# Stable carbon isotope signatures of background tropospheric chloromethane and CFC113

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**Abstract.** Samples of background air were collected in the lower troposphere of the Northern (high Arctic, northern Ontario, Vancouver and Houston) and Southern (Baring Head, New Zealand) Hemispheres over the period July 1999 until March 2001. These samples were analysed for the stable carbon isotope ratios of 1,1,1-trichlorotrifluoroethane (CFC113) and $CH_3Cl$ using a gas chromatography-continuous flow on-line combustion isotope ratio mass spectrometry combination. For $CH_3Cl$ the global average of the stable carbon isotope ratio is $-36.2 \pm 0.3$‰ (error of mean). The average is based on 78 data points, standard deviation for all measurements is 2.3‰, and the 90% confidence interval is $-35.8$ to $-36.6$‰. However, the number of data points from the Southern Hemisphere is rather limited and thus this observation is not necessarily representative for the entire Southern Hemisphere. A simple isotopic budget of $CH_3Cl$ shows the most important parameters needing to be defined are the kinetic isotope effect of $CH_3Cl$ destruction by OH radicals and the source composition of $CH_3Cl$ emitted by the oceans and biomass burning of C-4 plants. Present budgets of atmospheric $CH_3Cl$ show a significant deficit in the source strength. We estimate that the average stable carbon isotope ratio of the additional $CH_3Cl$ emissions required to balance the budget is $-41.9 \pm 7.8$‰. The average CFC113 isotopic composition based on 38 measurements is $-23.3 \pm 1.6$‰ (error of mean), $\sigma = 9.6$‰ with no significant difference between the hemispheres.

## Introduction

Chloromethane ($CH_3Cl$) with an average atmospheric concentration in the range of 500–600 ppt represents one of the largest reservoirs of gaseous chlorine in the atmosphere. It contributes 43% of the total reactive Cl in the troposphere and is increasingly important as a source for Cl atoms in the stratosphere (Khalil et al. 1999, Khalil & Rasmussen 1999). It comprises the

only significant source of natural Cl atoms to the stratosphere, contributing up to 25% (Keene et al. 1999) of stratospheric Cl. Since the emission rates of trace gases can be influenced by various factors, a quantitative understanding of the atmospheric $CH_3Cl$ budget is essential in order to allow predictions of potential future developments of $CH_3Cl$ emissions, e.g. as a consequence of climate change.

However, our current understanding of the global budget of tropospheric $CH_3Cl$ is completely unsatisfactory. The quantified sources can only account for approximately half of the emissions required to balance the known sinks. The major sink of $CH_3Cl$ in the troposphere is loss by reaction with OH-radicals (3.37 Tg $CH_3Cl$/yr). Minor sinks include loss to the stratosphere and uptake by soils (0.28 and 0.25 Tg $CH_3Cl$/yr respectively). Current estimates of emissions only total 2.03 Tg $CH_3Cl$/yr (Keene et al. 1999; Rhew et al. 2000), which is approximately 50% of the atmospheric loss rate.

The most important known $CH_3Cl$ source is biomass burning, contributing 0.90 Tg $CH_3Cl$ annually. Oceanic emissions are estimated to account for 0.65 Tg $CH_3Cl$/yr, salt marsh emissions 0.17 Tg $CH_3Cl$/yr (Rhew et al. 2000), and fungi, coal combustion, incineration and industry emit a total of 0.31 Tg $CH_3Cl$/yr (Keene et al. 1999).

Clearly, either the emissions from the identified sources are underestimated, the sinks are overestimated, or there are other unknown sources of $CH_3Cl$. Since the dominant atmospheric loss process of $CH_3Cl$, reaction in the troposphere with OH radicals, is well understood, an overestimate of the loss rates is an unlikely explanation for the very substantial imbalance in the $CH_3Cl$ budget.

Stable carbon isotope ratio measurements have been used very successfully to constrain the atmospheric budgets of a number of important trace gases such as carbon dioxide, carbon monoxide, and methane (e.g. Kaplan 1975; Lowe et al. 1994; Mook et al. 1983). With the recent development of techniques to measure the stable carbon isotope ratio of volatile organic compounds in the atmosphere (Rudolph et al. 1997) the use of isotope composition measurements to improve our insight into the atmospheric cycle of $CH_3Cl$ became feasible. However, there is still very little published data available on the stable carbon isotope ratios of ambient $CH_3Cl$. Knowledge of a representative average tropospheric distribution of the stable carbon isotope ratio of $CH_3Cl$ is an essential prerequisite for any attempt to use stable carbon isotope studies to improve our present understanding of the global $CH_3Cl$ budget. Currently there are only two published papers on ambient $CH_3Cl$ isotopic composition (Tsunogai et al. 1999; Rudolph et al. 1997). Rudolph et al. presented one measurement from a background station in New Zealand, Tsunogai et al. made measurements in urban and coastal areas of Japan and

over the Pacific Ocean between 5° N and 35° N latitude. These measurements gave stable carbon isotope ratios of $CH_3Cl$ in the range of –30 to –45‰ ($\delta^{13}C$ relative to Pee Dee Belemnite). Obviously, the limited geographic coverage of the available ambient measurements and the substantial spread of the data will severely limit the reliability of any budget constraints based on the presently existing ambient data. In this paper we present the results from seven campaigns comprising a total of 90 samples that allows significant reduction of the uncertainty of the average global stable carbon isotope ratio of $CH_3Cl$.

We also measured the isotopic composition of 1,1,1-trichlorotrifluoroethane (CFC113). CFC113 is a manufactured compound that was used in refrigeration, as a solvent, and a degreasing agent before its ban by the Montreal Protocol. In 1992 it was present in the atmosphere at a concentration of 82 ppt and had an atmospheric burden of 2.6 Tg (IPCC 1995). Present emissions are negligible and the dominant tropospheric loss process is transport to the stratosphere and subsequent photolysis. There is nothing published on the isotopic composition of CFC113 to date.

