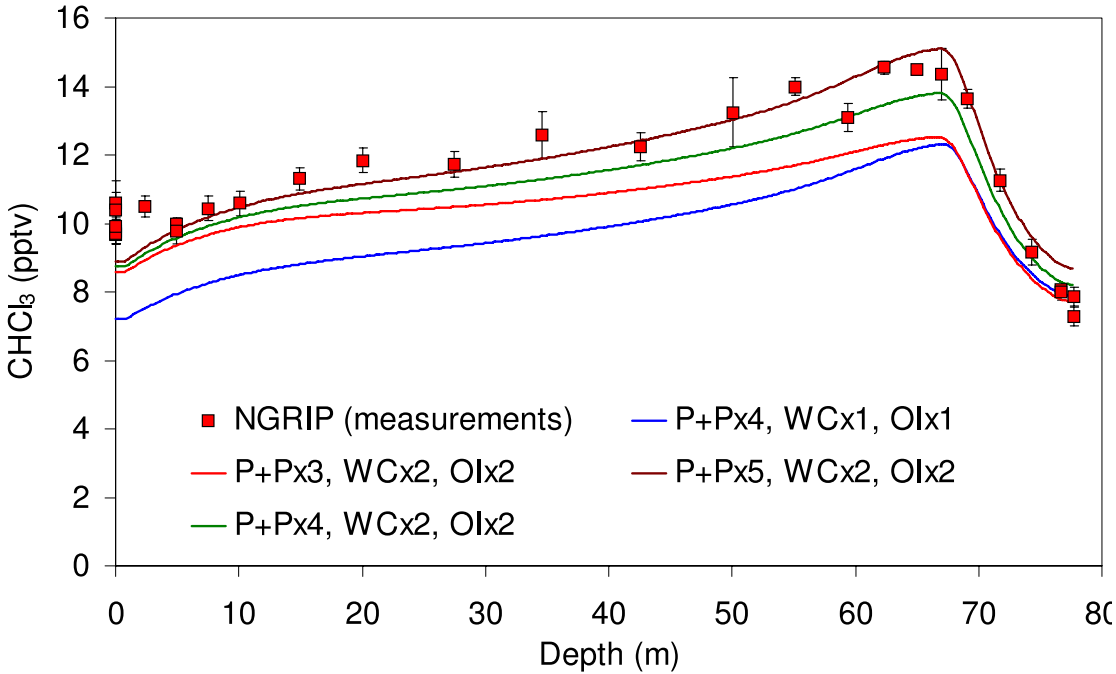

Fig. 10. A comparison of the effect of varying the magnitude of the various independent anthropogenic source components relative to the NGRIP firn air measurements of $CHCl_3$.

