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New insight into the atmospheric chloromethane budget gained using stable carbon isotope ratios

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Abstract. Atmospheric chloromethane (CH_3Cl) plays an important role in stratospheric ozone destruction, but many uncertainties still exist regarding strengths of both sources and sinks and the processes leading to formation of this naturally occurring gas. Recent work has identified a novel chemical origin for CH_3Cl, which can explain its production in a variety of terrestrial environments: the widespread structural component of plants, pectin, reacts readily with chloride ion to form CH_3Cl at both ambient and elevated temperatures (Hamilton et al., 2003). It has been proposed that this abiotic chloride methylation process in terrestrial environments could be responsible for formation of a large proportion of atmospheric CH_3Cl. However, more information is required to determine the global importance of this new source and its contribution to the atmospheric CH_3Cl budget.

A potentially powerful tool in studying the atmospheric CH_3Cl budget is the use of stable carbon isotope ratios. In an accompanying paper it is reported that the reaction of CH_3Cl with OH radical, the dominant sink for atmospheric CH_3Cl, is accompanied by an unexpectedly large fractionation factor (Gola et al., 2005). Another recently published study shows that CH_3Cl formed by the abiotic methylation process at ambient temperatures has a unique stable carbon isotope signature, extremely depleted in ^{13}C, unequivocally distinguishing it from all other known sources (Keppler et al., 2004). Using these findings together with data existing in the literature, we here present three scenarios for an isotopic mass balance for atmospheric CH_3Cl. Our calculations provide strong support for the proposal that the largest source of atmospheric CH_3Cl (1800 to 2500 Gg yr^{-1}) is the abiotic methylation of chloride in terrestrial ecosytems, primarily located in tropical and subtropical areas where turnover of biomass is highest. Furthermore our calculations also indicate that the microbial soil sink for CH_3Cl is likely to be much larger ($>$1000 Gg yr^{-1}) than that previously assumed.

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1 Introduction

Chloromethane (CH_3Cl) is the most abundant halocarbon in the atmosphere with a reported average mixing ratio in the range of 530 to 560 pptv (Montzka and Fraser, 2003; Simmonds et al., 2004; Trudinger et al., 2004; Aydin et al., 2004; Yoshida et al., 2004), corresponding to a total atmospheric burden of around 4000 to 5000 Gg (giga gram=10^9 gram). Although largely of natural origin CH_3Cl is responsible for around 16% of chlorine-catalysed ozone destruction in the stratosphere (Montzka and Fraser, 2003). With large reductions in anthropogenic emissions of many ozone-depleting gases mandated under the Montreal Protocol, halogenated gases with natural sources will become relatively more important as a source of chlorine in the stratosphere in the future. A better understanding of the atmospheric budget of chloromethane is therefore required for reliable prediction of future ozone depletion.

Until 1996 most of the CH_3Cl input to the atmosphere was considered to originate from the oceans, but investigations in recent years have clearly demonstrated that terrestrial sources dominate the atmospheric budget (Moore et al., 1996; Harper and Hamilton, 2003; Montzka and Fraser, 2003). The latest consensus assessment by the World Meteorological Organization (WMO) (Montzka and Fraser, 2003) considered the major terrestrial sources of CH_3Cl to be biomass burning (Lobert et al., 1999; Andreae and Merlet, 2001), wood-rotting fungi (Watling and Harper, 1998), coastal salt marshes (Rhew et al., 2000), and tropical vegetation (Yokouchi et al., 2002). In addition decomposition of soil organic matter can act as a source for atmospheric

Table 1. Known sources of tropospheric CH_3Cl and corresponding carbon isotope signatures.

Sources	Source (best estimate)[a] ($Gg\,yr^{-1}$)	Source (full range)[a] ($Gg\,yr^{-1}$)	Carbon isotope signature (per mil)	Uncertainty magnitude (per mil)
Terrestrial				
Biomass burning	911[b]	655 to 1125	−47[c]	12
Tropical plants	910	820 to 8200	−71[d]	2
Fungi	160	43 to 470	−43[e]	2
Salt marshes	170	65 to 440	−62[d, f]	3
Wetlands	40	6 to 270	?	
Coal combustion	105	5 to 205	−47[g]	12
Incineration	45	15 to 75	−47[g]	12
Industrial	10		−51[h]	
Rice	5		?	
Decay of organic matter in topsoil	?	?	?	
Senescent and leaf litter	?	30 to 2500	−135[i]	12
Marine				
Oceans	600	325 to 1300	−38[j]	4
Total sources	2956 + ?	1964 to 14585		

