Mass spectrometric measurement of hydrogen isotope fractionation for the reactions of chloromethane with OH and Cl

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Abstract

Chloromethane (CH₃Cl) is an important provider of chlorine to the stratosphere but yet lacks detailed knowledge of its budget. Stable isotope analysis is potentially a powerful tool to constrain CH₃Cl flux estimates. The largest degree of isotope fractionation is expected to occur for deuterium in CH₃Cl in the hydrogen abstraction reactions with its main sink reactant tropospheric OH and its minor sink reactant Cl atoms. We determined the isotope fractionation by stable hydrogen isotope analysis of the fraction of CH₃Cl remaining after reaction with hydroxyl and chlorine radicals in a 3.5 m³ Teflon smog-chamber at 293 ± 1K. We measured the increasing stable hydrogen isotope values of the unreacted CH₃Cl using compound specific thermal conversion isotope ratio mass spectrometry. The isotope fractionations of CH₃Cl for the reactions with hydroxyl and chlorine radicals were found to be -242 ± 7 mUr (or ‰) and -280 ± 11 mUr, respectively. For comparison, we performed
similar experiments using methane (CH$_4$) as the target compound with OH and obtained a fractionation constant of -205 ± 6 mUr which is in good agreement with values previously reported. The observed large kinetic isotope effects are helpful when employing isotopic analyses of CH$_3$Cl in the atmosphere to improve our knowledge of its atmospheric budget.

1 Introduction

Chloromethane (often named methyl chloride) is the most abundant chlorine containing trace gas in the Earth’s atmosphere, currently with a global mean mixing ratio of ~540 ± 5 parts per trillion by volume (pptv) and an atmospheric lifetime of 1.0–1.2 years (Carpenter et al., 2014). The global emissions of CH$_3$Cl have been estimated to be in the range of 4 to 5 Tg yr$^{-1}$ (1 Tg = 10$^{12}$ g) stemming from predominantly natural but also anthropogenic sources (Montzka and Fraser, 2003; WMO, 2011; Carpenter et al., 2014). However, current estimates of the CH$_3$Cl global budget and the apportionment between sources and sinks are still highly uncertain. Known natural sources of CH$_3$Cl include tropical plants (Yokouchi et al., 2002; Yokouchi et al., 2007; Umezawa et al., 2015), wood-rotting fungi (Harper, 1985), oceans (Moore et al., 1996), plants of salt marshes (Rhew et al., 2003; Rhew et al., 2000), aerated and flooded soil (Redeker et al., 2000; Keppler et al., 2000), senescent leaves and leaf litter (Hamilton et al., 2003; Derendorp et al., 2011) and wild fires. Anthropogenic CH$_3$Cl release to the atmosphere comes from the combustion of coal and biomass with minor emissions from cattle (Williams et al., 1999) and humans (Keppler et al., 2017). In addition, it has been reported that emissions from industrial sources, particularly in China, might be much higher than previously assumed (Li et al., 2016).

The dominant sink for atmospheric CH$_3$Cl results from the reaction with photochemically-produced hydroxyl radicals (OH), currently estimated at about 2.8 Tg yr$^{-1}$ (Carpenter et al., 2014). Furthermore, in the marine boundary layer the reaction of CH$_3$Cl with chlorine radicals (Cl) represents another sink estimated to account for up to 0.4 Tg yr$^{-1}$ (Khalil et al., 1999; Montzka and Fraser, 2003). Microbial CH$_3$Cl degradation in soils may be a relevant additional global sink (McAnulla et al., 2001; Harper et al., 2003; Miller et al., 2004; Jaeger et al., 2018a) but its impact on the global CH$_3$Cl budget is still highly uncertain. The microbial CH$_3$Cl soil sink strength has been estimated to range from 0.1 to 1.6 Tg yr$^{-1}$ (Harper et al., 2003; Keppler et al., 2005; Carpenter et al., 2014). Moreover, small proportions of tropospheric CH$_3$Cl are lost to the stratosphere (146 Gg yr$^{-1}$, 1 Gg = 10$^9$ g) and
to cold polar oceans (370 Gg yr⁻¹) though oceans in total are a net source (Carpenter et al.,
2014).