**Experimental procedure**

Whole air samples were collected in the field and transferred for analysis to the laboratory. Following a cryogenic enrichment procedure, the stable carbon isotope ratios of $CH_3Cl$ and CFC113 were determined by isotope ratio mass spectrometry in combination with a gas chromatographic separation and continuous flow on-line combustion. The procedure was very similar to a method described by Rudolph et al. (1997), but a few modifications were made and therefore a brief description of the technique is presented here.

*Ambient Sampling*

Sampling locations, characterisation of sampled air masses, number of samples, sampling periods, and sampling frequency are tabulated in Table 1. The ambient air samples were collected in evacuated electropolished 3L stainless steel canisters at a pressure of approximately 2 atm above ambient. For background samples, as well as the aircraft samples, the canisters were pressurised using metal bellows pumps in order to minimise the risk of sample contamination. Tests showed that metal bellows pumps did not cause detectable levels of contamination for any of the compounds studied here. For urban or semi-urban samples Teflon diaphragm pumps were used. For these samples of somewhat higher trace gas levels the use of Teflon diaphragm pumps caused no detectable change in the trace gas concentration. The advantage

of Teflon diaphragm pumps is their lower power consumption and thus the possibility to use batteries as power supply. This increased the flexibility in selection of sampling locations.

*Pre-concentration*

A two step process was used to enrich the analytes from between 1 and 20 L of air. Prior to the enrichment steps $CO_2$ was removed by passing the sample air through a 30 cm × 1/2" stainless steel tube filled with Ascarite II. In order to maintain the $CO_2$ removal efficiency at a high level (>99.9%), the Ascarite trap was conditioned prior to each measurement by passing humidified He at a flow rate of 30 $cm^3$ $min^{-1}$ for 30 minutes through the trap. After every second analysis the trap was replaced by a new trap containing fresh Ascarite. Prior to use all traps were conditioned for at least 8 hours in a He flow at 80 °C to eliminate contamination. Testing of this procedure (including the introduction of a $CH_3Cl$ standard before and after the trap) showed that there were no losses or fractionations for $CH_3Cl$ and that $CO_2$ removal is highly efficient (>99.9%) for sample volumes of 30 L or less. It must be noted that no tests of the analytical method specific for CFC113 were performed. Thus all stable carbon isotope ratios presented for CFC113 are based on the assumption that the tests conducted for $CH_3Cl$ were also valid for CFC113.

After the $CO_2$ trap, the sample flowed through a two-stage water trap (15 cm × 1" stainless steel and then 50 cm × 3/8" stainless steel, both held at –30 °C during pre-concentration) before passing through the first cryogenic trap. In this stainless steel trap of 30 cm length and 3/8" diameter packed with 80/100 mesh glass beads, the volatile organic compounds in the sample were cryogenically trapped at liquid Ar temperature (–186 °C). Sample flow rate through this trap was 100 ml/min. Consequently, for a 15 L sample this process took 2.5 hours. However, the sample enrichment procedure was usually performed during the chromatographic separation of the previous sample to reduce the overall analysis time. The trap was then heated to 160 °C and the halocarbons transferred in a flow of 5–12 ml/min of He to a second trap (8 cm × 1/16" stainless steel) held at –196 °C with liquid $N_2$ for cryogenic focussing. For sample injection this trap was flash heated and the pre-concentrated halocarbons were transferred to the separation columns by the carrier gas.

*Separation and analysis*

The samples were separated on a Varian Series 3600 gas chromatograph using a combination of a 60 m (0.32 mm ID, 5 $\mu$m film) HP1 column and a 60 m (0.32 mmID) Chromatographic Specialties PoraPlot Q (PPQ) column. Flow

*Table 1.* Overview of sampling campaigns

| Campaign | Location | Number of Samples CH3Cl | Number of Samples CFC113 | Characterisation of sample air | Sampling Period | Frequency |
|---|---|---|---|---|---|---|
| Alert, seasonal cyckes | Alert, Nunavut, Canada (82.5 °N, 62.3 °W) | 42 | 31 | Background | Jul 1999– Mar 2001 | One sample every fortnight |
| Fraserdale | Fraserdale, Ontario, Canada (49.9 °N, 81.6 °W) | 12 | 0 | Background, continental | Apr 2000– Feb 2001 | One sample every three weeks |
| Vancouver | Fraser Valley, British Columbia, Canada (48.3 °N, 123.7 °W) | 1 | 0 | Rural | 5 May 2000 | |
| Houston | Houston, Texas, United States (29.8 °N, 95.3 °W) | 16 | 0 | Background into urban plumes, aircraft campaign | 29, 31 Aug 12 Sep 2000 | 3 flights |
| New Zealand background | Baring Head, New Zealand (41.4 °S, 174.9 °E) | 16 | 5 | Background | Jul–Sep 1999 Feb–Aug 2000 | Approx. one sample every three weeks |
| New Zealand urban | Auckland, New Zealand (36.8 °S,175.7 °E) | 2 | 0 | Suburban, close to motorway | 3, 14 March 2000 | |
| Polar Sunrise 1999 | Alert, Nunavut, Canada (82.5 °N, 62.3 °W) | 0 | 2 | Background | 3, 20 May 1999 | |