[a] Values for source (best estimate) and source (full range) were taken from Montzka and Fraser (2003), except for emissions associated with senescent and leaf litter which are from Hamilton et al. (2003).
[b] Although lower estimates for CH_3Cl emissions from biomass burning have been reported by Andreae and Merlet (2001) and Yoshida et al. (2004) the value in the table is used in our model.
[c] Thompson et al. (2002)
[d] Harper et al. (2003) and unpublished results (Hamilton, Yokouchi, Yukawa and Harper)
[e] Harper et al. (2001)
[f] Bill et al. (2002)
[g] based on the assumptions made in the text
[h] mean of values reported by Rudolph et al. (1997), Holt et al. (1997) and Harper et al. (2001)
[i] Keppler et al. (2004)
[j] Komatsu et al. (2004)
? denotes that no value has been provided

CH_3Cl (Keppler et al., 2000), but the importance of this source remains uncertain. Despite the progress in identifying new sources, the best estimate in the latest WMO Report (Montzka and Fraser, 2003) still revealed a significant shortfall of >1000 $Gg\,yr^{-1}$ between known sources and the modelled sinks. However, very recently Hamilton et al. (2003) made the interesting discovery that the widespread plant structural component, pectin, reacts readily with chloride ion to form chloromethane. Furthermore it was established that the reaction occurs abiotically at ambient temperatures in senescent and weathering plant material. They calculated that this process acting on senescent leaves and leaf litter could be responsible for formation of a large proportion of chloromethane entering the atmosphere (up to 2500 $Gg\,yr^{-1}$ from tropical and sub-tropical regions) and may also provide the mechanism for release of chloromethane during biomass burning, possibly for emissions from living tropical vegetation and importantly also the abiotic soil emissions reported by Keppler et al. (2000). Including this new emission source allows global CH_3Cl sources to balance and even possibly outweigh the best estimates of total sinks. Table 1 summarises existing information on estimated emission fluxes from known sources. The estimates of the strengths of many sources have large uncertainties. For example the possible CH_3Cl flux from tropical ferns and trees ranges from 800 to 8200 $Gg\,yr^{-1}$ (Yokouchi et al., 2002) whilst CH_3Cl emissions in the tropics and sub-tropics by senescent leaves and leaf litter ranging from 30 to 2500 $Gg\,yr^{-1}$ have been suggested (Hamilton et al., 2003).

As regards sinks for atmospheric CH_3Cl, the dominant loss process for atmospheric CH_3Cl is via reaction with photochemically produced OH radicals (Table 2) and is considered responsible for some 3200 $Gg\,yr^{-1}$ (Montzka and Fraser, 2003). The reaction of CH_3Cl with chlorine radicals in the marine boundary layer constitutes another significant sink that has been estimated at 370 $Gg\,yr^{-1}$. Small proportions of tropospheric CH_3Cl are lost to the stratosphere (200 $Gg\,yr^{-1}$) and to mid- and high-latitude waters (75 $Gg\,yr^{-1}$). Another sink for atmospheric CH_3Cl, is degradation by soil microorganisms for which Montzka and Fraser

Table 2. Known sinks of tropospheric CH_3Cl and the mean fractionation factors reported for each.

Sinks	Sink (best estimate)[a] ($Gg\,yr^{-1}$)	Sink (full range)[a] ($Gg\,yr^{-1}$)	Kinetic isotope effect (KIE) ε (per mil)	Error in ε (per mil)
Reaction with OH in troposphere	−3180	−2380 to −3970	59[b]	8
Loss to stratosphere	−200	−100 to −300	0[c]	5
Reaction with Cl in marine boundary layer	−370	−180 to −550	70[b]	10
Microbial degradation in soil	−180 (-1600)	−100 to −1600	47[d]	3
Loss to polar cold ocean waters	−75	−37 to −113	?	?
Total sinks	−4005 (−5425)	−2797 to −6533		

[a] Values for sink strength (best estimate and full range) were taken from Montzka and Fraser (2003), except for the value shown in brackets for the sink (best estimate) for microbial degradation in soil which is from that suggested by Harper and Hamilton (2003) and discussion in the text of this manuscript.

