Isotopic characterization ($^2$H, $^{13}$C, $^{37}$Cl, $^{81}$Br) of the abiotic sinks of methyl bromide and methyl chloride in water and implications for future studies.

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Abstract. Methyl bromide and methyl chloride are each the largest natural sources of halogens to the stratosphere and hence substantially contribute to stratospheric ozone loss. The atmospheric budgets of both compounds are, despite considerable efforts, still unbalanced with known sinks outweighing known sources. Stable isotope analysis may be capable to provide additional process level information and source differentiation of methyl halides and it is particularly powerful if isotopes of multiple elements in these compounds are measured. In the current study triple-elemental isotope analysis ($^2$H, $^{13}$C, $^{37}$Cl/$^{81}$Br) was applied to investigate the two main abiotic degradation processes of methyl halides (CH$_3$X) in water: hydrolysis and halide exchange. Both nucleophilic substitution reactions caused large carbon and significant bromine isotope effects in CH$_3$Br and small secondary inverse hydrogen isotope effects. Calculated loss rates indicated that exchange with chloride (Cl) may be a major abiotic sink for CH$_3$Br in oceans whereas hydrolysis may contribute to degradation in freshwater and soils. For CH$_3$Cl only hydrolysis was observed with large carbon and chlorine isotope effects and a secondary inverse hydrogen isotope effect. Halide exchange could not be detected for CH$_3$Cl at ambient temperatures and may not be a significant sink for this compound. This study demonstrates, to our knowledge, the first triple-elemental isotope analyses of CH$_3$Cl and CH$_3$Br. The presented results have important implications for source apportionment of tropospheric CH$_3$X if viewed in conjunction with results from previous studies.
1 Introduction

Methyl chloride (CH\textsubscript{3}Cl, chloromethane) and methyl bromide (CH\textsubscript{3}Br, bromomethane) are each the largest natural sources of chlorine and bromine to the stratosphere where they together contribute with about 30% to halogen induced ozone loss (Carpenter et al., 2014). Other than chlorofluorocarbons, CH\textsubscript{3}Cl and CH\textsubscript{3}Br are emitted by both anthropogenic and natural sources such as fumigation, marine macroalgae (Laturnus, 2001), salt marshes (Rhew et al., 2000), soils (Rhew et al., 2007), biomass burning (Reinhardt and Ward, 1995) and tropical plants (Saito and Yokouchi, 2008). Main sinks for both of these compounds are reaction with OH and Cl radicals in the troposphere (Rudolph et al., 2000), uptake by oceans (Hu et al., 2013) and soils (Rhew, 2011) and loss to the stratosphere (Carpenter et al., 2014). Despite considerable efforts, the atmospheric budgets of both compounds are still unbalanced with known degradation processes exceeding the best estimates of the sources by approximately 20% (Yvon-Lewis et al., 2009; Carpenter et al., 2014).

Hydrolysis and halide exchange were identified as major abiotic sinks for methyl halides in oceans besides microbial degradation (Tokarczyk and Saltzman, 2001; Hu et al., 2013). Hydrolysis may also contribute to degradation of CH\textsubscript{3}Br in soils (Papiernik et al., 2000). These nucleophilic substitution reactions (S\textsubscript{N}2) of CH\textsubscript{3}X (CH\textsubscript{3}Cl and CH\textsubscript{3}Br) follow second order reaction kinetics where the attacking nucleophiles are either water (H\textsubscript{2}O) and hydroxide ions (OH\textsuperscript{-}) for neutral (R1) and alkaline (R2) hydrolysis, respectively, or halide ions (R3) such as Cl\textsuperscript{-} and Br\textsuperscript{-} (Y\textsuperscript{-}) for halide exchange (Elliott and Rowland, 1993; Jeffers and Wolfe, 1996; King and Saltzman, 1997):

\[
\begin{align*}
\text{CH}_3\text{X} + \text{H}_2\text{O} & \rightarrow \text{CH}_3\text{OH} + \text{H}^+ + \text{X}^- \\
\text{CH}_3\text{X} + \text{OH}^- & \rightarrow \text{CH}_3\text{OH} + \text{X}^- \\
\text{CH}_3\text{X} + \text{Y}^- & \rightarrow \text{CH}_3\text{Y} + \text{X}^- 
\end{align*}
\]

In principle, hydrolysis of chlorinated aliphatic compounds may occur due to neutral (R1) and/or alkaline hydrolysis (R2) depending on the pH and the reacting organic compound. For instance, solely neutral hydrolysis (R1) was detected for CCl\textsubscript{4} whereas some chlorinated ethenes only reacted with hydroxide ions (R2) (Jeffers et al., 1989). For CH\textsubscript{3}X it was shown that alkaline hydrolysis required a hydroxide concentration larger than 0.1 mol l\textsuperscript{-1} and hence only neutral hydrolysis may be of concern in most environments (Jeffers and Wolfe, 1996). Consequently, reactions R1 and R3 form large sinks for methyl bromide (Moore and Webb, 1996; Lobert et al., 1995; Yvon and Butler, 1996). For methyl chloride, microbial degradation seems to be more important, especially in subarctic and arctic ocean waters due to lower reaction rates (Hu et al., 2013). Still, the importance of these reactions as a sink compared to microbial degradation in oceans and soils is not well understood.

