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1 **Isotopic characterization (²H, ¹³C, ³⁷Cl, ⁸¹Br) of abiotic sinks of methyl**
2 **bromide and methyl chloride in water and implications for future studies**

3 Axel Horst*¹, Magali Bonifacie², Gérard Bardoux², and Hans Hermann Richnow¹

4 ¹Department of Isotope Biogeochemistry, Helmholtz Centre for Environmental Research – UFZ,
5 Permoserstr.15, 04318 Leipzig, Germany

6 ²Institut de Physique du Globe de Paris, Sorbonne Paris Cité, Université Paris-Diderot, UMR 7154
7 CNRS, 1 rue Jussieu, F-75005 Paris, France

8 **Corresponding author:* axel.horst@ufz.de

9 ORCID 0000-0002-3475-2425

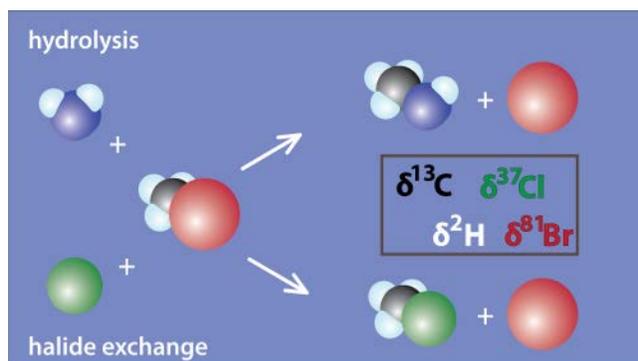
10 The authors declare no competing financial interest

11

12 Abstract

13 Methyl bromide (CH_3Br) and methyl chloride (CH_3Cl) significantly contribute to stratospheric
14 ozone depletion. The atmospheric budgets of both compounds are unbalanced with known sinks
15 outweighing known sources. Stable isotope analysis may be capable to provide additional
16 information for better differentiation of sources and sinks, respectively, and is particularly
17 powerful if isotopes of multiple elements in each compound are used. In the current study, triple-
18 element isotope analysis (^2H , ^{13}C , $^{37}\text{Cl}/^{81}\text{Br}$) was applied to investigate the two main abiotic
19 degradation processes of methyl halides (CH_3X) in fresh and seawater: hydrolysis and halide
20 exchange. For CH_3Br both nucleophilic substitution reactions caused significant carbon and
21 bromine isotope effects accompanied by a secondary inverse hydrogen isotope effect. Calculated
22 loss rates indicated that exchange with chloride (Cl^-) may be the dominating abiotic sink for CH_3Br
23 in oceans. For CH_3Cl only hydrolysis was observed at significant rates causing large carbon and
24 chlorine isotope effects and a secondary inverse hydrogen isotope effect. This study demonstrates,
25 to our knowledge, the first triple-element isotope analyses of CH_3Cl and CH_3Br . The presented
26 results have important implications for source apportionment of tropospheric CH_3X if viewed in
27 conjunction with previously measured isotope effects caused by other main sinks of methyl
28 halides.

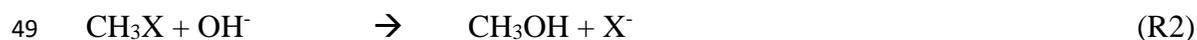
29 TOC graphic



31 **Introduction**

32 Methyl chloride (CH₃Cl, chloromethane) and methyl bromide (CH₃Br, bromomethane) together
33 contribute about 30 % to halogen induced ozone loss even though atmospheric concentrations are
34 very low: 540 pptv and 7 pptv respectively¹. CH₃Cl and CH₃Br are emitted by both anthropogenic
35 and natural sources such as fumigation for quarantine and pre-shipment treatment², marine
36 macroalgae³, salt marshes⁴, soils⁵, biomass burning⁶ and tropical plants⁷. Main sinks for both of
37 these compounds are reaction with OH and Cl radicals in the troposphere⁸, uptake by oceans⁹ and
38 soils¹⁰. The atmospheric budgets of both compounds are unbalanced with known degradation
39 processes exceeding the best estimates of known sources by approximately 20 %^{1, 11}. A better
40 understanding of emission and degradation processes will be necessary in order to better quantify
41 emission and degradation of CH₃X and to improve budget estimates.