[b] Gola et al. (2005)

[c] Thompson et al. (2002) and discussion in this manuscript

[d] mean of Miller et al. (2001, 2004)

? denotes that no value has been provided

(2003) gave a best estimate of 180 $Gg\,yr^{-1}$. However we believe that compelling evidence is now emerging from microbial studies for a much larger soil sink for CH_3Cl. The ubiquitous occurrence in soil from pristine environments of microbial species capable of utilizing CH_3Cl as sole carbon and energy source implies a widespread and substantial soil sink for CH_3Cl (Harper, 2000; McAnulla et al., 2001; Harper and Hamilton, 2003; Miller et al., 2004). If the microbial sink for CH_3Cl in soil is assumed to account for a similar proportion of the atmospheric burden as with CH_3Br, the magnitude of the soil sink would be of the order 1600 $Gg\,yr^{-1}$ (Harper and Hamilton, 2003). Since the atmospheric concentration of CH_3Cl is around 60 fold higher than that of CH_3Br it may well act as a far better substrate for microorganisms than atmospheric CH_3Br. Hence even a soil sink of 1600 $Gg\,yr^{-1}$ for CH_3Cl may be a considerable underestimate. For the purpose of this paper the values of the oceanic source and sink quoted by Montzka and Fraser (2003) will be used. These numbers do in fact represent a net source in warm waters and a net sink in colder waters (the temperature threshold between these waters being around 12°C). A rigorous isotopic budget would take into account the fact that the gross sources and sinks are larger, the loss processes, for example, not being restricted to cold waters.

A potentially powerful tool in the investigation of the atmospheric CH_3Cl budget is the use of stable carbon isotope ratios ($^{13}C/^{12}C$). For example, this technique has been applied with some success to investigate sources and sinks of atmospheric methane (Miller et al., 2002; Quay et al., 1999) carbon monoxide (Röckmann et al., 1998, 2002) and nitrous oxide (Kim and Craig, 1993; Röckmann et al., 2003) (see Gros et al., 2004 for further references). Furthermore $^{13}C/^{12}C$ ratio measurements are useful in studying non-methane volatile organic compounds (VOCs) in atmospheric samples (Rudolph et al., 1997; Tsunogai et al., 1999). Measurements of the $^{13}C/^{12}C$ isotopic ratio of VOCs including CH_3Cl are usually reported with respect to a standard in "delta" notation where $\delta^{13}C$ is defined as:

$$\delta^{13}\mathrm{C}(\text{per mil}) = (\mathrm{R_{sample}}/\mathrm{R_{standard}} - 1)\times 1000 \text{ per mil} \quad (1)$$

with $R={}^{13}C/{}^{12}C$, where $R_{standard}$ is the $^{13}C/^{12}C$ ratio of an international standard, usually Vienna Pee Dee Belemnite (V-PDB), with a value of $R_{standard}=0.0112372$.

In this paper using an isotopic mass balance approach we attempt to shed light on the question of which CH_3Cl source in the terrestrial environment provides the largest input to the atmosphere. We have utilised recently published information on the $\delta^{13}C$ values of CH_3Cl sources and the latest measurements for the kinetic isotope effects (KIEs) associated with sink processes to determine which source/sink distribution pattern provides the best fit with the observed carbon isotope ratio of atmospheric CH_3Cl.

2 Stable isotope composition of known sources of tropospheric CH_3Cl

The isotope signatures of several CH_3Cl sources have been measured. Values of $\delta^{13}C$ for CH_3Cl released during biomass burning were first measured by Rudolph et al. (1997) and subsequently by Czapiewski et al. (2001). Both studies showed that CH_3Cl emitted is relatively depleted in ^{13}C with $\delta^{13}C$ values ranging from −38 per mil to −68 per mil. For instance, burning of wood of manuka (*Leptospermum scoparium*) resulted in a $\delta^{13}C$ for CH_3Cl released of −45.1±0.6 per mil (Rudolph et al., 1997) which is considerably depleted compared with the unburnt fuel (Δ=17 per mil; in this paper we define the isotope difference between two pools as $\Delta=\delta^{13}C_{pool1}-\delta^{13}C_{pool2}$). Combustion of wood of *Eucalyptus* spp. yielded $\delta^{13}C$ values for CH_3Cl emissions of −51.7 per mil (Czapiewski et al., 2001) which was also highly depleted in comparison with unburnt fuel (Δ=24.8 per mil). Globally the bulk of biomass burning involves C_3 plant material but approximately one-third is associated with tropical and sub-tropical grasslands which are dominated by C_4 plants (Harper et al., 2001). Thompson et al. (2002) assumed that the isotopic fractionation of CH_3Cl relative to the parent fuel is similar for the combustion of material from both C_3 and C_4 plants (Δ=25±12 per mil) and suggested an average $\delta^{13}C$ for CH_3Cl emissions during biomass burning of −47±12 per mil although this has not been confirmed experimentally.