Stable isotope analysis was suggested as a diagnostic tool to overcome the limitations of solely quantifying concentration levels of these compounds (Hunkeler et al., 2008). Isotopic fingerprints of gases emitted by the various sources and isotope fractionation caused by the different sinks adds an additional level of process information that may help to improve budget estimates. For hydrolysis and halogen exchange reactions only two isotope studies have been carried out to date. Kalin et al. (2001) determined the isotopic enrichment factor (\(\varepsilon_C\)) for substitution of Br with Cl in CH\textsubscript{3}Br (\(\varepsilon = -41.5\) mUr; 1 mUr = 0.001
Baesman and Miller (2005) found a slightly larger carbon isotope enrichment factor of -57±5 mUr for this reaction. The enrichment factor ($\varepsilon$) for hydrolysis of CH$_3$Br was -51± 6 mUr (Baesman and Miller, 2005). These two studies demonstrated, that hydrolysis and halide exchange are associated with a generally large carbon isotope effect.

Several studies measured the carbon isotopic composition of various sources and sinks and an overview of these isotopic signatures was presented (Keppler et al., 2005). Despite these achievements, stable isotope measurements have not yet contributed to better budget estimates of CH$_3$Cl and CH$_3$Br because the ranges for isotopic source signatures are often overlapping and coincide with the tropospheric $\delta^{13}$C of CH$_3$X. Significant improvement may be expected if isotopic values of several elements are measured simultaneously for one compound and this technique has been successfully applied to describe the fate of groundwater contaminants (Kuder et al., 2013; Franke et al., 2017). For methyl chloride and methyl bromide no multi-element isotopic studies are available yet. Apart from carbon isotope analysis, hydrogen isotope measurements have been demonstrated for CH$_3$Cl (Nadalig et al., 2013; Keppler et al., 2018; Jaeger et al., 2018). For CH$_3$Br bromine isotope analysis was presented in two studies (Horst et al., 2013; Horst et al., 2014).

In order to improve future budget estimates of ozone depleting methyl halides, multi-element isotope analyses may contribute important information but before any isotope based models are applicable, source signatures and the isotope fractionation caused by sink processes needs to be determined. Hence the objective of the presented study was to characterize the isotopic enrichment factors ($\varepsilon$) caused by hydrolysis and halide exchange reactions with CH$_3$Cl and CH$_3$Br, an important abiotic sink for these compounds. We determined the isotope fractionation of all available stable isotopes, that is, hydrogen and carbon isotopes for both compounds and chlorine as well as bromine isotopes for methyl chloride and methyl bromide, respectively. To our knowledge, the presented data are the first three-dimensional isotope measurements of each of these compounds. The implications of our results for future multi-dimensional isotope studies of methyl halides are discussed.

2 Material and Methods

2.1 Chemicals

Both compounds were purchased as compressed gases and with a purity of more than 99%. Methyl chloride was obtained from Linde Deutschland whereas methyl bromide was purchased from Gerling, Holtz & Co (Germany). A commercially available sea salt without any additives (Aquasale, Heilbronn, Germany) was purchased to prepare brines with a concentration of 3.5% which is similar to seawater.

2.2 Preparation of samples and experiments

Stock solutions with a concentration of 10 mmol/L CH$_3$Br and CH$_3$Cl were prepared for hydrolysis and 5 mmol/L for Cl exchange experiments by injecting the corresponding amount of organic into a 2 L crimp-sealed glass bottle filled with distilled water or a brine (3.5%). Additionally, a stock solution with a lower concentration of 0.22 mmol/L CH$_3$Br was
prepared to carry out a hydrolysis experiment at a lower concentration. The brine was prepared by mixing distilled water with the sea salt and boiling this solution for 10 min. All experiments were carried out in unbuffered solution. Stock solutions were shaken overnight before further usage. For each experiment, 6 to 10 septum bottles (60 mL) were filled with 40 mL of solution, crimp-sealed and all bottles shaken for at least 3 hours. Then, the starting concentration was determined by injecting aliquots of the headspace of all samples and three standards thus applying a three-point calibration. Bottles were stored overhead at 23±1°C. Sampling of the bottles occurred in different time intervals. For methyl bromide, sampling occurred every 3-5 days whereas for methyl chloride up to two months passed before another bottle was sampled. The sampled bottles were then frozen at -18°C and stored until further usage.