A potentially powerful tool in the investigation of the budgets of atmospheric volatile organic
compounds is the use of stable isotope ratios (Brenninkmeijer et al., 2003; Gensch et al.,
2014). Stable isotope analysis, when used in combination with CH₂Cl flux measurements, has
the potential to better constrain the atmospheric CH₃Cl budget as suggested by Keppler et al.
(2005) and Saito & Yokouchi (2008). The isotopic composition of tropospheric CH₃Cl
depends on the isotopic source signatures and the kinetic isotope effects (KIE) of the sinks.
Several studies have investigated the stable carbon isotope source signature of CH₃Cl
produced via biotic and abiotic processes, however, for a more detailed overview we refer
readers to the studies reported by Keppler et al. (2005) and Saito & Yokouchi (2008).
Moreover, a few studies have measured the KIE of stable carbon isotopes of CH₃Cl during
oxidation or biodegradation by bacterial isolates (Miller et al., 2001; Nadalig et al., 2013;
Nadalig et al., 2014) or in soils under laboratory conditions (Miller et al., 2004; Jaeger et al.,
2018a). The first, and so far, only available analysis of the KIE for reaction of CH₂Cl with
OH has been reported by Gola et al. (2005) and revealed an unexpectedly large stable carbon
isotope fractionation. The experiments were carried out in a smog chamber using long path
Fourier-transform infrared spectroscopy (FTIR) detection. However, in view of the
unexpected isotope fractionation we consider it important to confirm this result using other
measurement methods such as stable isotope ratio mass spectrometry (IRMS).

So far isotopic investigations of CH₃Cl have predominantly focused on stable carbon isotope
measurements. Stable hydrogen isotope measurements including both sources and sinks of
CH₃Cl have become available only recently (Greule et al., 2012; Nadalig et al., 2014; Nadalig
et al., 2013; Jaeger et al., 2018b; Jaeger et al., 2018a). Moreover, relative rate experiments
have been carried out for three isotopologues of CH₃Cl and their reactions with Cl and OH.
The OH and Cl reaction rates of CH₂DCl were measured by long-path FTIR spectroscopy
relative to CH₂Cl at 298 ± 2 K and 1 atm (Sellevåg et al., 2006) (Table 1).

In this manuscript, using a 3.5 m³ Teflon smog chamber and IRMS measurements, we
present results from kinetic studies of the hydrogen isotope fractionation in the atmospheric
OH and Cl loss processes of CH₃Cl. Furthermore, we also measured the isotope fractionation
for the reaction between methane (CH₄) and OH using a similar experimental design and
compared this value with those from previous studies.
2 Materials and Methods

2.1 Smog chamber experiments with chloromethane

The isotope fractionation experiments were performed in a 3.5 m³ Teflon smog-chamber (fluorinated ethylene propylene, FEP 200A, DuPont, Wilmington, DE, USA) with initial CH₂Cl mixing ratio of about 10 parts per million by volume (ppmv). Atomic chlorine were generated via photolysis of molecular chlorine (Cl₂) (Rießner Gase, 0.971% Cl₂ in N₂) by a solar simulator with an actinic flux comparable to the sun in mid-summer in Germany (Bleicher et al., 2014). Hydroxyl radicals were generated via the photolysis of ozone (O₃) at 253.7 nm in the presence of water vapor (RH = 70%) (produced by double-distilled water in a three-neck bottle humidifier) and/or H₂. To obtain efficient OH formation, a Philips TUV lamp (55 W) was welded in Teflon film (FEP 200) and mounted inside the smog chamber. O₃ was monitored by a chemiluminescence analyzer (UPK 8001). The chamber was continuously flushed with purified, hydrocarbon-free zero air (zero-air-generator, cmc instruments, <1 ppbv of O₃, <500 pptv NOₓ, <100 ppbv of CH₄) at a rate of 4 L min⁻¹ to maintain a slight overpressure of 0.5-1 Pa logged with a differential pressure sensor (Kalinsky Elektronik DS1). The quality of the air inside the chamber in terms of possible contamination was controlled by monitoring NO and NOₓ (EcoPhysics CLD 88p, coupled with a photolytic converter, EcoPhysics PLC 860). Perfluorohexane (PFH) with an initial mixing ratio of ~25 parts per billion by volume (ppbv) was used as an internal standard to correct the resulting concentrations for dilution. The temperature was set to 20±1°C and monitored, together with the relative humidity, by a Teflon-cased sensor (Rotronic, HC2-IC102). To guarantee constant mixing and small temperature gradients, a Teflon fan was mounted and operated inside the chamber. More detailed specification of the smog chamber can be found elsewhere (e.g. Wittmer et al., 2015). The mixing ratios of CH₃Cl and PFH were monitored by gas chromatography-mass spectrometry (GC-MS, Agilent Technologies, Palo Alto, CA) with a time resolution of 15 minutes throughout the experiments. Aliquots (5 ml) were withdrawn from the chamber with a gas tight syringe, injected into a stream of He (30 ml min⁻¹) and directed to a pre-concentration unit that was attached to the GC-MS. The pre-concentration unit consisted of a simple 8 port valve (VICI Valco) equipped with two cryotrap made of fused silica, which were immersed in liquid nitrogen for trapping the analytes. Prior to each sample measurement, a gaseous standard (5 ml of 100 ppmv CH₃Cl in N₂) was measured. Figure 1 shows the design of the smog chamber used in our experiments.
In the CH₃Cl and OH experiments (1 and 2) 2000 ppmv H₂ was used to scavenge chlorine atoms originating from the photolysis or oxidation of formyl chloride (HCOCl), which forms as an intermediate in the reaction cascade. Under the experimental conditions typically more than 70% of the CH₃Cl was degraded within 7 to 10 h. From each experiment (CH₃Cl + OH and CH₃Cl + Cl) 10 to 15 canister samples (2 L stainless steel, evacuated <10⁻⁴ mbar) were collected at regular time intervals for subsequent stable hydrogen isotope measurements at Heidelberg University.