rates were 1.5 ml/min, the carrier gas was He. The sample was pre-separated on the HP1 column and the fraction of the column effluent containing $CH_3Cl$ was transferred to the PPQ column for further separation. CFC113 was separated on the HP1 column only. The temperature was held at $-30\,°C$ for 30 mins, then a $3\,°C$/min ramp to $180\,°C$ was applied. About 0.5 ml/min of the column effluent was transferred via a deactivated fused silica capillary to an Ion Trap mass spectrometer for peak identification and verification of peak purity. The remainder of the carrier gas flow entered a commercial (Finnigan MAT) combustion interface similar to that described by Matthews and Hayes (1978) to convert the analyte into $CO_2$, and about 0.3 ml/min of the flow was transferred via an open split to a Finnegan Mat 252 Isotope Ratio Mass Spectrometer (IRMS). The isotopic composition of the $CO_2$ from each individual compound was measured against a $CO_2$ reference gas (with $\delta^{13}C_{VPDB} = -35.4‰$) from the reference open split. This on-line reference was calibrated to the primary scale Vienna Pee Dee Belemnite (VPDB) scale on a daily basis using two lab carbonate standards with $\delta^{13}C_{VPDB}$ of $-2.57‰$ and $-45.78‰$. All delta values in this paper are reported relative to this scale, and presented errors, unless otherwise stated, are the standard error of the mean.

## Results

*Chloromethane*

*Concentration*
$CH_3Cl$ concentrations were not measured separately in any of the campaigns. However, for the Alert data set the $CH_3Cl$ concentrations have been determined from the 44 mass trace peak area of $CH_3Cl$ relative to the 44 mass trace peak area of propane, for which the concentration was measured independantly using GC-FID methods. $CH_3Cl$ and propane underwent separation on the same columns and elute within 50s of each other. We estimate the error in the $CH_3Cl$ concentration is 10%, mainly due to the uncertainty of the propane concentration, and the possibility of minor changes in the column flow rate between elution of the $CH_3Cl$ peak and the propane peak, which effect the fraction of analyte reaching the IRMS. The $CH_3Cl$ concentrations are shown in Figure 1 along with the 7-year monthly average at Alert during the period 1991–1996 (Gautrois et al. 2002). Yokouchi et al. (1998) also measured $CH_3Cl$ at Alert and observed similar concentrations, although the magnitude of the seasonal variation was slightly less than that of Gautrois et al. According to both of these studies, $CH_3Cl$ at Alert has an average concentration of 500 ppt and shows a seasonal variation of approximately 150–230 ppt with a maximum concentration in winter. Within the uncer-
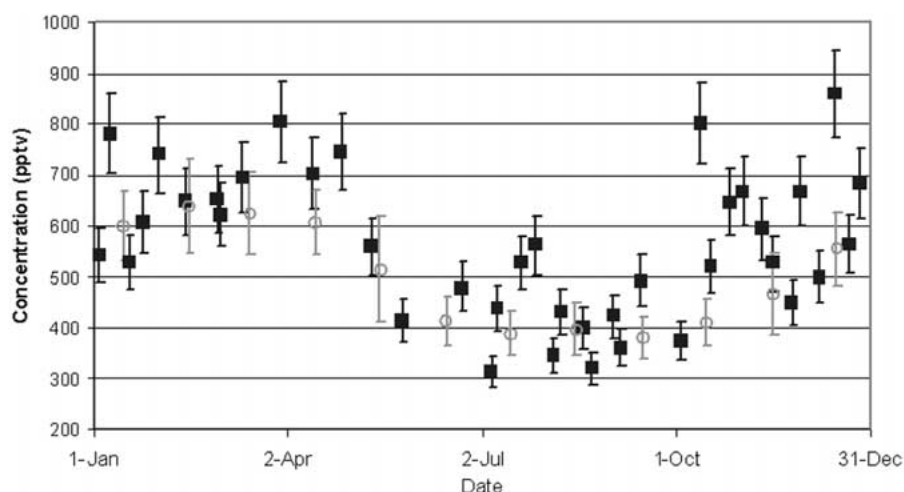
*Figure 1.* Concentration of CH$_3$Cl at Alert. Solid squares represent concentrations from this work; open circles represent monthly averages from observations during 1991 to 1996 (Gautrois et al. in prep.). The error bars represent the measurement error, and the error of the mean, respectively.

tainty of measurements and the expected interannual variability, our CH$_3$Cl concentrations are compatible with these other studies. Unfortunately it was not possible to calculate the concentrations for other campaigns using this method because the chromatography differed and associated errors became too large.

*Isotopic composition*

Table 2 summarises the CH$_3$Cl stable carbon isotopic composition data. The average isotopic composition of background tropospheric CH$_3$Cl in the Northern Hemisphere from our observations is –36.1 ± 0.3‰, $N = 68$.

The stable carbon isotopic composition and the concentrations for CH$_3$Cl at Alert are plotted against each other in Figure 2. The plot shows no correlation between isotopic composition and concentration ($R^2 = 0.001$), however there are three clearly outlying data points with concentrations greater than 1.4 ppb. These data, likely to be contaminated or influenced by unusually high local or regional emissions, have been removed from the data set.

The seasonal averages are shown in Table 3. The average summer (June until August) composition is –36.5 ± 0.7‰, $N = 9$, the average for winter (December until February) is –35.8 ± 0.4‰, $N = 11$, and the annual average is –36.4 ± 0.3‰, $N = 39$ at Alert. Within their statistical uncertainty of less than 1‰ these values are the same. At Fraserdale the average winter composition, –35.0 ± 0.7‰, $N = 3$, and the annual average is –36.0 ± 0.6‰, $N =$