2.3 Stable isotope analysis of carbon, hydrogen, chlorine, and bromine

Stable isotope analysis was carried out by following closely previously published protocols for carbon (Chevallier et al., 2018), hydrogen (Renpenning et al., 2015), chlorine (Horst et al., 2017; Renpenning et al., 2018) and bromine (Horst et al., 2011). Subsequently a brief description is provided for each method. Further details may be found in the cited literature. Delta values for all isotopes are calculated according the following expression:

\[ \delta^i E \ (U_r) = \frac{(R)_{\text{sample}}}{(R)_{\text{standard}}} - 1 \]  

(1)

Here, \( i \) indicates \( ^2\text{H}, ^{13}\text{C}, ^{37}\text{Cl}, \) and \(^{81}\text{Br} \) and \( R \) the isotopic ratio \( ^2\text{H}/^1\text{H}, ^{13}\text{C}/^{12}\text{C}, ^{37}\text{Cl}/^{35}\text{Cl}, \) and \(^{81}\text{Br}/^{79}\text{Br} \) for hydrogen, carbon, chlorine, and bromine, respectively. The delta values are given in \( U_r \) (Urey) according to recent IUPAC recommendations (Brand et al., 2014). \( U_r \) and the more commonly used permil scale (‰) are interchangeable: 1 m\( U_r = 0.001 = 1 \) ‰, but \( U_r \) is, in contrast to ‰, a SI unit and hence common SI prefixes such as milli- and micro- become available and expressions such as ppm and permeg may also be expressed in \( U_r \).

Carbon isotope measurements were carried out using gas chromatography (Agilent 7890A) coupled via a combustion furnace and a ConFlo IV interface to isotope ratio mass spectrometry (IRMS, Thermo Finigan MAT 253). Sample introduction into the gas chromatographic system (GC) occurred via injecting an aliquot of the headspace of the sample bottles with a gas-tight syringe. For all isotope analyses a ZB1 chromatographic column (Phenomenex, USA) was kept at 100°C for all analyses. Isotope ratios of all samples and, additionally, an external in-house working standard were analyzed following a previously published protocol (Chevallier et al., 2018). The delta values (\( \delta^{13}\text{C} \)) indicate the relative difference of the measured ratios versus the international standard V-PDB (Vienna Pee Dee Belemnite). The analytical accuracy for a single measurement by this method is usually better than 0.5 m\( U_r \).

Hydrogen isotope analysis of halogenated compounds was achieved by using a recently developed chromium reactor (Renpenning et al., 2015) which suppresses the generation of HCl and HBr by converting halogens to CrCl\(_3\) which is trapped at the end of the reactor. This chromium reactor is connected to an Agilent 7890A GC and, via the ConFlo IV interface, to a Thermo Finigan MAT 253. Raw \( \delta^2\text{H} \) are obtained by using Equation 1. Values are normalized to the Vienna Standard Mean Ocean Water (V-SMOW) by applying a two-point calibration approach (Coplen, 1988), that is, a set of in house reference
compounds (alkanes) were used to adjust the delta values measured by the individual mass spectrometer to the international V-SMOW scale. The accuracy for a single measurement by this method is usually better than 5 mUr.

Stable chlorine and stable bromine isotope analyses were carried out by coupling gas chromatography (Thermo Scientific Trace 1310 GC) over a heated transferline (250°C) to a Neptune MC-ICPMS (multiple-collector inductively coupled plasma mass spectrometry, Thermo Fisher Scientific, Germany). Equation 1 was applied to calculate the raw-δ\(^{37}\)Cl and raw-δ\(^{81}\)Br.

Here, \(\epsilon\) denotes \(^{37}\)Cl and \(^{81}\)Br and R the isotopic ratios of \(^{37}\)Cl/\(^{35}\)Cl and \(^{81}\)Br/\(^{79}\)Br, respectively. For chlorine, a two-point calibration approach was applied to normalize raw-δ\(^{37}\)Cl values to the SMOCl scale (Standard Mean Ocean Chloride). Three organic in-house reference compounds (TCE-2, TCE-6, CH\(_3\)Cl) are typically used for this procedure (Horst et al., 2017). The accuracy for the analysis of a single sample is better than 0.2 mUr.

For bromine isotope analysis, appropriate organic reference material was not available prior to this study. To produce several CH\(_3\)Br with a different δ\(^{81}\)Br a distillation approach was applied. Liquid methyl bromide was filled in a 500 mL stainless steel gas cylinders (Swagelok Germany) which was connected via a 6.3 mm stainless steel tube to an empty 500 mL cylinder immersed in liquid nitrogen. When 50% and 95% of the transfer was completed subsamples of 50 mL of CH\(_3\)Br were transferred to 150 mL stainless steel cylinders. The original stock CH\(_3\)Br-1 and the two distilled CH\(_3\)Br-2 and CH\(_3\)Br-3 were then measured against each other with both GC-MC-ICPMS and DI-IRMS. Additionally characterization versus standard mean ocean bromide (SMOB) was carried out with dual inlet isotope ratio mass spectrometry (DI-IRMS) following a protocol published by Eggenkamp and Coleman (2000) which was adapted recently at IPGP (Eggenkamp and Coleman, 2000; Louvat et al., 2016). The international standard NIST SRM 977 salt was used as a working reference material with δ\(^{81}\)Br\(_{vsSMOB}\) = -0.64‰ to provide δ\(^{81}\)Br values versus SMOB. To ensure accuracy of the δ\(^{81}\)Br\(_{vsSMOB}\) data, two reference materials were routinely analysed; one KBr salt and HBr solutions with previously characterized δ\(^{81}\)Br\(_{vsSMOB}\) values as secondary reference materials. KBr and HBr solutions were precipitated as AgBr, dried and filtered. CH\(_3\)Br was then generated by reacting AgBr with CH\(_3\)I at 80°C. The samples CH\(_3\)Br-1 to CH\(_3\)Br-3 were then measured against the reference CH\(_3\)Br working gas (ie. CH\(_3\)Br made out of NIST SRM 977), together with the two secondary standards distributed along with measurements of unknown samples in all runs. Four to five replicate measurements of each sample were made on four consecutive days of analyses in a Thermo Fisher Delta Plus XP at the Institut de Physique du Globe de Paris. CH\(_3\)Br-1 to CH\(_3\)Br-3 were then used as reference compounds for GC-MC-ICPMS measurements following the mentioned two-point calibration approach. The accuracy of this method was usually better than 0.2 mUr.