Figure 1: Scheme of the experimental smog chamber
2.2 Smog chamber degradation experiments with methane

The CH\textsubscript{4} degradation experiments were carried under the same conditions as the CH\textsubscript{3}Cl degradation experiments but without PFA as an internal standard. Instead we used the flushing flow rate of zero air to account for the dilution during the experiment. The initial CH\textsubscript{4} mixing ratio was 6 ppmv. Throughout these experiments CH\textsubscript{4} mixing ratios were monitored with a Picarro G225i cavity ring down spectrometer directly connected to the chamber.

2.3 Stable hydrogen isotope analysis using isotope ratio mass spectrometry

2.3.1 Chloromethane

Stable hydrogen isotope ratios of CH\textsubscript{3}Cl were measured by an in-house built cryogenic pre-concentration unit coupled to a Hewlett Packard HP 6890 gas chromatograph (Agilent Technologies, Palo Alto, CA) and an isotope ratio mass spectrometer (IRMS) (Isoprime, Manchester, UK) as described in detail by Greule et al. (2012). Diverging from the method of Greule et al. (2012) a ceramic tube reactor without chromium pellets at 1450°C was instead used for high-temperature conversion (HTC). A tank of high-purity H\textsubscript{2} (Alphagaz 2, hydrogen 6.0, Air Liquide, Düsseldorf, Germany) with a $\delta^{2}$H value of ~−250 mUr (milliurey $= 0.001 = 1\%$, cf. section below) versus VSMOW was used as the working gas. All measured sample $\delta^{2}$H values were monitored for their relative trueness by analyzing an in-house working standard of known $\delta^{2}$H value. The CH\textsubscript{3}Cl working standard was calibrated against IAEA standards NBS 22, LVSEC (carbon), VSMOW and SLAP (hydrogen) using TC/EA-IRMS (elemental analyser-isotopic ratio mass spectrometer, IsoLab, Max Planck Institute for Biogeochemistry, Jena, Germany) resulting in a $\delta^{2}$H value of $−140.1 ± 1.0$ mUr vs. VSMOW ($n = 10$, $1\sigma$). The $H_3^+$ factor, determined daily during this investigation (two different measurement periods), was in the range of 5.75 - 6.16 (first period) and 8.90 - 9.21 (second period). The mean precision based on replicate measurements ($n = 6$) of the CH\textsubscript{3}Cl working standard was 2.1 mUr and 3.8 mUr for the first and second measurement periods, respectively. Samples were analyzed three times ($n = 3$), and the standard deviations (SD) of the measurements were in the range of 1.2 to 103.8 mUr. Lowest SD were observed for samples with lowest $\delta^{2}$H values ($−140$ mUr) and highest mixing ratios and higher SD for samples with highest $\delta^{2}$H values ($+800$ mUr) and lowest mixing ratios.
To comply with International System of Units (SI) guidelines, we follow the proposal of Brand and Coplen (2012) and use the symbol Ur, after H.C. Urey (Urey, 1948), as the isotope delta value unit. Thus, an isotope-delta value expressed traditionally as −50 ‰ can be written −50 mUr. Similarly as for the δ²H values, throughout the manuscript we also report the isotope enrichment factor ε in mUr.

Please note that the above described 1-point calibration of the δ²H data might be affected by an additional error ("scale compression") and particularly might affect the uncertainties of the very positive δ²H values. Unfortunately CH₃Cl working standards with distinct isotopic signatures spanning the full range of measured δ²H values (-150 to ~+800 mUr) are not currently available to eliminate or minimize such an error.

### 2.3.2 Methane

Stable hydrogen isotope ratios of CH₄ were analyzed using an in-house built cryogenic pre-concentration unit coupled to a Hewlett Packard HP 6890 gas chromatograph (Agilent Technologies, Palo Alto, CA) and an isotope ratio mass spectrometer (DeltaPlus XL, ThermoQuest Finnigan, Bremen, Germany). The working gas was the same as that used for δ²H analysis of CH₃Cl (c.f. section 2.3.1.).

All δ²H values obtained from analysis of CH₄ were corrected using two CH₄ working standards (isometric instruments, Victoria, Canada) calibrated against IAEA and NIST reference substances (not specified by the company). The calibrated δ²H values of the working standard in mUr vs. V-SMOW were -144 ± 4 mUr and -138 ± 4 mUr.