It has been argued that CH_3Cl release by tropical ferns and trees such as dipterocarps could represent the single largest global source of atmospheric CH_3Cl (Yokouchi et al., 2002) although no mechanism has been suggested. Values for $\delta^{13}C$ for CH_3Cl released from two species of glasshouse-grown tropical ferns (*Cyathea smithii* and *Angiopteris evecta*) of −72.7±1.4 per mil and −69.3±0.9 per mil reported by Harper et al. (2003) showed considerable depletion (Δ=42.3 and 43.4 per mil) relative to bulk biomass. This is consistent with the average value obtained for three families of tropical ferns reported by Komatsu et al. (2004). An even greater ^{13}C fractionation has been observed in CH_3Cl emissions by leaves of a glasshouse-grown dipterocarp (*Shorea guiso*) for which a $\delta^{13}C$ value of −75.2±1.7 per mil was determined by Hamilton, Yokouchi, Yukawa and Harper (unpublished results). Harper et al. (2001) measured the $\delta^{13}C$ of CH_3Cl released by different batches of tubers of the potato (*Solanum tuberosum*). The overall mean $\delta^{13}C$ for CH_3Cl emissions was −62.2±4.6 per mil, again showing a substantial depletion (Δ=34.5 per mil) relative to the bulk biomass of the tubers. The same group also reported $\delta^{13}C$ values of CH_3Cl released by glasshouse-grown material of the halophyte *Batis maritima* of −65.7±3.4 per mil, with significant depletion (Δ=36.8 per mil) observed relative to biomass. Later in situ studies on CH_3Cl emissions by *Batis maritima* in Californian salt marsh largely confirmed these observations with weighted daily mean $\delta^{13}C$ values of −62±3 per mil recorded (Bill et al., 2002).

Wood rotting fungi are another significant terrestrial source of atmospheric CH_3Cl (Watling and Harper, 1998). Laboratory studies on the fungus *Phellinus pomaceus* cultured on wood showed ^{13}C depletion in CH_3Cl released relative to the wood substrate. The $\delta^{13}C$ measured for this source was −43.3±0.2 per mil, a fractionation of 17.9 per mil relative to the substrate (Harper et al., 2001).

$\delta^{13}C$ values for industrially produced CH_3Cl from various sources have been variously reported as −41.9±0.3 per mil (Rudolph et al., 1997), −58.4±0.3 per mil (Holt et al., 1997) and for two different batches −46.9±0.8 per mil and −61.9±0.5 per mil (Harper et al., 2001). The isotopic composition of CH_3Cl emissions from coal combustion and incineration has not yet been measured. However as coals have a $^{12}C/^{13}C$ distribution similar to land plants (Hoefs, 1980) we assume that the CH_3Cl fractionation from both sources is the same as that calculated for biomass burning. Any uncertainty regarding this value will not have a significant effect on the atmospheric CH_3Cl ^{13}C signature as both sources combined contribute only about 3% to the total CH_3Cl budget.

The most abundant C_1 units of terrestrial plants, the methoxyl groups (OCH_3) of pectin and lignin, which are responsible for CH_3Cl emissions from senescent leaves and leaf litter referred to earlier in this paper, have a unique carbon isotope signature exceptionally depleted in ^{13}C (Keppler et al., 2004). The carbon isotope signatures of pectin and lignin methoxyl groups of leaf tissue from trees, grasses and halophytes including plants from C_3, C_4 and CAM plant categories were found to be in the range of −33 to −77 per mil and the depletion of the plant methoxyl pool relative to bulk plant biomass ranged from −11 to −46 per mil with the pectin C_1 pool generally more depleted than the lignin C_1 pool. Keppler et al. (2004) reported that CH_3Cl released during low temperature heating of plant leaf tissue was even more depleted in ^{13}C than either of the C_1 plant methoxyl pools. They found $\delta^{13}C$ values of −147, −139 and −119 per mil for CH_3Cl emitted at 40°C from dried leaf tissue of two tree species, European ash (*Fraxinus excelsior*) and wych elm (*Ulmus glabra*), and the grass species, cocksfoot (*Dactylis glomerata*), respectively. These $\delta^{13}C$ values are the lowest ever observed in a terrestrial carbon compound produced by natural processes and represent a striking depletion of 119, 108 and 90 per mil relative to the respective biomass. A large kinetic isotope effect (KIE) is obviously involved in the process leading to CH_3Cl release during heating of such plant material. At the higher temperature of 225°C these researchers also reported very low $\delta^{13}C$ values for CH_3Cl emissions from a variety of C_3 plants (−89.7±10.3 per mil, Δ=60.2 per mil relative to biomass), a C_4 plant, maize (*Zea mays*, −91.3 per mil, Δ=80.3 per mil relative to biomass) and for two CAM plants, saltwort (*Batis maritima*, −78.3 per mil, Δ=52.7 per mil relative to biomass) and scarlet paintbrush (*Crassula falcata*, −81.4 per mil, Δ=63.5 per mil relative to biomass). Clearly therefore, the depletion of ^{13}C in CH_3Cl released during heating of leaf tissue is widespread amongst all plant categories, although this depletion was found to decrease as the heating temperature increased.