42 Previous studies suggested that ocean uptake is driven by the abiotic processes hydrolysis and
43 halide exchange as well as microbial degradation^{9, 12, 13}. To a minor extent, hydrolysis may also
44 contribute to degradation of CH₃Br in soils¹⁴. Hydrolysis and halide exchange of CH₃X (CH₃Cl
45 and CH₃Br) are both nucleophilic substitution reactions (S_N2) following second order reaction
46 kinetics. The attacking nucleophiles are either water (H₂O), hydroxide ions (OH⁻), or halide ions
47 such as Cl⁻ and Br⁻ (Y⁻)¹⁵⁻¹⁷:



51 In principle, hydrolysis of chlorinated aliphatic compounds may occur due to neutral (R1) and/or
52 alkaline hydrolysis (R2) depending on the pH and the reacting organic compound. For instance,

53 solely neutral hydrolysis (R1) was detected for CCl_4 whereas some chlorinated ethenes only
54 reacted with hydroxide ions (R2)¹⁸. For CH_3X it was shown that alkaline hydrolysis required a
55 hydroxide concentration of more than 0.1 mol L^{-1} and hence only neutral hydrolysis is considered
56 to be relevant in most environments¹⁶. Consequently, reactions R1 and R3 were suggested to
57 constitute large sinks for methyl bromide¹⁹⁻²¹. For methyl chloride, microbial degradation seems
58 to be more important, especially in subarctic and arctic ocean waters due to low reaction rates of
59 abiotic processes⁹. Still, the overall importance of these reactions as a sink of methyl halides
60 compared to microbial degradation in oceans and soils is generally not well understood.

61 Stable isotope analysis was suggested as a diagnostic tool to overcome the limitations of solely
62 quantifying concentration levels of these compounds²². Several studies measured the carbon
63 isotope composition of various sources and sinks and an overview of these isotopic signatures was
64 published for CH_3Br ²³ and CH_3Cl ²⁴, respectively. Important new information could be derived
65 from stable carbon isotope measurements but both studies also revealed the fact that the ranges of
66 the source signatures are overlapping and often coincide with the tropospheric $\delta^{13}\text{C}$ of CH_3X . For
67 that reason, stable carbon isotope measurements have not yet contributed to better budget estimates
68 of CH_3Cl and CH_3Br . Significant improvements may be expected if the isotopic compositions of
69 several elements are measured in one compound. Such multi-element isotope approaches have
70 recently become available with improved measurement techniques and were successfully applied
71 to describe, for instance, the fate of organic contaminants in groundwater^{25, 26}. For CH_3Cl ,
72 hydrogen isotope measurements were presented recently²⁷⁻²⁹ and bromine isotope analysis was
73 demonstrated in two studies for CH_3Br ^{30, 31} but overall no multi-element isotope studies have been
74 published yet for methyl halides.

75 Future estimates of the atmospheric budget of methyl halides may significantly benefit from the
76 additional information provided by multi-element isotope analyses but before any isotope-based
77 models are applicable, source signatures and the isotope fractionation caused by sink processes
78 need to be determined. Knowledge about the isotope fractionation caused by sinks is particularly
79 important for two reasons. Firstly, it provides the link between the isotopic source signatures of
80 these compounds and the tropospheric isotopic composition of methyl halides. Secondly, the
81 extent of isotope fractionation can be used to estimate the loss rate caused by the individual
82 processes, a method commonly used to determine contaminant degradation in groundwater^{22, 32-37}.
83 Consequently the characterization of the individual sink processes is a crucial prerequisite for the
84 application of future isotope based models.