The H³⁺ factor determined daily during the two week measurement period was in the range 2.38–2.43. The daily average precision based on replicate measurements of the CH₄ working standard was 4.9 mUr (n = 7). Samples were analyzed 3 times (n = 3), and the SD of the measurements were in the range of 1.4 to 40.9 mUr. Lowest SD were observed for samples with lowest δ³H values (~-140 mUr) and highest mixing ratios and higher SD for samples with highest δ³H values (~+800 mUr) and lowest mixing ratios.
2.4 Kinetic isotope effect, fractionation constant $\alpha$ and the isotope enrichment constant $\varepsilon$

The isotopic composition of atmospheric compounds might be altered by the kinetic isotope effects of physical, chemical or biological loss processes. The kinetic isotope effect (KIE) is usually defined as:

$$KIE = \frac{k_1}{k_2}$$  \(1\)

where $k_1$ and $k_2$ are the reaction rate constants for loss of the lighter and the heavier isotopologues, respectively. The KIE is typically expressed as isotope fractionation $\varepsilon$ (also termed isotope enrichment constant) or isotope fractionation constant $\alpha$.

In this study the isotope fractionation constant $\alpha$ and the isotope enrichment constant $\varepsilon$ are derived from the slope of the Rayleigh plot according to (Clark and Fritz, 1997; Elsner et al., 2005) and equation 2:

$$\ln \frac{R_t}{R_0} = \ln \left(\frac{\delta^2 H_t + 1000}{\delta^2 H_0 + 1000}\right) = \ln \left(\frac{\delta^2 H_0 + \delta^2 H_1 + 1}{\delta^2 H_0 + 1}\right) \cong (\alpha - 1) \cdot \ln f = \varepsilon \cdot \ln f$$  \(2\)

Where $R_t$ and $R_0$ are the $^2$H/$^1$H ratios in CH$_3$Cl or CH$_4$ at the different time points and time zero, respectively, and $f$ is the remaining CH$_3$Cl or CH$_4$ fraction at the different time points. Negative values of $\varepsilon$ indicates that the remaining CH$_3$Cl or CH$_4$ is enriched in the heavier isotope and corresponds to $\alpha<1$, meaning that over the entire experiment, the heavier CH$_3$Cl or CH$_4$ react by this factor more slowly than the lighter CH$_3$Cl or CH$_4$.

The kinetic isotope effect is then calculated as:

$$KIE = \frac{1}{\alpha}$$  \(3\)

To correct for ongoing analyte dilution the remaining fraction $f$ has been calculated as follows

$$f = c_{xT}c_{oi}/(c_{x0}c_{iT})$$  \(4\)

where $c_{x0}$ and $c_{xT}$ are the mixing ratios of CH$_3$Cl at time zero and time t and $c_{oi}$ and $c_{iT}$ are the respective concentrations of the internal standard PFH.
3 Results

The first experiment of CH₃Cl degradation with OH was performed on the 25/02/2014 and repeated under similar conditions on the 03/02/2015. Under the experimental conditions (see methods section) more than 70% of the CH₃Cl was degraded within 7 to 10 h. The results from these two experiments are shown in Figure 2. Both the trend of changes in δ²H values of CH₃Cl as well as the remaining fraction of CH₃Cl observed in the two independent experiments are in good agreement (Figure 2a). The calculated ε values for experiments 1 and 2 are -264 ± 8 mUr and -220 ± 6 mUr, respectively (Figure 2b), with a correlation coefficient R² of the slope of the regression line of 0.99 for both experiments.

Figure 2: Reaction of CH₃Cl and OH. Two independent experiments (triangles and dots) were carried out using an initial mixing ratio of ~10 ppmv CH₃Cl. More than 70% of the CH₃Cl was degraded within 8 to 10 h. (a) Measured δ²H values (filled circles and triangles) of CH₃Cl versus residual fraction (open circles and triangles) of CH₃Cl (calculated from changes of CH₃Cl and PFH). Error bars of δ²H value of CH₃Cl indicate the standard deviation (SD) of the mean of three replicate measurements. Some error bars lie within the symbol. (b) Rayleigh plot (equation 2). Error bars were calculated by error propagation including uncertainties in δ²H values of CH₃Cl and the remaining fraction. Dashed lines represent 95% confidence intervals of the linear regressions (bold lines).
The CH$_3$Cl degradation with Cl experiment was conducted on the 18/02/2014. Here, over 90% of CH$_3$Cl was degraded during reaction with Cl radicals within 7 to 8 hours (Figure 3a). The calculated $\varepsilon$ of experiment 3 is $-280 \pm 11$ mUr (Figure 3b) with a correlation coefficient of the slope of the regression line of 0.99. Due to limited analytical resources it was not possible to repeat this experiment.