### 2.4 Enrichment factors

The isotopic enrichment factor describes the change in the isotopic composition between the substrate and the instantaneous product caused by a reaction or a process of subsequent reactions (Scott et al., 2004). It further characterizes the constant change in the isotopic composition of the substrate reservoir due to the preferential loss of heavy or light isotopes during a reaction or process. In the current study, isotopic enrichment factors (\(\epsilon_{H}, \epsilon_{C}, \epsilon_{Cl}, \epsilon_{Br}\)) for CH\(_3\)Cl and CH\(_3\)Br were determined by using the Rayleigh equation (Mariotti et al., 1981):
\[
\ln \left( \frac{\delta^E + 1000}{\delta^E_0 + 1000} \right) \approx \ln(f) \epsilon_x
\]

where \(\delta^E\) is the isotopic signature (\(\delta^{2}H, \delta^{13}C, \delta^{37}Cl, \delta^{81}Br\)) of the organic after partial degradation, \(\delta^E_0\) indicates the initial delta value (\(\delta^{2}H_0, \delta^{13}C_0, \delta^{37}Cl_0\)), and \(f\) is the fraction of organic remaining.

3 Results and Discussion

3.1 Reaction rates

Experiments were performed to investigate the degradation of CH\(_3\)Br and CH\(_3\)Cl dissolved in distilled water (hydrolysis) and seawater (halide exchange reactions). All experiments were carried out at a temperature of 23±1°C (296 K). No buffer was added to the stock solutions because buffer catalysis was reported as a complicating factor in previous studies (Perdue and Wolfe, 1983; Elliott and Rowland, 1995; Jeffers and Wolfe, 1996). Furthermore, hydrolysis of CH\(_3\)Cl and CH\(_3\)Br is relatively independent of the pH because it mainly undergoes neutral hydrolysis (R1). Alkaline hydrolysis (R2) was only observed at \(\text{OH}^-\) concentrations of more than 0.1 mol L\(^{-1}\) (Jeffers and Wolfe, 1996). Hence R2 is only supposed to be of relevance in environmental settings at pH values above 10 (Schwarzenbach et al., 2003). The independence of hydrolysis reactions of CH\(_3\)X from the pH was also confirmed by Baesman and Miller (2005) who measured the carbon isotope fractionation of CH\(_3\)Br at different pH and additionally in un-buffered solutions. No significant difference was observed in that study for isotope enrichment factors obtained from unbuffered solutions compared to those with a fixed pH. Hence, in the current study all experiments were carried out without adding buffers. Results for the calculated loss rates of the individual experiments are summarized in Table 1 and compared to previously published values.

For hydrolysis of CH\(_3\)Br two experiments were carried out. At high concentrations (10 mmol/L) an abrupt change in the reaction rate is visible (Fig S1.1). As mentioned above, a changing pH and accompanied shift from alkaline to neutral hydrolysis is not a likely scenario. Still, additional effects and reactions may be a conceivable explanation. When the hydrolytic degradation of CH\(_3\)Br proceeds, additional nucleophiles (Br-) are released into the solution. These released nucleophiles may strongly interact with CH\(_3\)Br in the transition state of a bond cleavage and hence a very different rate constant may be obtained (Schwarzenbach et al., 2003). Additionally to reaction rates, an effect on the Br isotopic composition was observed as discussed more detailed further below. To avoid any of such additional reactions and their effects, a second experiment was run at a lower concentration (0.22 mmol/L) and samples were primarily taken until 70% of the substrate was left, the point where the reaction rate changed in the first experiment. In this range hydrolysis of methyl bromide followed first order kinetics which is also a prerequisite for the validity of the Rayleigh equation for quantification of isotope fractionation (Fig S1.2). The experimentally determined loss rate of 1.3 ± 0.2 % d\(^{-1}\) is slightly smaller compared to a value of 2.1 ± 0.2 % d\(^{-1}\) reported by Jeffers and Wolfe (1996). For experiments with added sea salt the loss rate was about one order of magnitude larger (11.5 ± 2.3 % d\(^{-1}\)) compared to hydrolysis in distilled water and followed first order kinetics. This larger reaction rate indicates that halide exchange is taking place. The experimentally determined loss rate agrees within
analytical uncertainty with 15.4 ± 6.0 % d⁻¹ published by a previous study (King and Saltzman, 1997). For the reaction of methyl chloride in distilled water the experimentally determined loss rate of 0.15 ± 0.05 % d⁻¹ is in good agreement with 0.14 ± 0.02 % d⁻¹ reported earlier (Elliott and Rowland, 1995). The reaction of CH₃Cl with H₂O and salt delivered a loss rate (0.12 ± 0.02 % d⁻¹) comparable to hydrolysis in distilled water. This may indicate that halide exchange of CH₃Cl at ambient temperatures is much slower than hydrolysis and not likely to have any additional effect on the combined loss rate and the isotopic composition. Data from both reactions of CH₃Cl follow first order kinetics. Overall, the magnitude of loss rates obtained from our experiments agreed with previous studies carried out in unbuffered solutions. All but one experiment followed first order kinetics and hence the Rayleigh equation was used to determine isotopic enrichment factors from these experiments.