*Table 2.* Average isotopic composition of CH3Cl (all values in ‰[a])

| Campaign | Alert[b] | Fraserdale | Vancouver | Houston | New Zealand[c] | New Zealand Background[d] | New Zealand Urban | Northern Hemispheric Average | Global Average |
|---|---|---|---|---|---|---|---|---|---|
| Average $\delta^{13}$C | −36.40 | −35.99 | −38.88 | −35.17 | −42.13 | −37.23 | −40.64 | −36.08 | −36.22 |
| Error of mean | 0.26 | 0.64 | 0.5[e] | 0.83 | 1.85 | 0.82 | 8.90 | 0.27 | 0.26 |
| Standard Deviation | 1.63 | 2.12 | – | 3.20 | 7.18 | 2.47 | 8.90 | 2.22 | 2.27 |
| Median | −36.62 | −35.75 | – | −35.34 | −39.00 | −37.79 | −40.64 | −36.37 | −36.61 |
| 25th Percentile | −37.67 | −37.01 | – | −37.42 | −47.04 | −38.56 | −43.79 | −37.56 | −37.69 |
| 75th Percentile | −35.53 | −34.57 | – | −34.00 | −37.56 | −36.75 | −37.50 | −34.90 | −35.01 |
| 90% Confidence interval | ±0.43 | ±1.01 | – | ±1.32 | ±2.95 | ±1.28 | ±10.35 | ±0.44 | ±0.42 |
| Number of samples | 39 | 12 | 1 | 16 | 16 | 10 | 2 | 68 | 78 |

[a]Relative to VPDB.
[b]Excluding contaminated samples.
[c]Including all samples taken in New Zealand Background campaign.
[d] Excluding samples possibly directly impacted by recent emissions.
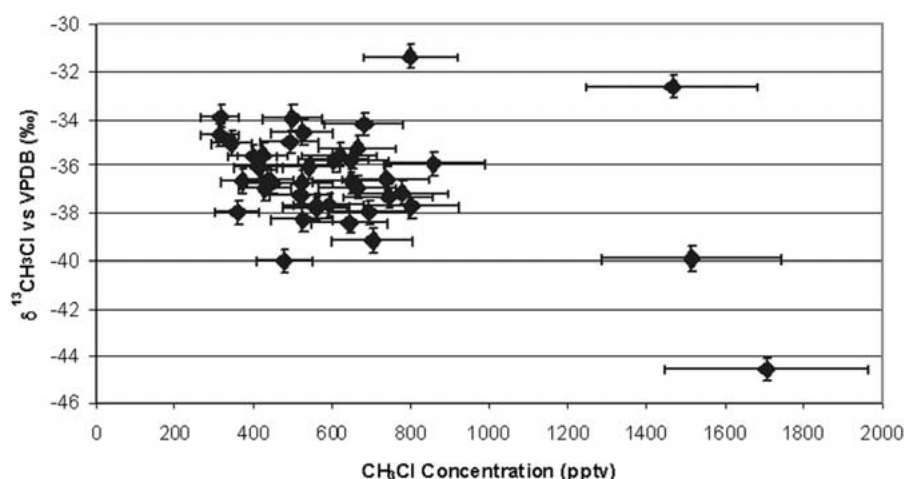[e]Error of measurement.

*Figure 2.* Concentrations and isotopic composition of CH₃Cl at Alert.

12, are also the same as the averages of our measurements at Alert. Only the stable carbon isotope ratio for summer, with $-38.5 \pm 1.4‰$, $N = 3$, is slightly lower than our observations at Alert. However this summer average is based on a very small number of measurements. Our other background tropospheric $CH_3Cl$ stable carbon isotope measurements in the Northern Hemisphere fall into a very similar range (Table 2). The average is $-36.1 \pm 0.3‰$, $N = 68$. The data median is $-36.4‰$, and the confidence interval at the 90% level is $-35.6‰$ to $-36.5‰$. The 25th and 75th percentiles are $-37.6‰$ and $-34.9‰$ respectively. This is within the range of results previously found by Tsunogai et al. (1999) of $-44$ to $-30‰$ for marine and coastal $CH_3Cl$, but our measurements allow the determination of a considerably better defined representative average. There is no statistically significant difference between background samples from the different locations at different latitudes in the Northern Hemisphere.

The stable isotope ratios of $CH_3Cl$ in background samples from the Southern Hemisphere show a less uniform picture (Table 2). The available data are limited to a relatively small region, New Zealand, and show a larger variability than the Northern Hemispheric measurements. The average of all our Southern Hemispheric measurements is $-42.1 \pm 1.9‰$, $N = 16$, noticeably lighter than our Northern Hemispheric average, however the substantial difference between the median and the mean (Table 2) indicates a somewhat skewed distribution. The frequency distributions for the Northern Hemispheric and New Zealand stable carbon isotope ratio measurements are compared in Figure 3. Data from the Northern Hemisphere present an approximately symmetrical frequency distribution, however the New Zealand

*Table 3.* Seasonal averages of isotopic composition of CH3Cl in two Northern Hemispheric background sites (all values in ‰[a])

| Season | Summer (Jun–Aug) | Autumn (Sep–Nov) | Winter (Dec–Feb) | Spring (Mar–May) | Seasonal Variation Winter–Summer |
|---|---|---|---|---|---|
| Campaign | Alert | Alert | Alert | Alert | Alert |
| Average $\delta^{13}$C | –36.53 | –36.28 | –35.83 | –37.35 | 0.69 |
| Error of mean[b] | 0.69 | 0.56 | 0.37 | 0.50 | 0.78 |
| Standard deviation | 1.94 | 1.86 | 1.17 | 1.22 | |
| Number of samples | 9 | 12 | 11 | 7 | |
| Campaign | Fraserdale | Fraserdale | Fraserdale | Fraserdale | Fraserdale |
| Average $\delta^{13}$C | –38.50 | –34.74 | –35.02 | –36.19 | 3.47 |
| Error of mean[b] | 1.44 | 1.03 | 0.71 | 1.20 | 1.61 |
| Standard deviation | 2.04 | 1.78 | 1.00 | 1.20 | |
| Number of samples | 3 | 4 | 3 | 2 | |

[a]relative to VPDB
[b]for seasonal variation this value is the error of the difference.