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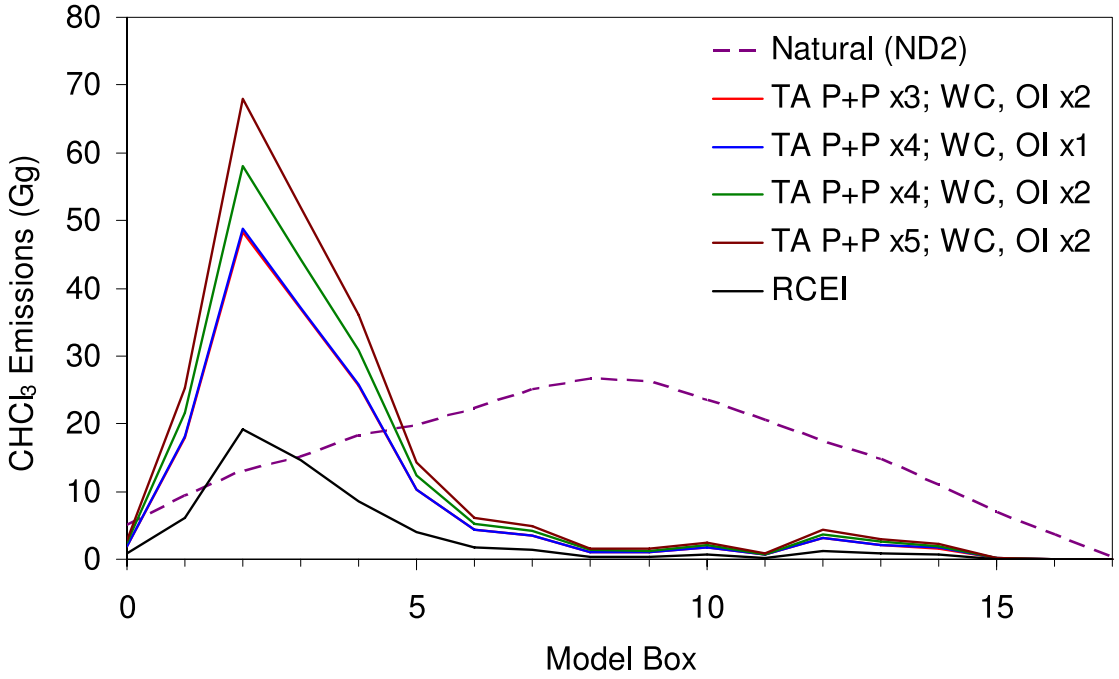

Fig. 11. A comparison of the latitudinal distribution of the increased magnitude anthropogenic emissions relative to the distribution of natural emissions.

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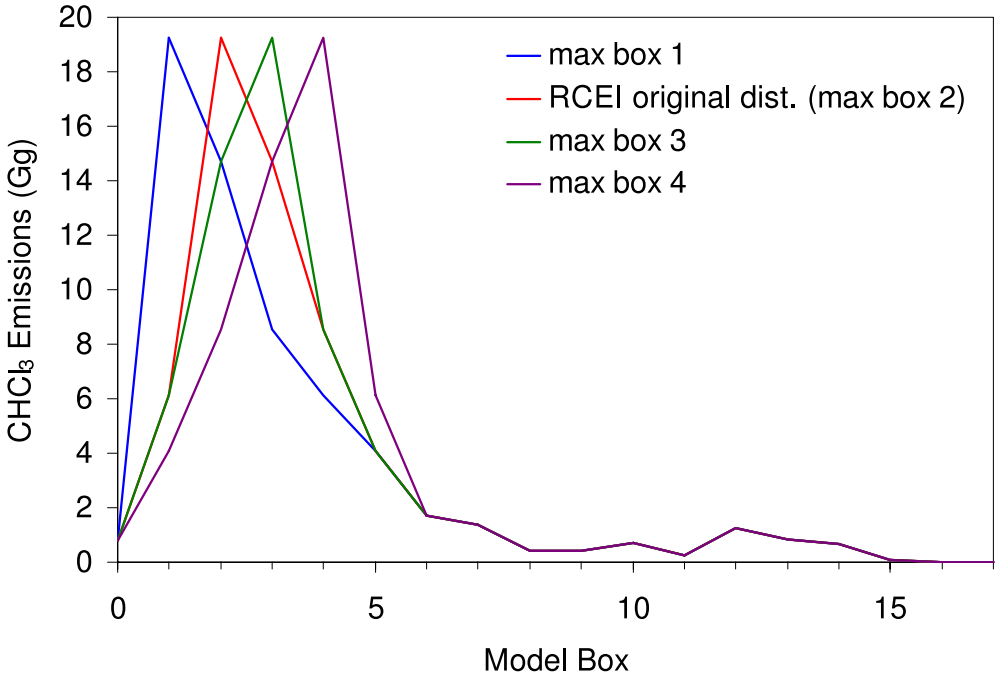

Fig. 12. The four various anthropogenic distributions used to demonstrate the sensitivity of the model to slight shifts in the location of the maximum emissions.