3.2 Hydrolysis

For quantification of the isotope fractionation caused by hydrolysis, CH₃X were dissolved in distilled water without any additives. Experiments for the hydrolysis of CH₃Br were carried out at two different concentrations (10 mmol/L and 0.22 mmol/L). At high concentration the reaction did not follow first order kinetics and, strictly speaking, the Rayleigh equation may not be valid to determine isotopic enrichment factors. Still the carbon isotopic data followed a linear regression and the εₓ of -48.8 ± 9.2 mUr is indistinguishable from -58.3±6.8 mUr determined for the experiment carried out at a low concentration. Both εₓ are consistent with a previously published carbon isotope enrichment factor of -51.0 ± 6.0 mUr (Baesman and Miller, 2005). The reported value of that previous study is the average εₓ measured at 287 K and 306 K. The low variability of the εₓ in that study indicates that isotope fractionation of CH₃Br by hydrolysis is largely independent of the temperature within the tested ranges. The current CH₃Br hydrolysis experiment was carried out at 23°C (296 K) which is within the range investigated by Baesman and Miller (2005). Hence it may be assumed that enrichment factors obtained in the current study are also independent of temperature and they may be valid in most environmental compartments. Hydrogen isotope enrichment factors could only be measured for samples at high concentrations. CH₃Br concentrations of 0.22 mmol/L were too low to meet the isotopic detection limit. The enrichment factor determined at 10 mmol/L (+42 ± 20 mUr ) needs to be considered with some precaution because of changing kinetics during this experiment. The magnitude and the positive value indicate, however, isotope fractionation according to a secondary inverse isotope effect (Fig 2, Table 2). The existence of such a secondary inverse effect for the investigated SN2 reactions is also confirmed by all subsequent hydrogen isotope measurements (see below). Secondary effects usually occur adjacent to a reactive position in a molecule and may be due to the changing structure of the molecule or influences of bond vibrations, for example (Melander and Saunders, 1980). The positive εₓ indicates that the remaining CH₃X in water becomes successively depleted in deuterium throughout the reaction. Secondary inverse isotope effects of hydrogen are, in fact, a common feature for nucleophilic substitution reactions of methyl derivatives and this was investigated in several experimental studies in the gas phase as well as in computational studies (Gronert et al., 1991; Viggiano et al., 1991; Wolfe and Kim, 1991; Hennig et al., 2006). Accordingly, the inverse isotope effects may be explained with transition state theory. The C-H bond lengths in the transition
state are independent of the halogen. Furthermore, the reaction probability of the molecules containing a C-D bond is larger compared to the C-H bond due to a symmetric excitation of the stretching vibration. Even though our measured enrichment factors of +42 mUr were smaller than those in the cited articles (up to +200 mUr in gas phase experiments), they qualitatively confirm these inverse effects for different nucleophiles attacking methyl halides dissolved in water (see also discussion further below).

For bromine isotopes an $\varepsilon_{Br}$ of $-1.2 \pm 0.4$ mUr was measured for the experiment carried out at 0.22 mmol/L (see Figure 2(a)) but no $\varepsilon_{Br}$ could be determined for the experiment run at 10 mmol/L. As pointed out above, a second reaction took place after hydrolysis of 30% of the substrate that additionally influenced the isotopic composition (Fig 1). At first, the $\delta^{81}$Br of the substrate became more enriched but then converged towards the starting value again. For carbon and hydrogen isotopes no such trend was visible and hence experimental errors such as leakage may be excluded. A conceivable reason for this phenomenon may be the equilibration of the substrate CH$_3$Br with bromine ions in the solution. During hydrolysis bromine ions are released due to reaction R1. With rising concentration, Br$^-$ might have become important as a nucleophile itself and reacted with the remaining CH$_3$Br. Simultaneously, the rate constant changed at this point (Fig S1.1). To avoid this hypothesized re-equilibration effect with Br$^-$, samples were only taken during degradation of the first 30% of the substrate (f > 0.7).