samples do not. Since the atmospheric lifetime of $CH_3Cl$ (1.3 years) is substantially greater than the hemispheric mixing time (3 months) the hemispheric background troposphere should be well mixed with respect to $CH_3Cl$ and therefore the distribution of delta values should be narrow. The wide range of observed values indicates that some of the samples from New Zealand must have been impacted by relatively recent $CH_3Cl$ emissions, which are depleted in $^{13}$C. Biomass burning in the tropics and subtropics of the Southern Hemisphere is a very important source of $CH_3Cl$ (Andreae 1991). Rudolph et al. (1997) and von Czapiewski et al. (2001) measured the isotopic composition of $CH_3Cl$ of biomass burning. Both studies show that $CH_3Cl$ emitted from biomass burning is relatively light, $\delta^{13}$C values range from –38‰ to –68‰. Other known emissions of $CH_3Cl$ for which the isotopic composition has been measured also have low $\delta^{13}$C values (Table 4). Obviously, even a very moderate impact of emissions of very light $CH_3Cl$ into the studied air mass might decrease its ambient stable carbon isotope ratio by several per mil. Our Southern Hemispheric data do not allow any conclusions on the representativeness of the unusually low values. If we exclude these data from the average, we obtain a value of $-37.2 \pm 0.8$‰, $N = 10$. This value, within its statistical uncertainty, is the same as the Northern Hemispheric average. Our data thus indicate that $CH_3Cl$ in the Southern Hemisphere has
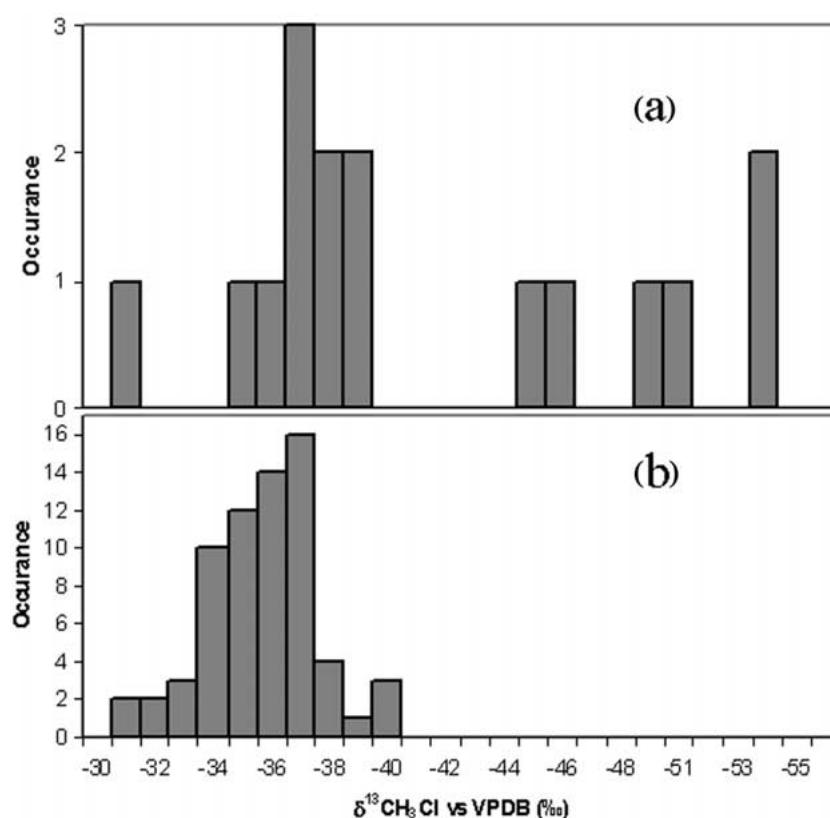
*Figure 3.* Frequency distributions of the isotopic composition of $CH_3Cl$ in the (a) Southern Hemispheric and (b) Northern Hemispheric data sets.

a stable carbon isotope ratio very similar to that of the Northern Hemisphere, although there are a number of observations that indicate depletion in $^{13}C$ relative to the Northern Hemisphere. The suburban New Zealand samples had $CH_3Cl$ isotopic compositions of $-46.9 \pm 0.5‰$ and $-34.4 \pm 0.5‰$.

*CFC113*

The measured CFC113 isotopic compositions are shown in Table 5. The global average stable carbon isotopic composition of ambient CFC113 is 23.3 $\pm$ 1.6‰, $N = 38$. The Alert campaign was analysed with a slightly different chromatographic separation, which caused occasional partial peak merging with an unknown species. This interference did not occur in either the Polar Sunrise 1999, or the New Zealand Background measurements. This analytical problem is responsible for the high variability in the Alert data set.

*Table 4.* Known Sources of Tropospheric $CH_3Cl$

| Sources | Source Strength[a] (TgCH$_3$Cl/yr) | Source Composition (‰) | Error in Composition (‰) |
|---|---|---|---|
| Biomass burning | 0.90 | –47[b] | 12[b] |
| Fungi | 0.15 | –43[c] | 2[c] |
| Salt Marshes | 0.17[d] | –62[e] | 3[e] |
| Industry | 0.01 | –41.9 and –60[f] | |
| Ocean | 0.65 | ? | |
| Coal combustion | 0.11 | ? | |
| Incineration | 0.04 | ? | |
| TOTAL | 2.03 | | |

[a]Khalil et al. 1999a.
[b]Weighted average of C3 and C4 plants, see text for details.
[c]Harper et al. 2001, not including higher plants.
[d]Rhew et al. 2000.
[e]Bill et al. 2002.
[f]Composition of manufactured CH3Cl (Rudolph et al. 1997 and Tsunogai et al. 1999).