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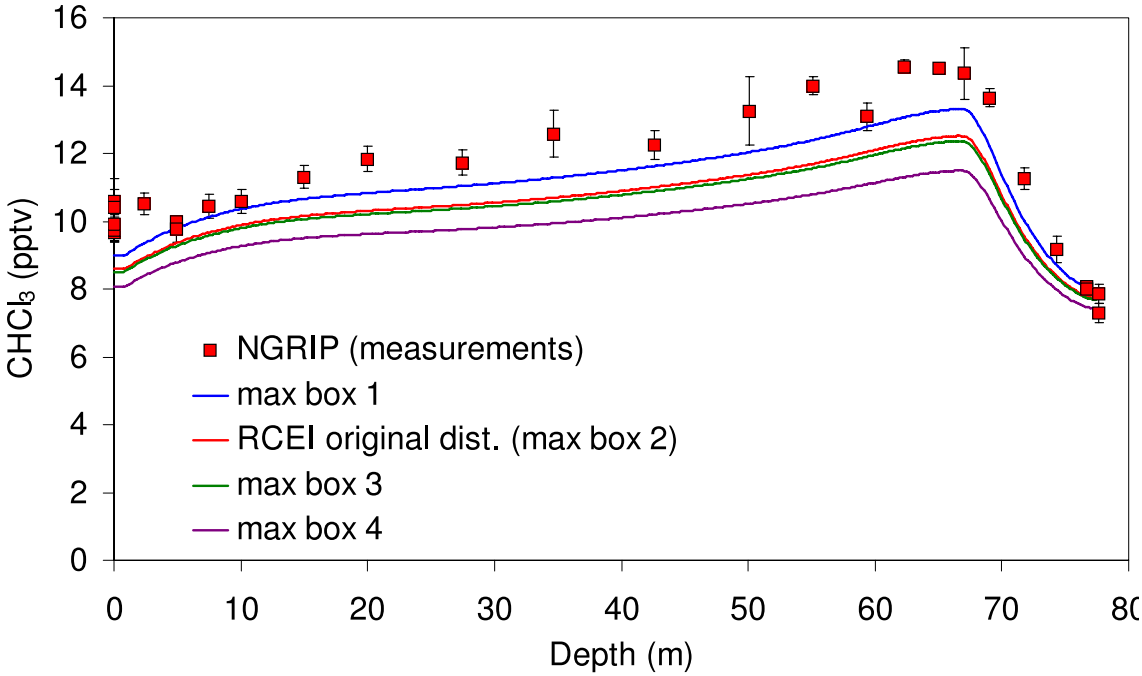

Fig. 13. A comparison of the effect on the model output at NGRIP for the four anthropogenic distributions shown in Fig. 12.

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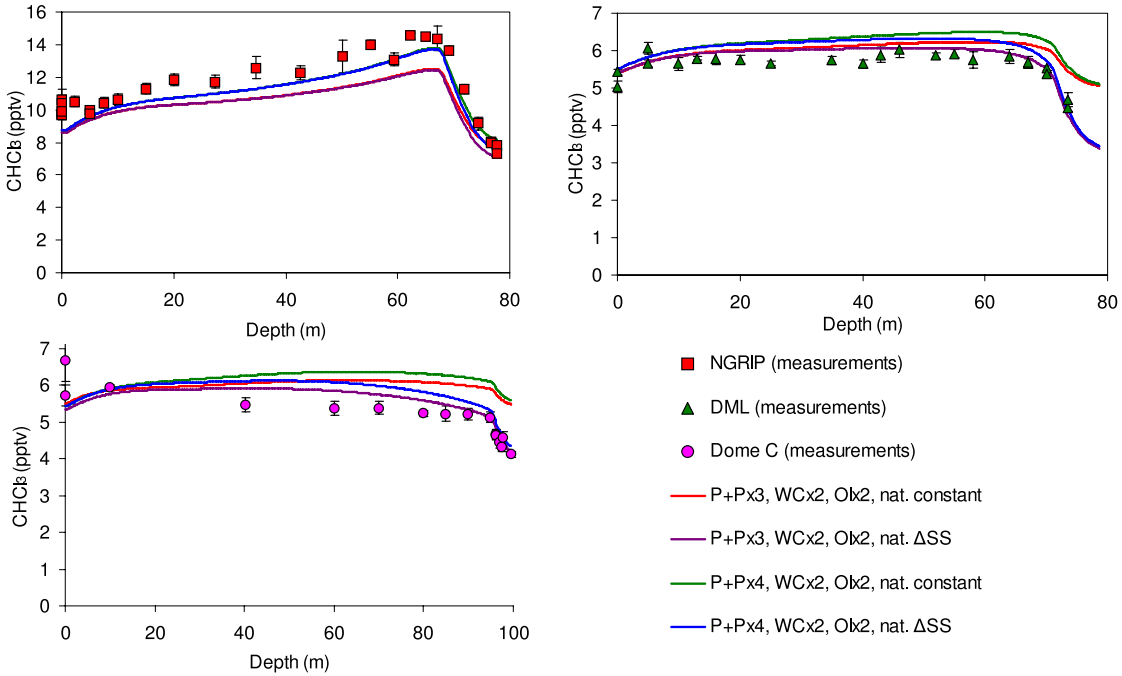