The only $\delta^{13}C$ values for CH_3Cl from an oceanic source are those reported by Komatsu et al. (2004). On the basis of measurements made in the NW Pacific Ocean and Tokyo Bay a mean value of −38±4 per mil was recorded which would appear to indicate approximate equilibrium between seawater and the troposphere.

Table 1 summarises existing information on the mean $\delta^{13}C$ value and range reported for each source.

3 Kinetic isotope effects associated with known sinks for tropospheric CH_3Cl

The isotopic composition of atmospheric CH_3Cl can be significantly altered by the kinetic isotope effects of loss processes. Kinetic fractionations occur due to differences in reaction rates of different isotopologues in irreversible physical, chemical, or biological processes. The resulting kinetic isotope effect (KIE) associated with a loss process is defined as:

$$\mathrm{KIE} = \frac{k_{12}}{k_{13}} \tag{2}$$

where k_{12} and k_{13} are the rate constants for loss of the lighter $^{12}CH_3Cl$ isotopologue and the heavier $^{13}CH_3Cl$ isotopologue, respectively. The KIE is typically expressed as a fractionation constant (ε) in per mil:

$$\varepsilon=(\mathrm{KIE}-1)\times 1000 \text{ per mil} \tag{3}$$

where a positive ε indicates that loss causes the remaining sample to be enriched in the heavier isotope.

The dominant loss process for atmospheric CH_3Cl is via reaction with the photochemically produced OH radical in the atmosphere (Montzka and Fraser, 2003). Previously it has been assumed (Harper et al., 2001 and 2003; Thompson et al., 2002) that the KIE for this reaction would be small and similar to that observed for the reaction of methane (CH_4) with OH radical. The carbon KIE for reaction of CH_4 had been measured in the laboratory by Cantrell et al. (1990) (k12/k13=1.0054, ε=5.4) and more recently by Saueressig et al. (2001) (k12/k13=1.0039, ε=3.9). However the first measurement of the KIE for reaction of CH_3Cl with OH has recently been reported by Gola et al. (2005) and reveals an unexpectedly large fractionation factor of ε=59 per mil ±8 per mil. The reaction of CH_3Cl with chlorine radicals in the marine boundary layer constitutes another significant loss process. The KIE for this reaction is reported as 70 per mil±10 per mil (Gola et al., 2005).

As explained by Thompson et al. (2002), loss of tropospheric CH_3Cl to the stratosphere is caused by turbulent mixing and the transport process itself is not considered to result in an isotope fractionation. Isotope fractionation during exchange of CH_3Cl between the oceans and the atmosphere has not yet been quantified, so the treatment of marine fluxes has to be approximate.

As discussed in the introduction, the microbial degradation of CH_3Cl in the soil is potentially a large sink for atmospheric CH_3Cl, possibly second in importance to the reaction with OH radical. Recent work by Miller et al. (2001 and 2004) has shown a KIE of 1.045 and 1.049, respectively, for degradation of CH_3Cl by soil bacteria. Thus a microbial sink accounting for around 20–30% of atmospheric CH_3Cl significantly affects the $\delta^{13}C$ value of atmospheric CH_3Cl.

The known CH_3Cl sinks in the environment and their associated fractionation factors as well as the uncertainties are presented in Table 2. Figure 1 summarises diagrammatically the atmospheric CH_3Cl budget showing the carbon isotope signatures of sources and fractionation constants associated with sinks.