**Figure 3:** Reaction of CH$_3$Cl and Cl. Initial mixing ratio of CH$_3$Cl was $\sim$10 ppmv. More than 90% of the CH$_3$Cl was degraded within 7 to 8 h. (a) Measured $\delta^2$H values (filled circles) of CH$_3$Cl versus residual fraction (open diamonds) CH$_3$Cl. Error bars of $\delta^2$H values of CH$_3$Cl indicate the standard deviation (SD) of the mean of three replicate measurements. Some error bars lie within the symbol. (b) Rayleigh plot (equation 2). Data are expressed as the mean $\pm$ standard error of the mean, n = 3. Error bars were calculated by error propagation including uncertainties in $\delta^2$H values of CH$_3$Cl. Dashed lines represent 95% confidence intervals of the linear regressions (bold line).
The experiment to determine the isotope enrichment constant of the degradation of CH$_4$ by hydroxyl radicals was conducted on the 02/02/2015. Over 80% of CH$_4$ was degraded during...
reaction with OH radicals within 7 hours (Figure 4a). The calculated \( \varepsilon \) of experiment 4 is \(-270^{205 \pm 6}\) mUr (Figure 4b) with a correlation coefficient of the slope of the regression line of 0.99.

**Figure 4:** Reaction of CH\(_4\) and OH. Initial mixing ratio of CH\(_4\) was \(-6\) ppmv. More than 80\% of the CH\(_4\) was degraded within 7 h. (a) Measured \( \delta^2\text{H} \) values of CH\(_4\) versus residual fraction of CH\(_4\). Error bars of \( \delta^2\text{H} \) values of CH\(_4\) indicate the standard deviation (SD) of the mean of three replicate measurements. Some error bars lie within the symbol. (b) Rayleigh plot (equation 2). Error bars were calculated by error propagation including uncertainties in \( \delta^2\text{H} \) values of CH\(_4\) and the remaining fraction. Dashed lines represent 95\% confidence intervals of the linear regressions (bold line).
Discussion

Chloromethane reacts with both hydroxyl and chlorine radicals in the atmosphere. The first degradation step of CH$_3$Cl in both reactions is the abstraction of a hydrogen atom to yield CH$_2$Cl and H$_2$O or HCl, respectively (Spence et al., 1976; Khalil and Rasmussen, 1999). In both reactions hydrogen is directly present in the reacting bond, and thus influenced by the so-called primary isotope effect (Elsner et al., 2005). Particularly for hydrogen these primary kinetic isotope effects are in general large as they involve a large change in relative mass of the atoms being abstracted. In the following we would like to discuss and compare our results with (i) previous work conducted by (Sellevåg et al., 2006), (ii) with OH degradation experiments of CH$_4$ and (iii) with the very recent report of biochemical degradation of CH$_3$Cl in soils and plants (Jaeger et al., 2018b; Jaeger et al., 2018a).

Although our experimental results show relatively large hydrogen isotope fractionations with $\varepsilon$ values of -242 (mean result from two independent experiments) and -280 mUr, for reaction of CH$_3$Cl with OH and Cl radicals, respectively, they are smaller than the isotope fractionations previously measured and theoretically calculated by (Sellevåg et al., 2006) (Table 1). These researchers employed smog chamber experiments at 298 K and used FTIR measurements to determine the stable hydrogen isotope fractionation of CH$_3$Cl and reported $\varepsilon$ values of -410 and -420 mUr for the reaction of CH$_3$Cl with OH and Cl radicals, respectively.
They also performed theoretical calculations of $\epsilon$ for the reactions of CH$_2$DCl with OH and Cl radicals and reported $\epsilon$ values in the range of -330 to -430 and -540 to -590 mUr, respectively (Table 1). Whilst we do not know the reasons for the large discrepancies in the experimental $\epsilon$ values observed here and those reported by Sellevåg et al. (2006), we suggest that they may be due to differences in the experimental smog chamber set-up or the different measurement techniques employed in each of the studies. However, we also conducted similar smog chamber experiments for the degradation of CH$_4$ with hydroxyl radicals (see methods section and Figure 4) and calculated an $\epsilon$ value of -205 ± 6 mUr for the reaction of CH$_4$ with OH radicals at a temperature of 293 ± 1 K. In Table 1 we compare our results with those from a number of previous studies (Saueressig et al., 2001; Sellevåg et al., 2006; DeMore, 1993; Gierczak et al., 1997; Xiao et al., 1993), which were conducted at temperatures ranging from 277 to 298 K (Table 1). The $\epsilon$ values for the reaction of CH$_4$ with OH radicals from all studies ranged from -145 to -294 mUr with a mean value of -229 ± 44 mUr with the most negative $\epsilon$ value of -294 ± 18 mUr reported by Sellavag and coworkers (2006). The $\epsilon$ value found in this study (-205 ± 6 mUr) was in good agreement with previous experimentally reported values conducted at similar temperatures. This finding gave us confidence that our experimental design and the measurements made using GC-IRMS were reliable.