Fig. 14. A comparison of the effect of varying the magnitude of the anthropogenic and soil sources on the model fit relative to the NGRIP, Dome C and DML firn air measurements of $CHCl_3$.

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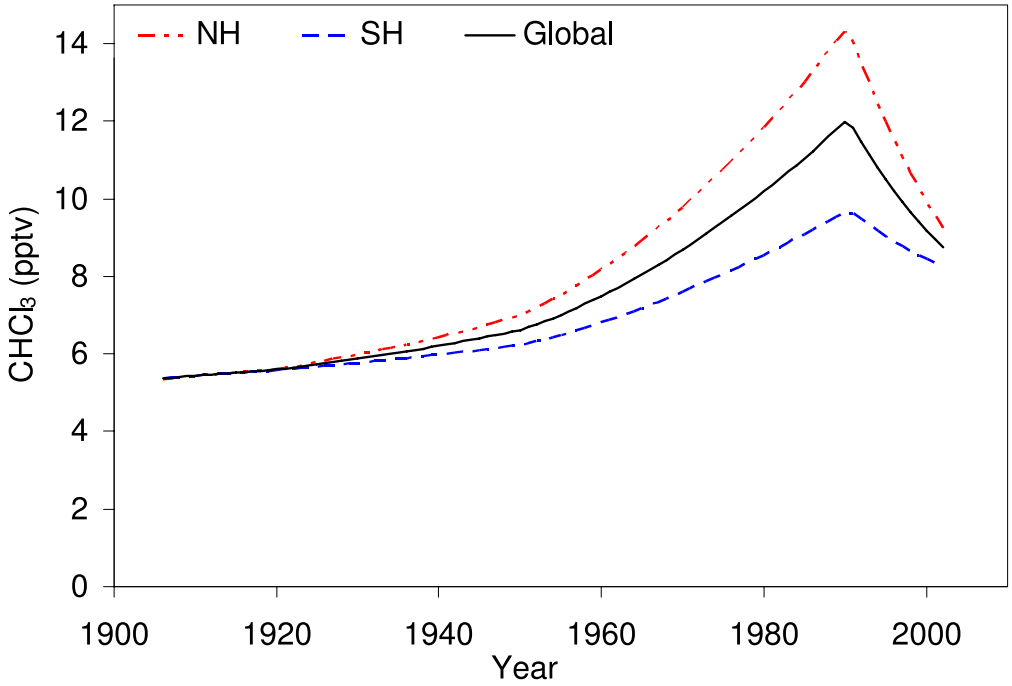

Fig. 15. The best fit modelled global and hemispheric atmospheric evolutions of $CHCl_3$ during the 20th Century.

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