4 Budget modelling of atmospheric CH_3Cl using stable carbon isotope signatures of sources and sinks

Assuming the budget is at steady state the isotopic composition of atmospheric CH_3Cl reflects the weighted average isotopic signature of all the sources, and the weighted average kinetic isotope effect of all the loss mechanisms:

$$\delta^{13}\mathrm{C}^{\mathrm{atm}}=\sum_{i=l}^{n}\Phi_i^{\mathrm{source}}\times\delta^{13}\mathrm{C}_i^{\mathrm{source}}+\sum_{j=l}^{n}\Phi_j^{\mathrm{sink}}\times\varepsilon_j^{\mathrm{sink}} \tag{4}$$

where $\delta^{13}\mathrm{C}^{\mathrm{atm}}$ and $\delta^{13}C_i^{\mathrm{source}}$ are the carbon isotope composition of CH_3Cl in the atmosphere and of the different sources i in per mil. Φ_i and Φ_j are the CH_3Cl flux fraction for each source and sink. ε_j is the fractionation constant of each sink j in per mil. Equation (4) is an approximation that is commonly used in calculations relating to global budgets, however, a more exact calculation requires that a small correction be applied as follows (Kaiser, 2005):

$$\delta^{13}\mathrm{C}^{\mathrm{atm}}=\sum_{i=l}^{n}\Phi_i^{\mathrm{source}}\times\delta^{13}\mathrm{C}_i^{\mathrm{source}}\left(1+\sum_{j=l}^{n}\Phi_j^{\mathrm{sink}}\times\varepsilon_j^{\mathrm{sink}}\right)+\sum_{j=l}^{n}\Phi_j^{\mathrm{sink}}\times\varepsilon_j \tag{5}$$

To date measurements of $\delta^{13}C$ for atmospheric CH_3Cl including marine, urban, rural, and remote sites have been reported by Rudolph et al. (1997), Tsunogai et al. (1999), and Thompson et al. (2002) with values ranging between −30 and −47 per mil. Thompson et al. (2002) reported $\delta^{13}C$ measurements for CH_3Cl from both Northern and Southern hemisphere. Although the number of data points from the Southern hemisphere was rather limited Thompson et al. (2002) reported a global average value $\delta^{13}C$ of CH_3Cl of −36.2±0.3 per mil and this value is employed in the calculations below.

Several attempts at modelling the atmospheric CH_3Cl budget using carbon isotope ratios have been made (Harper et al., 2001, 2003; Thompson et al., 2002; Komatsu et al., 2004) but all have been hampered by the lack of data concerning isotopic fractionation of some important sources and the KIE associated with the major sinks. The recent discoveries made by Gola et al. (2005), Hamilton et al. (2003) and Keppler et al. (2004) are critically important in the development of a much refined isotopic mass balance for atmospheric CH_3Cl.

As mentioned above, the largest uncertainty in sinks is that due to microbial degradation of atmospheric CH_3Cl. In this paper we present three scenarios based on different strengths for the microbial sink and different emissions for