Compared to primary isotope effects, changes in bonding are much smaller in the case of secondary isotope effects, where positions adjacent to the reacting bond are only slightly affected by the proximity to the reaction centre (Elsner et al., 2005; Kirsch, 1977). It was suggested that for the same element, secondary isotope effects are generally at least 1 order of magnitude smaller than primary isotope effects (Kirsch, 1977; Westaway, 1987; Merrigan et al., 1999).

We therefore compared our results from chemical degradation experiments with those from recently reported biochemical degradation experiments (Jaeger et al., 2018a; Jaeger et al., 2018b). So far, the only known pathway for biochemical consumption of CH$_3$Cl is corrinoid- and tetrahydrofolate-dependent and is termed cmu (abbreviation for chloromethane utilization). This pathway was characterized in detail for the aerobic facultative methylotrophic strain *Methylobacterium extorquens* CM4 (Vannelli et al., 1999) and involves genes that were also detected in several other chloromethane-degrading strains (Schafer et al., 2007; Nadalig et al., 2013; Nadalig et al., 2011). During degradation of CH$_3$Cl the methyl group is transferred to a corrinoid cofactor by the protein CmuA. In this case the carbon-
chlorine bond of CH₃Cl is broken and thus since the hydrogen atoms are adjacent to the
reacting bond only a secondary isotope effect would be expected. Indeed, the first ε values
reported (Jaeger et al., 2018a; Jaeger et al., 2018b) for CH₃Cl biodegradation by different
soils and plants (ferns) are in the range of -50 ± 13 mUr and -8 ± 19 mUr, respectively, and
thus showing considerably smaller kinetic isotope effects than for chemical degradation of
CH₃Cl by OH and Cl radicals measured in either this study or reported by Sellevåg et al.

5 Conclusions and future perspectives
We have performed experiments to measure the hydrogen isotope fractionation of the
remaining unreacted CH₃Cl following its degradation by hydroxyl and chlorine radicals in a
3.5 m³ Teflon smog-chamber at 293 ± 1K. δ²H values of CH₃Cl were measured using GC-
IRMS. The calculated isotope fractionations of CH₃Cl for the reactions with hydroxyl and
with chlorine radicals were found to be smaller than either the experimentally measured (by
FTIR) or theoretical values reported by Sellevåg et al. (2006). We also performed
degradation experiments of CH₄ using the same smog-chamber facilities yielding an isotope
enrichment constant for the reaction of CH₄ with hydroxyl radicals of -205 ± 6 mUr which is
in excellent agreement with previous reported results. Although stable hydrogen isotope
measurements of CH₃Cl sources are still scarce, some recent studies have reported first data
on δ²H values of CH₃Cl sources and ε values on sinks (Greule et al., 2012; Jaeger et al.,
2018a; Jaeger et al., 2018b; Nadalig et al., 2014; Nadalig et al., 2013).

We have summarized all available information regarding δ²H values of environmental CH₃Cl
sources in Table 2. Furthermore, the known CH₃Cl sinks and their associated isotope
enrichment constants are presented in Table 3. Eventually Figure 5 displays the global CH₃Cl
budget showing the known hydrogen isotope signatures of sources and isotope enrichment
constants associated with sinks.

Figure 5. Scheme of major sources and sinks involved in the global CH₃Cl cycle (modified
after Keppler et al., 2005) with known (experimentally determined) corresponding δ²H values
and isotope enrichment constants, respectively. Red straight and dashed lines of arrows
indicate sources and sinks of CH₃Cl, respectively. Questions marks indicate where currently
no data exist. All values are given in mUr.
Our results suggest that stable hydrogen isotope measurements of both sources and sinks of CH$_3$Cl and particularly the observed large kinetic isotope effect of the atmospheric CH$_3$Cl sinks might strongly assist with the refinement of current models of the global atmospheric CH$_3$Cl budget. In contrast to the large hydrogen fractionation of CH$_3$Cl by chemical degradation of OH and Cl radicals, the isotope fractionation of CH$_3$Cl biodegradation are in the range of an order of magnitude lower. This therefore holds the opportunity to improve our understanding of the global CH$_3$Cl budget once the $\delta^2$H value of atmospheric CH$_3$Cl has been measured. The stable hydrogen isotopic composition of tropospheric CH$_3$Cl depends on the isotopic source signatures and the kinetic isotope effects of the sinks, primarily the reaction with OH and consumption by soils and potentially plants.