85 Hence the objective of the presented study was to characterize the isotopic enrichment factors (ϵ)
86 caused by hydrolysis and halide exchange reactions with CH_3Cl and CH_3Br , potentially important
87 abiotic sinks for these compounds. We determined the isotope fractionation of all available stable
88 isotopes in each compound, that is, hydrogen and carbon isotopes in both compounds and chlorine
89 as well as bromine isotopes for methyl chloride and methyl bromide, respectively. To our
90 knowledge, the presented data are the first three-dimensional isotope measurements for each of
91 these substances. The implications of our results for future multi-dimensional isotope studies of
92 methyl halides are discussed.

93

94 **Materials and Methods**

95 **Chemicals.** Methyl chloride and methyl bromide were purchased as compressed gases and with a
96 purity of more than 99 %. Methyl chloride was obtained from Linde (Germany) whereas methyl
97 bromide was purchased from Gerling, Holtz & Co (Germany). A commercially available sea salt
98 without any additives (Aquasale, Heilbronn, Germany, major ion composition given in Table S1)
99 was purchased to prepare brines with a concentration of 35 g kg⁻¹ (psu) which is similar to the
100 average salt content of seawater.

101 **Preparation of samples and experiments.** Stock solutions with a concentration of 10 mmol L⁻¹
102 CH₃Br and CH₃Cl were prepared for hydrolysis experiments and 5 mmol L⁻¹ for halide exchange
103 experiments by injecting the corresponding amount of gas into the headspace of a 1 L crimp-sealed
104 glass bottle filled with distilled water and brine (3.5 %), respectively. Additionally, a stock solution
105 of 0.2 mmol L⁻¹ CH₃Br was prepared to carry out a hydrolysis experiment at a lower concentration.
106 The brine was prepared by mixing distilled water with the sea salt and boiling this solution for
107 10 min. All experiments were carried out in unbuffered solution (see also Results and Discussion
108 for further explanations). After preparation, stock solutions were shaken overnight for
109 equilibration before further usage. For each experiment, 6 to 10 septum bottles (60 mL) were filled
110 with 40 mL of solution, crimp-sealed and all bottles shaken for at least 3 hours. Then, the starting
111 concentration was determined by injecting aliquots of the headspace of all samples. At least three
112 standards were analyzed to quantify the sample concentrations via a three-point calibration
113 (Supporting Information 3). To avoid gas-leakage through the pinched septa, the sample bottles
114 were kept upside-down throughout the entire experiment. Furthermore, samples were kept at a
115 dark place maintaining a temperature of 23 ± 1°C. Sampling of the bottles took place in different
116 time intervals. For methyl bromide, sampling occurred every 3-5 days whereas for methyl chloride

117 up to two months passed before another sample was collected. After sampling, each bottle was
118 frozen to -18°C for conservation and stored until the end of the experiment at this temperature.
119 Before analysis, all samples of one experiment were heated simultaneously to 25°C in a water bath
120 and subsequently shaken for two hours to ensure equal treatment of all samples and complete
121 equilibration in the sample bottles.

122 **Stable isotope analysis of carbon, hydrogen, chlorine and bromine.** Stable isotope analysis was
123 carried out by injecting aliquots of the headspace gas (50 to 1000 μL depending on concentration
124 and element) into the injector (split mode) of the gas chromatographic systems (GC) using a gas
125 tight syringe with push-button valve (VICI Precision Sampling). The GC was either connected to
126 gas source isotope ratio mass spectrometry (IRMS) for hydrogen and carbon isotope analysis or to
127 multiple collector inductively coupled plasma mass spectrometry (MC-ICPMS) for chlorine and
128 bromine isotope analyses. The analytical procedures followed closely the methods described and
129 published in previous studies for carbon³⁸, hydrogen³⁹, chlorine^{40, 41} and bromine⁴² isotopes.
130 Descriptions of the methods are provided for each method in the Supporting Information 1,
131 including also a cross calibration for bromine isotopes following previously published protocols⁴³,
132 ⁴⁴ (Supporting Information 2).