The degradation experiment of CH$_3$Cl in distilled water (hydrolysis) was carried out over 232 days and sampling occurred in time steps of 1-3 months. Isotopic enrichment factors of $+25 \pm 6$ mUr ($^2$H), $-41.7 \pm 10.2$ mUr ($^{13}$C), and $-5.3 \pm 1.3$ ($^{37}$Cl) were derived from the Rayleigh plots (Figure 3). No equivalent data is available in the literature for comparison. Compared to hydrolysis of CH$_3$Br, enrichment factors for hydrogen and carbon showed a similar range and direction; that is, carbon isotope effects were normal and hydrogen isotope effects were inverse due to the secondary isotope effect caused by a nucleophilic substitution reaction. The chlorine isotope enrichment factor is about 3 times larger than the measured bromine isotope effect which is consistent with a previous estimate based on theoretical calculations for primary kinetic isotope effects (Willey and Taylor, 1978).

### 3.3 Halide exchange

The exchange of halide ions is the second abiotic degradation process investigated in this study. CH$_3$Br and CH$_3$Cl were dissolved (5 mmol/L) in artificial brine containing the main cations and anions in concentrations that are usually present in seawater. The enrichment factors obtained from experiments with CH$_3$Br were $+22 \pm 13$ mUr, $-63.3 \pm 5.1$ mUr, and $-1.2 \pm 0.2$ mUr for $^2$H, $^{13}$C, and $^{81}$Br, respectively. The carbon isotope enrichment factor agrees with the $-57.0 \pm 5.0$ reported by Baesman and Miller (2005). Another study published an $\varepsilon_C$ of $-41.2$ mUr for this reaction which is about 20 mUr smaller (Kalin et al., 2001). Compared to the hydrolysis experiments carried out in the current study, enrichment factors for halide exchange are indistinguishable if the analytical uncertainty is taken into account. For CH$_3$Br no obvious Br$^-$ exchange affected the bromine isotopic composition even though the absolute Br$^-$ content in these samples was high from the very
beginning of the experiment. The Cl\(^-\) concentration was more than 300 times larger and thus dominated the exchange reaction with CH\(_3\)Br which followed first order kinetics (Fig S1.3). The product of this reaction was CH\(_3\)Cl which could be identified during \(\delta^{13}\)C-CH\(_3\)Br measurements showing increasing yields. Simultaneous to halide exchange, also hydrolysis theoretically takes place but no obvious effect on the reaction rates or the isotopic composition was detectable. Reaction rates for hydrolysis were one order of magnitude smaller (Table 1) and the isotope fractionation caused by both processes is virtually indistinguishable. Hence, isotope effects in CH\(_3\)Br caused by the two main abiotic degradation processes in oceans cause a similar isotope fractionation and may be included as a combined sink in future isotope-based budget estimates for atmospheric CH\(_3\)X.

The reaction of CH\(_3\)Cl and salt in solution generated very similar enrichments factors as for hydrolysis of CH\(_3\)Cl in distilled water: +24 ± 19 mUr for hydrogen, −40.6 ± 13.9 mUr for carbon and −5.2 ± 1.0 mUr for chlorine. Based on the calculated loss rates it can be assumed that only hydrolysis took place. Further proof for this assumption was also delivered by the chlorine isotopic measurements. CH\(_3\)Cl used for the experiments had a \(\delta^{37}\)Cl of +6.02 mUr SMOC (Horst et al., 2017) whereas Cl\(^-\) in salt should be close to 0 mUr SMOC (Shouakar-Stash et al., 2005). In our experiments the reaction caused a shift of \(\delta^{37}\)Cl towards heavier values following clearly first order kinetics (Fig S1.5). In contrast, exchange of CH\(_3\)Cl with Cl\(^-\), if occurring at ambient temperatures, should have caused a shift of \(\delta^{37}\)Cl towards lighter values and without altering the concentration. Consequently, halide exchange in CH\(_3\)Cl may be considered negligible at ambient and lower temperatures.

It should be noted at this point that the errors for the methyl chloride experiments are relatively large. The degradation of CH\(_3\)Cl was very slow and even though the experiments run for 6 months only about 20% of the substrate was degraded. Hence the analytical errors of the isotope analysis and quantification had a relatively large influence on the quality of the regression and the determined enrichment factors. Still, results from both experiments are in good agreement and deliver first insights into the magnitude of isotope fractionation of all three elements in CH\(_3\)Cl.

### 3.4 Implications for future isotope-based studies of CH\(_3\)X

The results presented here provide a first glimpse into the capabilities of triple-elemental isotope analysis of CH\(_3\)X for identification and characterization of sources and sinks. Previous attempts to use stable isotopes for source apportionment of CH\(_3\)X have mainly relied on stable carbon isotope measurements (Bill et al., 2004; Keppler et al., 2005). Even though important new information could be derived in these studies estimates of tropospheric CH\(_3\)X budgets were not unambiguous due to overlap of reported ranges of isotopic source signatures and their similarity to the tropospheric composition of CH\(_3\)X.