*Table 5.* Average isotopic composition of CFC113 (all values in ‰[a])

| Campaign | Polar Sunrise 1999 | Alert Zealand | New Average of Background | Global Sample Ambient CFC113 | Commercial |
|---|---|---|---|---|---|
| Average $\delta^{13}$C | –22.70 | –23.53 | –22.24 | –23.32 | –31.3 |
| Error of mean | 1.27 | 1.95 | 0.66 | 1.58 | 0.5[b] |
| Standard Deviation | 1.27 | 10.69 | 1.32 | 9.64 | – |
| Median | –22.70 | –24.74 | –23.10 | –23.10 | – |
| 25th Percentile | –23.15 | –29.08 | –23.10 | –28.58 | – |
| 75th Percentile | –22.25 | –21.28 | –21.80 | –21.55 | – |
| 90% Confidence interval | ±1.48 | ±3.15 | ±0.97 | ±2.57 | – |
| Number of samples | 2 | 31 | 5 | 38 | 1 |

[a]Relative to VPDB.
[b]Estimated measurement error.

The Northern Hemispheric average stable isotopic composition is –23.5 ± 1.8‰ N=33, and the Southern Hemispheric average is –22.2 ± 0.7‰, $N$ = 5. There is no significant difference in the isotopic composition of ambient CFC113 between the hemispheres. For comparison, a commercial sample (Sigma Aldrich Lot # BI00453TU, produced in December 1999 by Aldrich) of CFC113 was analysed and its stable carbon isotope ratio was found to be –31.3 ± 0.5‰.

## Discussion

### Chloromethane

Seasonal variation in the concentration of $CH_3Cl$ has been observed in the high and mid latitudes and the tropics of both hemispheres (although at different magnitudes) and is the result of the seasonal variation of the OH radical concentrations (Khalil & Rasmussen 1999b). The kinetic isotope effect (KIE) of $CH_3Cl$ and OH is not known. To date, all measured KIEs of hydrocarbons reacting with OH have been positive (Rudolph et al. 2000). Assuming that the KIE of $CH_3Cl$ and OH is positive, as atmospheric $CH_3Cl$ is photochemically aged its isotopic composition becomes heavier, ie. enriched in $^{13}C$. Thus, we expect that it would be heavier in summer than during the winter. However, the seasonal variation seen in the Fraserdale data set shows the winter isotopic composition to be slightly heavier than the summer composition. This is an indication that $CH_3Cl$ at Fraserdale is impacted by lighter sources during the summer than during the winter. Thus the seasonal variation at Fraserdale can be explained by a regional impact of biomass burning. A seasonal variation of 3.5‰ would only require a 15% additional contribution from biomass burning during the summer. Summertime biomass burning is known to occur at mid and boreal latitudes, and there is substantial burning in Canada. Further away from the sources, for example at Alert where the burning forests are at least 1000 km or more away, the effect will be diluted.

It is possible to construct a simple global budget for $CH_3Cl$ using the isotopic compositions and associated errors to constrain the contribution of different sources. However, substantial difficulties lie with firstly the parameters which are completely unknown, and secondly that the uncertainties of the 'known' parameters are not understood. Most notably, errors in the magnitude of the sources and sinks of tropospheric $CH_3Cl$ are, for the most part, undefined. Although accuracy in the magnitude of sources and sinks is critical to any budget, for the purposes of this paper we have used the most likely magnitudes and neglected their associated errors in the budget calcula-

tions. This is a substantial weakness in the discussion of the isotopic budget of $CH_3Cl$, however since so little is understood about the sources of atmospheric $CH_3Cl$, stable carbon isotope arguments can still be useful. There are also many gaps in our understanding of the effect of specific sources and sinks on the isotopic composition of atmospheric $CH_3Cl$. We use 'best guess' estimations of the effects and errors not explicitly stated in the literature.

An overview of identified $CH_3Cl$ sources and their isotopic compositions is shown in Table 4. As previously mentioned, only about half of the emissions required to balance the atmospheric $CH_3Cl$ budget have been identified. The most important known chloromethane source is biomass burning which emits 0.90 Tg $CH_3Cl$/yr (48% of known sources). As mentioned above, the two existing studies (Rudolph et al. 1997; von Czapiewski 2001) indicate that chloromethane emitted from biomass burning has stable carbon isotope ratios from –38‰ to –68‰, with an average of –52‰. However, both published studies used material from plants with a C-3 metabolism as fuel. Plants with a C-4 metabolism are enriched in $^{13}C$ relative to C-3 plants (parent material of –13‰ and –27‰ respectively) and are thought to be responsible for about a third of $CH_3Cl$ emissions from biomass burning (Lobert et al. 1999). Isotopic fractionation during combustion of C-3 plants is –25 ± 12‰. We assume that the fractionation relative to the parent fuel is the same for the combustion of material derived from C-3 and C-4 plants, that is –25 ± 12‰. The resulting average stable carbon isotope ratio of $CH_3Cl$ from biomass burning is –47 ± 12‰.

Current estimates place oceanic emissions of $CH_3Cl$ to be the second largest known source at 0.65 Tg $CH_3Cl$/yr, about 70% of the size of biomass burning emissions. Unfortunately, nothing is known about the stable carbon isotope ratio of $CH_3Cl$ produced and emitted by oceans. The composition of oceanic $CH_3Cl$ is unknown, and although fixed carbon in seawater is known to have a delta value of –22‰, the isotopic composition of oceanic emissions of $CH_3Cl$ is not necessarily representative of the source material.