133 Results from isotopic measurements are reported in delta values (δ) for all isotopes. Delta values
134 are calculated according to the following expression⁴⁵:

$$135 \quad \delta^i E (Ur) = \frac{(R)_{sample}}{(R)_{standard}} - 1 \quad \text{Equation 1}$$

136 Here, ⁱE indicates ²H, ¹³C, ³⁷Cl, and ⁸¹Br and R the isotopic ratio ²H/¹H, ¹³C/¹²C, ³⁷Cl/³⁵Cl, and
137 ⁸¹Br/⁷⁹Br for hydrogen, carbon, chlorine, and bromine, respectively. The delta values are given in
138 Ur (Urey) according to recent IUPAC recommendations⁴⁶. Urey, if expressed in milli-Urey (mUr),

139 and the more commonly used permil scale (‰) are interchangeable: 1 mUr = 0.001 = 1 ‰, but
140 Ur is, in contrast to permil a SI unit and hence common SI prefixes such as milli- and micro-
141 become available. Other terms for the expression of isotopic ratios such as ppm and permeg may
142 also be reported in Ur. Thus, the unit Urey provides a single unified approach for the expression
143 of all stable isotope ratios. The overall uncertainties of the analytical procedures, including
144 reproducibility, linearity, and scale normalization are usually better than 5 mUr (hydrogen),
145 0.5 mUr (carbon), 0.2 mUr (chlorine), and 0.1 mUr (bromine).

146 **Enrichment factors and dual element isotope ratios.** The isotopic enrichment factor describes
147 the change of the isotopic composition between the substrate and the instantaneous product caused
148 by a reaction or a process⁴⁷. It further characterizes the constant change of the isotopic composition
149 of the substrate reservoir due to the preferential loss of heavy or light isotopes during a reaction or
150 process. In the current study, isotopic enrichment factors (ϵ_H , ϵ_C , ϵ_{Cl} , ϵ_{Br}) for CH_3Cl and CH_3Br
151 were determined by using the Rayleigh equation⁴⁸:

$$152 \quad \ln \left(\frac{\delta^i E + 1000}{\delta^i E_0 + 1000} \right) \approx \ln(f) \epsilon_x \quad \text{Equation 2}$$

153 where $\delta^i E$ is the isotopic signature (δ^2H , $\delta^{13}C$, $\delta^{37}Cl$, $\delta^{81}Br$) of the organic after partial degradation,
154 $\delta^i E_0$ indicates the initial delta value (δ^2H_0 , $\delta^{13}C_0$, $\delta^{37}Cl_0$, $\delta^{81}Br_0$), and f is the fraction of organic
155 remaining after partial degradation. The procedure for quantifying f is provided in the Supporting
156 Information 3. The Rayleigh equation is appropriate to derive the isotopic enrichment factors for
157 first-order or pseudo-first-order reactions⁴⁹.

158 Λ -values (lambda) describe the ratio of the enrichment factors of isotopes of two different
159 elements⁴⁹. Λ -values are determined as the slope of a linear regression of isotopic signatures of

160 two elements (e.g. H and C) determined from samples of the same experiment. Λ -values may also
161 be estimated according to the following relationship⁴⁹:

$$162 \quad \Lambda_{x/y} \approx \frac{\varepsilon_x}{\varepsilon_y} \quad \text{Equation 3}$$

163 where ε_x and ε_y are the enrichment factors of two different elements determined for the same
164 mechanism in a certain compound.