Using the isotopes of multiple elements in a compound may add additional source and process level information. Triple element isotope analysis, as carried out in this study, showed a distinct pattern of isotopic enrichment factors which is particularly interesting if compared to those of other major sinks of CH\(_3\)X (Fig 4). Apart from the investigated sinks methylotrophic bacteria are capable of degrading large amounts of methyl halides in soils and seawater (Schäfer et al., 2007). Large carbon isotope enrichment factors were reported for this biotic sink but rather small secondary hydrogen isotope enrichment factors due cleavage of the C-X bond (Nadalig et al., 2013). Halogen isotope effects for aerobic
microbial degradation has not been measured yet but it is conceivable that they show a similarly large isotope fractionation as reported for anaerobic microorganisms (Franke et al., 2017) due to cleavage of the same bond. In contrast, reactions in the gas phase show very different isotope effects. Degradation of CH₃X in the troposphere is mainly caused by OH and Cl radical reactions (Carpenter et al., 2014) which cause a C-H bond breakage. Consequently, reported hydrogen and carbon isotope effects are large (Gola et al., 2010; Keppler et al., 2018). Halogens are not involved in radical reactions and should only show small secondary isotope effects (Melander and Saunders, 1980).

Summarizing these results reveals an interesting view on isotope effects in the gas phase and in water. All currently known sinks in water show similar isotope effects, namely, large carbon and halogen isotope effects but relatively small secondary hydrogen isotope effects. Likewise, major tropospheric sinks follow a similar reaction mechanism with similar isotope fractionation pattern. Radical reactions cause large carbon and hydrogen isotope fractionation (Gola et al., 2010; Keppler et al., 2018). Mass transport to the stratosphere is also considered to be a sink of tropospheric CH₃X but due to turbulent advective transport major changes in the isotopic composition are not expected. Consequently, known degradation processes in these two different compartments, water and troposphere, follow mainly two distinct mechanisms: C-H bond cleavage in the gas phase and C-X bond cleavage in the aqueous phase. Due to this fact triple elemental isotope analysis may present a very powerful tool for identification and quantification of degradation processes of CH₃X.

Particularly the non-reactive elements in the molecules may serve as a useful additional indicator for exchange processes between oceans and the troposphere and the reactions in the opposite compartment. For instance, large hydrogen isotope shifts observed in CH₃X dissolved in water should, according to this theory, only originate from tropospheric processes and hence are an indicator for ocean uptake. Vice versa, changes in the halogen isotopic composition in the marine boundary layer should give an estimate for partitioning of partially degraded CH₃X into the air or, in coastal environments, allow for a direct estimate of a coastal source that is not affected by radical reactions in the gas phase. Multi-element isotope analysis may also be particularly useful if samples are taken in the free troposphere. If changes in the halogen isotopic composition are negligible there, it may be assumed that observed changes in δ²H should be due to radical reactions only. Hydrogen isotopes in CH₃X would, in that case, provide a tool for in situ measurements of the OH sink which may be more precise than laboratory measurements and the current in situ estimates based on the variability of methyl chloroform concentrations in the atmosphere.
4 Conclusions

The degradation experiments of CH₃X in distilled water and seawater and associated isotope effects deliver novel information about these reactions but also have important implications for future isotope-based studies of CH₃X in the atmosphere. The isotope fractionation of all reactions exhibited similarly large carbon and halogen isotope effects and small inverse hydrogen isotope effects. These isotope effects are similar to those of other major sinks in water, such as oxidation by methylothrophic bacteria but very different from isotope fractionation caused by OH and Cl radical reactions, the major sinks in the gas phase. Hence the application of triple elemental isotope analysis provides a powerful tool for the identification of degradation in water and air, respectively, and it bodes well for future applications of this technique to further improve budget estimates of CH₃Br and CH₃Cl in the atmosphere. To fully benefit from the advantages of triple-elemental isotope analysis it will be necessary to determine three-dimensional isotopic fingerprints of the major sources (macroalgae, salt marshes, biomass burning, plants, soil) and isotope fractionation caused by other major sinks (OH radical reactions, microbial degradation in oceans and soils). Furthermore, the isotopic composition of tropospheric samples needs to be determined in long-term monitoring studies to produce sufficient data for future modelling approaches. Whereas sensitive methods for halogen and hydrogen isotopes have become available very recently, routine sampling of CH₃X for isotope analyses is still a difficult task. If these challenges are met, triple-elemental isotope analysis provides a realistic chance to better quantify the unbalanced atmospheric budget of CH₃X and to identify the missing sources.