Several attempts at modelling the global CH$_3$Cl budget using stable carbon isotope ratios have already been made (Harper et al., 2001; Harper et al., 2003; Thompson et al., 2002; Keppler et al., 2005; Saito and Yokouchi, 2008) but there are still major uncertainties regarding source and sink strengths as well as the respective stable isotope signatures. Therefore, we now suggest combining our knowledge of stable carbon and hydrogen isotopes of CH$_3$Cl in the environment. Such a two dimensional (2D) stable isotope approach of hydrogen and carbon can be used to better understand the processes of CH$_3$Cl biodegradation and formation. Furthermore, when this approach is combined with CH$_3$Cl flux estimates it
could help to better constrain the strength of CH$_3$Cl sinks and sources within the global CH$_3$Cl budget (Nadalig et al., 2014; Jaeger et al. 2018b)

We would highlight that currently no data is available for the $\delta^{2}$H value of atmospheric CH$_3$Cl. Although it will be a massive analytical challenge to obtain this value, we strongly consider that it would likely lead to a better refined isotopic mass balance for atmospheric CH$_3$Cl and thus to our better understanding of the global CH$_3$Cl budget.

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References


Table 1: Reported hydrogen isotope enrichment constants for the reaction of CH₃Cl with OH radicals and with Cl atoms and the reaction of CH₄ with OH radicals.

<table>
<thead>
<tr>
<th>Reaction</th>
<th>$\varepsilon / \text{mUr}$</th>
<th>Method and remarks</th>
<th>Reference</th>
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</thead>
<tbody>
<tr>
<td>CH₃Cl + OH</td>
<td>-242 mean</td>
<td>experimental: 3.5 m³ smog-chamber at 293 ± 1 K; Exp. 1 &amp; 2, this study</td>
<td>Sellevåg et al. 2006</td>
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<tr>
<td>CH₃Cl + OH</td>
<td>-410 ± 50</td>
<td>experimental: smog-chamber, long-path FTIR spectroscopy relative to CH₃Cl at 298 ± 2 K</td>
<td>Sellevåg et al. 2006</td>
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<tr>
<td>CH₃Cl + OH</td>
<td>-330 to -430</td>
<td>theoretical calculations</td>
<td>Sellevåg et al. 2006</td>
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<tr>
<td>CH₃Cl + Cl</td>
<td>-280 ± 11</td>
<td>experimental: 3.5 m³ smog-chamber at 293 ± 1 K; Exp. 3, this study IRMS</td>
<td>Sellavåg et al. 2006</td>
</tr>
<tr>
<td>CH₃Cl + Cl</td>
<td>-420 ± 40</td>
<td>experimental: smog-chamber, long-path FTIR spectroscopy relative to CH₃Cl at 298 ± 2 K</td>
<td>Sellavåg et al. 2006</td>
</tr>
<tr>
<td>CH₃Cl + Cl</td>
<td>-540 to -590</td>
<td>theoretical calculations</td>
<td>Sellavåg et al. 2006</td>
</tr>
<tr>
<td>CH₄ + OH</td>
<td>-205 ± 6</td>
<td>experimental: 3.5 m³ smog-chamber at 293 ± 1 K; Exp. 4, this study IRMS</td>
<td>Saueressig et al. 2001</td>
</tr>
<tr>
<td>CH₄ + OH</td>
<td>-227 ± 11</td>
<td>experimental: at 296 K, IRMS and tunable diode laser absorption spectroscopy</td>
<td>Gierczak et al., 1997</td>
</tr>
<tr>
<td>CH₄ + OH</td>
<td>-231 ± 45</td>
<td>experimental: at 277 K</td>
<td>Gierczak et al., 1997</td>
</tr>
<tr>
<td>CH₄ + OH</td>
<td>-251 ± 10</td>
<td>ab initio at 298 K</td>
<td>Xiao et al., 1993</td>
</tr>
<tr>
<td>CH₄ + OH</td>
<td>-145 ± 30</td>
<td>experimental: at 298 K</td>
<td>DeMore et al., 1993</td>
</tr>
<tr>
<td>CH₄ + OH</td>
<td>-294 ± 18</td>
<td>experimental: smog-chamber, long-path FTIR spectroscopy relative to CH₃Cl at 298 ± 2 K</td>
<td>Sellavåg et al. 2006</td>
</tr>
<tr>
<td>CH₄ + OH</td>
<td>-60 to -270</td>
<td>theoretical at 298 K</td>
<td>Sellavåg et al. 2006</td>
</tr>
</tbody>
</table>
### Table 2. Known sources of tropospheric CH\(_3\)Cl and corresponding \(\delta^2\)H values.