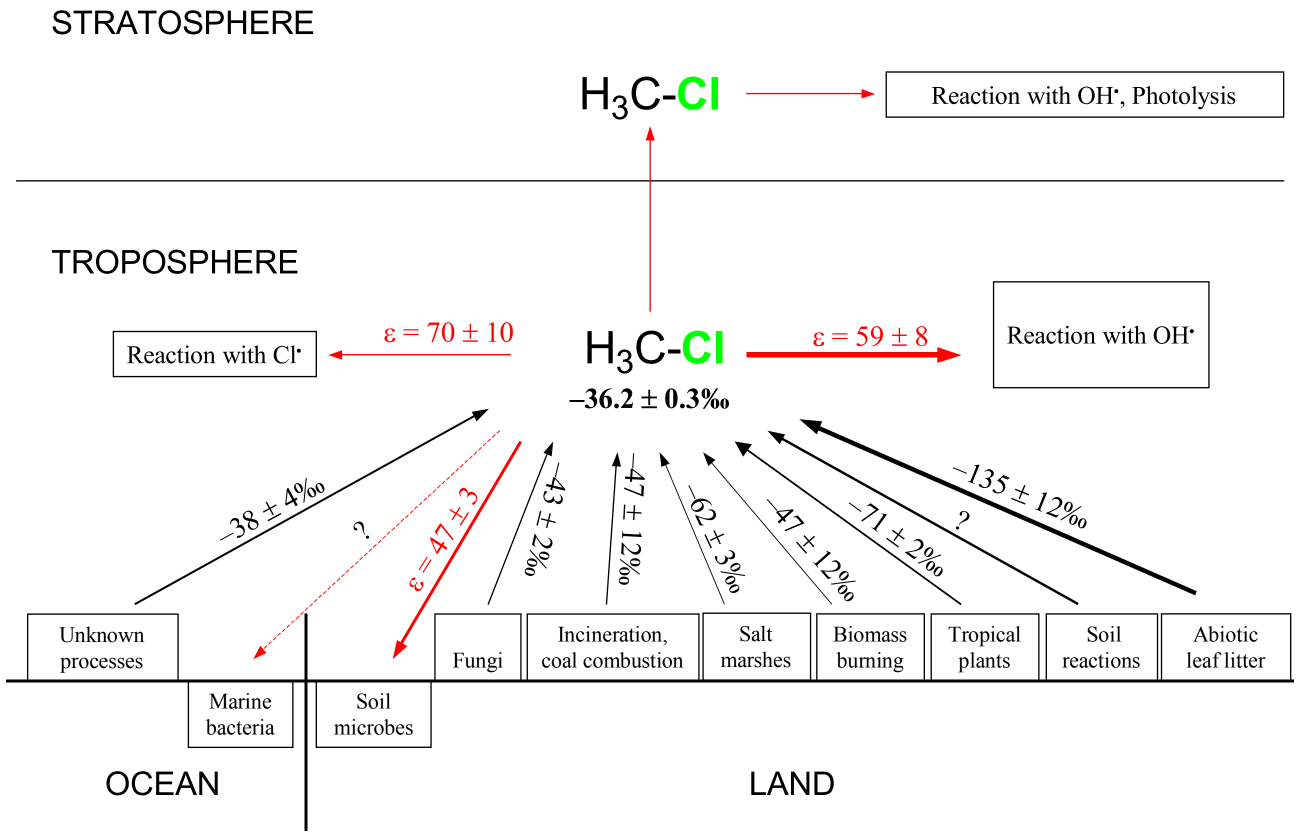

Fig. 1. Scheme of major sources and sinks involved in the global CH_3Cl cycle and the corresponding carbon isotope signatures and fractionation factors. Black arrows show sources and red arrows indicate sinks of CH_3Cl in the environment.

the missing source. Data for each scenario are listed in Table 3. The values for the missing sources are calculated by subtracting total known sources from total sinks. Scenario A uses the Montzka and Fraser (2003) values for the microbial sink (180 Gg yr^{-1}) and the total sink (4005 Gg yr^{-1}) of atmospheric CH_3Cl. In scenario B a microbial sink of 890 Gg yr^{-1} (mean of estimates from Montzka and Fraser, 2003; Harper and Hamilton, 2003) and a total sink of 4715 Gg yr^{-1} are used for the calculations. Finally, for scenario C we consider 1600 Gg yr^{-1} for the microbial sink and a total sink strength of 5425 Gg yr^{-1}.

First we determine the global average CH_3Cl composition of the sources from the atmospheric average ($\delta^{13}C^{\text{atm}}$=−36.2±0.3 per mil) and the weighted mean for all sinks based on scenario A, B and C ($\sum_{j=l}^{n}\Phi_j^{\text{sink}}\times\varepsilon_j^{\text{sink}}$=55.4±6.4 per mil, 54.2±5.5 per mil and 53.2±4.8 per mil. The resulting average $\delta^{13}C$ composition for all sources ($\delta^{13}C_{\text{total}}$) is calculated to be −86.8±6.4 per mil, −85.7±5.5 per mil and −84.9±4.8 per mil for Scenario A, B and C, respectively. Thus in all scenarios, the weighted mean of $\delta^{13}C$ values of total sources is in the range of −87 to −85 per mil.

In the second step we determine the isotope composition of the missing source ($\delta^{13}C_{\text{mis}}$). Using the weighted average of emissions from all known sources for which best estimates are available including biomass burning, fungi, salt marshes, tropical plants, coal combustion and incineration and assuming an isotopic signature of −50.0 per mil for the wetlands and rice paddie sources yields $\delta^{13}C_{\text{knownsources}}$=−53.3±3.6 per mil from which we can calculate the $\delta^{13}C_{\text{mis}}$ for each scenario as follows:

$$\delta^{13}C_{\text{mis}} = \frac{\left[\delta^{13}C_{\text{total}} - \delta^{13}C_{\text{knownsources}} \times (1-\Phi_{\text{mis}})\right]}{\Phi_{\text{mis}}} \quad (6)$$