Author contributions

AH and HHR designed the experiments. AH performed the experiments. AH, GB, and MB carried out the isotope analyses. AH took the lead in writing the manuscript with input by HHR and MB. All authors contributed to discussing the results and commenting on the article

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References


Figure 1. Bromine isotopic composition during hydrolysis of CH$_3$Br (10 mmol/L) and the change in concentration of the remaining substrate given as fraction remaining ($f$). Bromine isotopic composition is given as the $\Delta ^{81}\text{Br}$ which indicates the relative difference from the starting value (sample 0)
Figure 2. Rayleigh plots for reactions of CH$_3$Br. Panel (a), (b), and (c) show results of the reaction CH$_3$Br +H$_2$O (hydrolysis). Panel (d), (e), and (f) demonstrate isotope effects due to CH$_3$Br +H$_2$O + Y$^-$ (halide exchange).
Figure 3. Rayleigh plots for reactions of CH₃Cl. Panel (a), (b), and (c) show results of the reaction CH₃Cl + H₂O (hydrolysis). Panel (d), (e), and (f) present isotope effects due to CH₃Cl + H₂O + Y⁻ (halide exchange).
Figure 4. Schematic of known isotope fractionation effects in water and in the gas phase. All currently known gas phase reactions (OH, Cl radicals) cause C-H bond cleavage and consequently large C and H isotope effects but likely negligible Cl and Br effects. Abiotic and biotic degradation in water cause C-X bond cleavage and hence C, Cl and Br isotope effects are large but hydrogen isotope effects are relatively small compared to gas phase reactions.
Table 1: Loss rates for hydrolysis and halide exchange of CH₃Br and CH₃Cl

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Loss Rate [%·d⁻¹]</th>
<th>Loss Rate (Previous Studies) [%·d⁻¹]</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH₃Br + H₂O</td>
<td>1.3 ± 0.2</td>
<td>2.1 ± 0.2 a</td>
</tr>
<tr>
<td>CH₃Br + H₂O + Cl</td>
<td>11.5 ± 2.3</td>
<td>15.4 ± 6.0 b</td>
</tr>
<tr>
<td>CH₃Cl + H₂O</td>
<td>0.15 ± 0.05</td>
<td>0.14 ± 0.02 c</td>
</tr>
<tr>
<td>CH₃Cl + H₂O + Cl</td>
<td>0.12 ± 0.03</td>
<td>-</td>
</tr>
</tbody>
</table>

Loss rates were determined graphically from plots of ln[f] versus time and indicate the loss rate at 23°C±2 °C (296 K). The errors are given as the 95% confidence interval. Literature values are taken from a Jeffers and Wolfe 1996, b King and Saltzman 1997, c Elliot and Sherwood Rowland 1995;
Table 2: Isotopic enrichment factors ($\varepsilon$) measured throughout this study

<table>
<thead>
<tr>
<th>System</th>
<th>$\varepsilon_H$ mUr</th>
<th>$\varepsilon_C$ mUr</th>
<th>$\varepsilon_{Cl}$ mUr</th>
<th>$\varepsilon_{Br}$ mUr</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH$_3$Br + H$_2$O (10 $\mu$mol/L)</td>
<td>+42 ± 20</td>
<td>−48.8 ± 9.2</td>
<td>-</td>
<td>n.d.</td>
</tr>
<tr>
<td>CH$_3$Br + H$_2$O (0.22 $\mu$mol/L)</td>
<td>n.d.</td>
<td>−58.3 ± 6.8</td>
<td>−1.16 ± 0.42</td>
<td></td>
</tr>
<tr>
<td>CH$_3$Br + H$_2$O +Y$^-$</td>
<td>+22 ± 13</td>
<td>−63.3 ± 5.1</td>
<td>-</td>
<td>−1.22±0.23</td>
</tr>
<tr>
<td>CH$_3$Cl + H$_2$O</td>
<td>+25 ± 6</td>
<td>−41.7 ± 10.2</td>
<td>−5.3 ± 1.3</td>
<td>-</td>
</tr>
<tr>
<td>CH$_3$Cl + H$_2$O +Y$^-$</td>
<td>+24 ± 19</td>
<td>−40.6 ±13.9</td>
<td>−5.2 ± 1.0</td>
<td>-</td>
</tr>
</tbody>
</table>

Enrichment factors are derived from the Rayleigh plots in Fig 2 and Fig 3. Errors are given as the 95% confidence interval of the regression. Values in italics indicate that these data do not follow first order kinetics and epsilons only serve as an approximation.
Supplement 1: Graphs of concentration versus time to determine the rate law of the reactions. The slope of the regression is equivalent to \(-k\), the rate constant given in d\(^{-1}\).

FigS1.1: loss rate for CH\(_3\)Br in the experiment with (10 mmol/L) in water

![Graph](image1)

\[ y = -0.0240x - 0.0138 \quad R^2 = 0.9847 \]

FigS1.2: loss rate for CH\(_3\)Br + H\(_2\)O (low concentration (0.22mmol/L))

![Graph](image2)

\[ y = -0.0426x + 0.2374 \quad R^2 = 0.9997 \]
Fig S1.3: loss rate of CH$_3$Br in the experiment with H$_2$O + salt

Fig S1.4: loss rate of CH$_3$Cl in the experiment with H$_2$O
Fig S1.5: loss rate for CH3Cl + H2O + salt

\[ y = -0.0012x + 0.0084 \]

\[ R^2 = 0.9733 \]