Other known sources include fungi (0.15 Tg $CH_3Cl$/yr), salt marshes (0.17 Tg $CH_3Cl$/yr), and coal combustion, incineration, and industry (total of 0.16 Tg $CH_3Cl$/yr). $CH_3Cl$ produced by one species of fungi was measured to be –43.3‰ (Harper et al. 2001). The isotopic composition of emissions of $CH_3Cl$ from salt marshes ranges from –45‰ to –71‰, with a daily weighted mean of –62 ± 3‰ (Bill et al. 2002). Industrial $CH_3Cl$ has been measured to be –60‰ and –41.9‰ (Tsunogai et al. 1999; Rudolph et al. 1997). The isotopic composition of $CH_3Cl$ emissions from coal combustion and incineration are not known. Overall the isotopic composition of these minor sources is extremely uncertain. However, they contribute only about 10% to the total $CH_3Cl$ budget.

*Table 6.* Known Sinks of Tropospheric $CH_3Cl$

| Sinks | Sink Magnitude[a] (TgCH$_3$Cl/yr) | Fractionation Factor, $\epsilon$ (‰) | Error in $\epsilon$ (‰) |
|---|---|---|---|
| OH Destruction | 3.37 | 5[b] | 5[b] |
| Loss to Stratosphere | 0.28 | 5[b] | 5[b] |
| Soils | 0.25 | 46[c] | 20[b] |
| TOTAL | 3.91 | | |

[a]Khalil et al. 1999a.
[b]Estimate, see text for details.
[c]Miller et al. 2001.

The known $CH_3Cl$ sink mechanisms and their associated fractionation factors as well as uncertainties are summarised in Table 6. The total loss rate is 3.91 Tg $CH_3Cl$/yr. The dominant loss process of atmospheric $CH_3Cl$ by far is via reaction with OH-radicals (3.37 Tg $CH_3Cl$/yr). Currently the kinetic isotope effect (KIE) for reaction of $CH_3Cl$ with the OH radical is unknown.

Another loss of atmospheric chloromethane is the destruction by methylotrophic bacteria in soils. It is a minor sink of 0.25 Tg $CH_3Cl$/yr (6.5% of total loss), however it potentially has a significant fractionation effect. Miller et al. 2001 measured the fractionation of $CH_3Cl$ to be 46‰ for three strains of (whole cell) bacteria at elevated methyl halide concentrations. Although it is not clear how representative this study is to the effects on ambient atmospheric $CH_3Cl$, this fractionation factor has been included in the budget with an estimated error of 20‰.

And finally, 0.28 Tg $CH_3Cl$/yr of tropospheric $CH_3Cl$ is known to be lost to the stratosphere where it is destroyed by photolysis. Since this $CH_3Cl$ sink is via turbulent mixing, the transport process itself will not result in an isotopic fractionation. It cannot be excluded that stratospheric loss, which is via photolysis and reaction with OH-radicals, will be associated with an isotope fractionation. However, stratospheric loss is less than 10% of tropospheric removal and it is therefore extremely unlikely that this loss has a major impact on the isotopic composition of tropospheric $CH_3Cl$. We use the same fractionation and uncertainty for the stratospheric and tropospheric loss processes.

The global average tropospheric $CH_3Cl$ composition is equal to the weighted average of all emissions plus the weighted average of removal mechanisms (equation 1).

$$\delta_{obs} = \frac{\sum\limits_{all\cdot sources} \delta_i * S_i}{\sum\limits_{all\cdot sources} S_i} + \frac{\sum\limits_{all\cdot losses} \epsilon_j * L_j}{\sum\limits_{all\cdot losses} L_j} \tag{1}$$

where $\delta_{obs}$ is the global average isotopic composition of $CH_3Cl$, $\delta_i$ and $S_i$ are the isotopic composition and strength of source $i$, and $\epsilon_j$ and $L_j$ are the isotopic fractionation effect and magnitude of sink $j$. Reported uncertainties have been calculated using Gaussian error propagation from the errors associated with the source compositions and sink fractionations mentioned above.

An important parameter currently unknown is the KIE for the reaction of $CH_3Cl$ with OH-radicals ($\epsilon_{OH}$). This value can be determined in laboratory studies and such measurements can be made with high accuracy (Cantrell et al. 1990; Rudolph et al. 2000). Thus we express the average isotopic composition as a function of the KIE for the loss due to OH-radical reaction by rearranging (1):

$$\frac{\sum\limits_{all\cdot sources} \delta_i * S_i}{\sum\limits_{all\cdot sources} S_i} = \delta_{obs} - \frac{\epsilon_{OH}L_{OH} + \sum\limits_{NonOH\cdot losses} \epsilon_j * L_j}{\sum\limits_{all\cdot losses} L_j} \tag{2}$$

The resulting average source composition (of all sources) can be described by $-39.5\permil$ ($\pm 1.4\permil$) $- 0.86* \epsilon_{OH}$. Similiarly, the average composition of sources with an unknown stable isotope ratio (including oceanic, coal combustion, incineration and the deficit with a total of 2.67 Tg $CH_3Cl$/yr) is $-35.3\permil$ ($\pm 4.5\permil$) $- 1.26* \epsilon_{OH}$.

The current estimate for an oceanic source of $CH_3Cl$ is 0.65 Tg $CH_3Cl$/yr and we denote isotopic composition of these emissions as $\delta_{ocean}$. This enables us to describe the stable isotopic composition of the deficit ($\delta_{def}$) of 2.02 Tg $CH_3Cl$/yr in the atmospheric $CH_3Cl$ budget by the following expression:

$$\delta_{def} = -46.7\permil(\pm 6.0\permil) - 1.67 * \epsilon_{OH} - 0.32 * \delta_{ocean} \tag{3}$$

The deficit estimation includes a small contribution from minor sources with unknown stable carbon isotope ratios (Table 4), however it is extremely unlikely that these small emissions will significantly change the required stable carbon isotope ration of the shortfall in the $CH_3Cl$ budget. For example an isotopic composition of these small sources in the range between $-80\permil$ and $-5\permil$ will not result in a change of $\delta_{def}$ that exceeds its error of $6.0\permil$.