$\delta^{13}C_{\text{knownsources}}$ is weighted for known sources only whilst Φ_{mis} is normalised by the sum of all sources including the missing source. For scenario A values of Φ_{mis}=0.262, $\delta^{13}C_{\text{total}}$=−86.8±6.4 per mil and $\delta^{13}C_{\text{knownsources}}$=−53.3±3.6 per mil are used for calculations. Thus the isotope signature estimated for $\delta^{13}C_{\text{mis}}$ in scenario A is −181.3±26.5 per mil. Using a similar approach for scenario B (Φ_{mis}=0.373, $\delta^{13}C_{\text{total}}$=−85.7±5.5 per mil and $\delta^{13}C_{\text{knownsources}}$=−53.3±3.6 per mil) the estimated value for $\delta^{13}C_{\text{mis}}$ would be −140.2±15.9 per mil. In scenario C (Φ_{mis}=0.455, $\delta^{13}C_{\text{total}}$=−84.9±4.8 per mil and

$\delta^{13}C_{knownsources}$=$-53.3\pm3.6$ per mil) the respective value for $\delta^{13}C_{mis}$ is $-122.8\pm$ 11.4 per mil.

It is evident from those budget calculations that the missing global CH_3Cl source must have a highly depleted stable carbon isotope signature. Scenario A requires the missing source to have an isotopic composition which is much more depleted than any source reported to date. Based on our current knowledge it is most improbable that there is an as yet unidentified global CH_3Cl source of 1049 Gg yr^{-1} with a $\delta^{13}C$ signature of -181.3 ± 26.5 per mil. However, in scenarios B and C sources of 1759 or 2469 Gg yr^{-1} with respective signatures of -140.2 ± 15.9 per mil and -122.8 ± 11.4 per mil fit well with both the range of CH_3Cl emissions by senescent plants and leaf litter in the tropics and sub-tropics (Hamilton et al., 2003) and the $\delta^{13}C$ signature of these emissions ($\delta^{13}C=-135\pm12$ per mil; Keppler et al., 2004). Furthermore the source strengths of CH_3Cl used for scenario C are in general agreement with experimental observations by Scheeren et al. (2003) and a three dimensional global model study of atmospheric CH_3Cl published recently by Yoshida et al. (2004). On the basis of their measurements Scheeren and co-workers suggest a total global emission of 2000 Gg yr^{-1} from tropical forests whilst the Yoshida group hypothesise that a missing terrestrial source of 2900 Gg yr^{-1} is located between 30° N and 30° S. Our calculations also lend credence to the proposal that CH_3Cl degradation by soil microorganisms is a much bigger sink for atmospheric CH_3Cl (>1000 Gg yr^{-1}) than that postulated by Montzka and Fraser (2003). While it was acknowledged above that the gross source and sink fluxes for the ocean are underestimated in these isotopic budgets because only the net exchange is considered, our calculations indicate that inclusion of substantially larger marine source and sink in the budget does not significantly influence the conclusions of this work. This remains true even if liquid/gas phase fractionations in the oceanic sources and sinks of up to 5 per mil are envisaged. Only extreme fractionations would materially affect our conclusions and there is no evidence that such large isotope effects are likely.

The isotope mass balance presented here represents an important step in reducing the large uncertainties that have hitherto surrounded the atmospheric budget of CH_3Cl. It provides strong support for the contention that abiotic methylation of chloride in plants and soil organic matter provides the bulk of CH_3Cl released to the atmosphere. Further refinement of this budget will require not only accurate measurement of source strengths in the field and their respective isotopic signatures but also a recognition that source and sink processes, particularly those in the soil and the oceans, are not entirely independent. Thus isotope ratios measured for CH_3Cl may be expected to reflect the combined effect of both production and loss processes.

Table 3. Source and sink strengths of CH_3Cl^a used for three scenarios.

Scenario	A	B	C
Total sources	4005	4715	5425
Biomass burning	911	911	911
Tropical plants	910	910	910
Fungi	160	160	160
Salt marshes	170	170	170
Wetlands	40	40	40
Coal combustion	105	105	105
Incineration	45	45	45
Industrial	10	10	10
Rice	5	5	5
Oceans	600	600	600
Total known sources	2956	2956	2956
Missing source	1049	1759	2469
Total sinks	−4005	−4715	−5425
Reaction with OH in troposphere	−3180	−3180	−3180
Loss to stratosphere	−200	−200	−200
Reaction with Cl in marine boundary layer	−370	−370	−370
Loss to cold ocean waters	−75	−75	−75
Microbial degradation in soil	−180	−890	−1600

[a] Units are in Gg yr^{-1}

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