<table>
<thead>
<tr>
<th>Sources</th>
<th>Source (best estimate)(^a) (Gg yr(^{-1}))</th>
<th>Source (full range)(^a) (Gg yr(^{-1}))</th>
<th>Mean (\delta^2)H value mUr vs VSMOV</th>
<th>Uncertainty (\delta^2)H value ± mUr</th>
</tr>
</thead>
<tbody>
<tr>
<td>Open field biomass burning</td>
<td>355</td>
<td>142 to 569</td>
<td>-236(^b)</td>
<td>44</td>
</tr>
<tr>
<td>Biomass burning indoor</td>
<td>113</td>
<td>56 to 169</td>
<td>-236(^b)</td>
<td>44</td>
</tr>
<tr>
<td>Tropical and subtropical plants</td>
<td>2040</td>
<td>1430 to 2650</td>
<td>-202(^c)</td>
<td>10</td>
</tr>
<tr>
<td>Fungi</td>
<td>145</td>
<td>128 to 162</td>
<td>?</td>
<td></td>
</tr>
<tr>
<td>Salt marshes</td>
<td>85</td>
<td>1.1 to 170</td>
<td>?</td>
<td></td>
</tr>
<tr>
<td>Coal combustion</td>
<td>162</td>
<td>29 to 295</td>
<td>?</td>
<td></td>
</tr>
<tr>
<td>Industrial chemical production(^d)</td>
<td>363</td>
<td>278 to 448</td>
<td>-130(^e)</td>
<td>20</td>
</tr>
<tr>
<td>Oceans</td>
<td>700</td>
<td>510 to 910</td>
<td>?</td>
<td></td>
</tr>
<tr>
<td>Others(^f)</td>
<td>~58</td>
<td>27 to 86</td>
<td>?</td>
<td></td>
</tr>
<tr>
<td><strong>Total sources</strong></td>
<td><strong>3658 (4021)</strong></td>
<td><strong>2601 to 5459</strong></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

\(^a\) Values for source (best estimate) and source (full range) were taken from Carpenter and Reimann (2014), except for emissions associated with chemical production by the industry which are from Li et al. (2016). Value shown for total sources in brackets includes chemical production by the industry.  

\(^b\) Greule et al. 2012; please note that all values provided for CH\(_3\)Cl released from dried plants at elevated temperatures have been corrected by -23 mUr due to recalibration of the reference gas.  

\(^c\) Jaeger et al. (2018b)  
\(^d\) Li et al. (2016)  
\(^e\) taken from Greule et al. (2012), Nadalig et al. (2013) and Jaeger et al. (2018a & 2018b); please note that values provided by Greule et al. (2012) and Nadalig et al. (2013) for CH\(_3\)Cl from sources of the chemical industry have been corrected by -23 mUr due to recalibration of the reference gas  
\(^f\) including mangroves, wetlands, rice paddies and shrublands  

? denotes that no value has been provided.
Table 3. Known sinks of tropospheric CH$_3$Cl and the mean isotope enrichment constant $\varepsilon$ reported for each.

<table>
<thead>
<tr>
<th>Sinks</th>
<th>Sink (best estimate)$^a$ (Gg yr$^{-1}$)</th>
<th>Sink (full range)$^a$ (Gg yr$^{-1}$)</th>
<th>Isotope enrichment constant $\varepsilon$ / mUr</th>
<th>Uncertainty $\varepsilon$ ± mUr</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reaction with OH in troposphere</td>
<td>2832</td>
<td>2470 to 3420</td>
<td>-242$^b$</td>
<td>7$^b$</td>
</tr>
<tr>
<td>Loss to stratosphere</td>
<td>146</td>
<td>?</td>
<td>-410$^c$</td>
<td>50$^c$</td>
</tr>
<tr>
<td>Reaction with Cl in marine boundary layer</td>
<td>370$^d$</td>
<td>180 to 550$^d$</td>
<td>-280$^b$</td>
<td>11$^b$</td>
</tr>
<tr>
<td>Microbial degradation in soil</td>
<td>1058</td>
<td>664 to 1482</td>
<td>-50$^e$</td>
<td>13$^e$</td>
</tr>
<tr>
<td>Loss in ocean</td>
<td>370</td>
<td>296 to 445</td>
<td>0$^c$</td>
<td>10$^f$</td>
</tr>
<tr>
<td>Microbial degradation in plants$^g$</td>
<td>?</td>
<td>?</td>
<td>-8$^g$</td>
<td>19$^g$</td>
</tr>
<tr>
<td>Total sinks</td>
<td>4406 (4776)</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

$^a$ Values for sink strength (best estimate and full range) were taken from Carpenter and Reimann (2014), except for the value of the reaction with Cl-radicals in marine boundary layer and for total sinks shown in brackets which includes the potential sink strength by Cl-radicals in marine boundary layer (Montzka and Fraser, 2003).

$^b$ this study, mean value of two experiments

$^c$ Sellevåg et al. (2006)

$^d$ Thompson et al. (2002) and discussion in this manuscript

$^e$ Jaeger et al. (2018a)

$^f$ Nadalig et al. (2014)

$^g$ Jaeger et al. (2018b)

? denotes that no value has been provided.