As previously mentioned, $\epsilon_{OH}$ is unknown. However, the KIE for the reaction of methane with OH radicals is positive (Cantrell et al. 1990), similar to recent observations of Rudolph et al. (2000) who found that the carbon isotope fractionation associated with the reaction of several alkanes, alkenes, and benzene with OH radicals results in an enrichment of $^{13}$C in the remaining reservoir. Therefore it seems very likely that atmospheric removal of $CH_3Cl$ by OH radicals will results in an enrichment of $^{13}$C, although the magnitude of this effect is unknown. For the purposes of the following calculations, we have estimated the KIE (usually presented relative to unity as $\epsilon_{OH}$ = (KIE-1)*1000 with units of ‰) to be 5 ± 5‰ (5‰ being the $\epsilon_{OH}$ for $CH_4$ and OH) although the true $\epsilon_{OH}$ could well be outside this range. Considering only loss via OH destruction, the required average $CH_3Cl$ source composition is given by $\delta^{13}C_{observed} - \epsilon_{OH}$. Thus, using the measured global average $CH_3Cl$ composition, the required average $CH_3Cl$ source composition (over all sources) is –41.2 ± 5.0‰. Including all known losses, the required average $CH_3Cl$ source composition is –43.8 ± 4.5‰.

The quantity with the lowest uncertainty in the budget of $CH_3Cl$ is the atmospheric loss rate. We can separate the emissions required to balance the loss rate into three catagories: those for which there are some indicators as to the isotopic composition (biomass burning, fungi, industry, and salt marsh emissions), those for which the composition is not known (oceanic, coal combustion, and incineration), and the deficit in the budget. This deficit may be due to errors in the strength of known sources or the existence of presently unidentified emissions. The weighted average of emissions from biomass burning, fungi, industry and salt marshes is –48.7 ± 8.8‰ (1.23 Tg $CH_3Cl$/yr). This means, continuing the assumption that $\epsilon_{OH}$ = 5 ± 5‰, $CH_3Cl$ emitted from all other sources must have an average isotopic composition of –41.6 ± 7.8‰ (2.67 Tg $CH_3Cl$/yr).

Current understanding is that the large deficit in the atmospheric $CH_3Cl$ budget is not due to underestimation of the magnitiude of either the biomass burning source, or oceanic emissions. Lobert et al. 1999 constrained the upper limit of global biomass burning emissions to be 1.11 Tg $CH_3Cl$/yr. The ocean is insufficiently supersaturated in $CH_3Cl$ to account for more than a small percentage of the total $CH_3Cl$ budget (Moore et al. 1996). Clues as to unidentified sources include the results of Yokouchi et al. 2000, who found that levels of $CH_3Cl$ in marine air samples were correlated with $\alpha$-pinene, suggesting coastal terrestrial sources. Keppler et al. 2000 showed that alkylhalides could be produced abiotically from halide ions in organic matter (e.g. soil) via redox reactions, however the importance of this process is questionable and is reliant on the availability of the right source materials at sufficient concentration.

Since $\epsilon_{OH}$ will mostly likely be positive (see above), this budget indicates the unidentified sources of atmospheric $CH_3Cl$ are relatively low in $^{13}C$, that is significantly lower than carbon in fossil fuel and plant material. The results show that $CH_3Cl$ emitted from the oceans would have to be very strongly depleted in $^{13}C$ (composition of around –90‰) to allow the missing sources to have stable carbon isotope ratios similar to fossil fuel or terrestrial plant material. The required lightness, ie depletion in $^{13}C$, of the missing source/s is compatible with what has been observed for emissions from biological sources and also processes such as biomass burning.

*CFC113*

The average tropospheric CFC113 isotopic composition was –23.3 ± 1.6‰, *N* = 38 with no difference between the hemispheres. Since CFC113 has a lifetime of 85 years, and present day emissions are marginal due to the Montreal Protocol and its amendments, the global troposphere is well mixed with respect to CFC113. This means that the isotopic composition of tropospheric CFC113 will be homogenous and so the variability in the ambient observations is indicative only of the experimental uncertainty.

With only one recently produced commercial sample analysed, it is not justified to attach any significance to the difference in stable carbon isotope ratio between commercial and tropospheric CFC113. A substantial fractionation between emissions and ambient CFC113 is difficult to explain as CFC113 is unreactive. Also, the only significant tropospheric loss process is transport to the stratosphere. The fractionation due to stratospheric photolysis (the major loss mechanism in the stratosphere) of CFC113 is not known, however because of it's long lifetime fractionation would need to be extremely large to cause any discernable change in the isotopic composition of tropospheric CFC113. There is nothing published on the stable carbon isotopic composition of CFC113 to date, however McCauley et al. (1999) found isotopic variability of up to 15‰ in commercial samples of bromomethane, and as mentioned above industrial $CH_3Cl$ has been measured to be –60‰ and –41.9‰.

**Conclusions**

The global average stable carbon isotopic composition of tropospheric $CH_3Cl$ has a well defined average of –36.2 ± 0.3‰. However further study is warranted. In particular, current Southern Hemispheric data are inadequate. The magnitude of the seasonal cycles (over a longer period and more

geographic coverage), and the North-South Hemispheric gradient need to be better defined.

The measurement of atmospheric $CH_3Cl$ composition allows definition of the average isotopic composition of the unknown $CH_3Cl$ source/s, as a function of the KIE for reaction with OH-radical. This average unknown source composition is depleted in $^{13}C$ relative to known potential parent materials (plants, fossil fuel) implying substantial fractionation of emission processes.

Aside from the obvious identification of the unknown sources, the key uncertainties in the isotopic budget of $CH_3Cl$ are the KIE for loss via OH-radical and the isotopic composition of oceanic emissions. Also important is reducing the uncertainty in the isotopic composition of biomass burning emissions.

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