165 **Results and Discussions**

166 **Reaction rates.** Experiments were performed to investigate the abiotic degradation of CH₃Br and
167 CH₃Cl dissolved in water. Experiments in distilled water were carried out to study hydrolysis
168 reactions only. In brines (seawater) degradation may be due to both, hydrolysis and halide
169 exchange. All experiments were performed at a temperature of $23 \pm 1^\circ\text{C}$ (296 K). No buffer was
170 added to the stock solutions because buffer catalysis was reported as a complicating factor in
171 previous studies^{16, 50, 51}. Moreover, hydrolysis of CH₃Cl and CH₃Br is expected to primarily follow
172 reaction R1 in the environment. Alkaline hydrolysis of CH₃X (R2) only occurs at significant rates,
173 if OH⁻ concentrations exceed 0.1 mol L^{-1} ¹⁶. Consequently, reaction R2 is supposed to be important
174 only at pH 10 and above⁵². Therefore all hydrolysis reactions in this study, which were performed
175 at pH values smaller than 7, were assumed to be independent of the pH and to predominantly
176 follow reaction R1. Results for the calculated loss rates of the individual experiments are
177 summarized in Table 1 and are compared to previously published values.

178 For hydrolysis of CH₃Br two experiments were carried out at different concentrations. Reaction
179 rates of both experiments varied between $3.5 \pm 0.8 \% \text{ d}^{-1}$ at 10 mmol L^{-1} and $1.3 \pm 0.2 \% \text{ d}^{-1}$ at
180 0.2 mmol L^{-1} . The reaction rate obtained at high concentrations may, however, be influenced by

181 an additional equilibration effect with Br⁻ ions in the solution also represented by unusual bromine
182 isotope values (see discussion below). During hydrolytic degradation of CH₃Br, Br⁻ ions are
183 released into the solution according to reaction R1. Schwarzenbach et al⁵² (and references therein)
184 published relative nucleophilicities of nucleophiles reacting with CH₃Br. Taking into account these
185 nucleophilicities and the CH₃Br concentration of 10 mmol L⁻¹, released Br⁻ ions reached indeed a
186 concentration high enough to compete with water as a nucleophile. Both hydrolysis and Br⁻
187 exchange are equally important when about 75 % of Br⁻ is released due to transformation of CH₃Br
188 (Supporting Information 4). A second experiment was run at a lower concentration to avoid any
189 of such additional reactions. At 0.2 mmol L⁻¹ the release of Br⁻ ions due to transformation only
190 reached about 2 % of the amount necessary to compete with hydrolysis (Supporting Information
191 4) and no additional effect on the Br isotopic composition was detected. Consequently, hydrolysis
192 of methyl bromide at 0.2 mmol L⁻¹ followed first-order kinetics (pseudo-first order reaction, Figure
193 S4), a prerequisite to reliably apply the Rayleigh equation for quantification of isotopic enrichment
194 factors. The experimentally determined loss rate of $1.3 \pm 0.2 \text{ \% d}^{-1}$ was lower than at high
195 concentrations but the magnitude was close to the rate of $2.1 \pm 0.2 \text{ \% d}^{-1}$ reported by Jeffers and
196 Wolfe¹⁶.

197 For experiments with added sea salt the loss rate was about one order of magnitude larger
198 ($11.5 \pm 2.3 \text{ \% d}^{-1}$) compared to hydrolysis in distilled water and followed first-order kinetics
199 (pseudo-first order reaction, Figure S5). This experimentally determined loss rate agrees, within
200 analytical uncertainty, with $15.4 \pm 6.0 \text{ \% d}^{-1}$ published by a previous study¹⁷. The ten-times higher
201 rate together with the nucleophilic strength of Cl (Supporting Information 4) suggests that halide
202 exchange dominates the abiotic degradation of CH₃Br in seawater with hydrolysis only
203 contributing to a minor extent to the overall combined loss rate.

204 For hydrolysis of methyl chloride in distilled water the experimentally determined loss rate of
205 $0.15 \pm 0.05 \text{ \% d}^{-1}$ is in good agreement with $0.14 \pm 0.02 \text{ \% d}^{-1}$ reported previously⁵¹. The reaction
206 of CH_3Cl with H_2O and salt delivered a loss rate of $0.12 \pm 0.02 \text{ \% d}^{-1}$ which is indistinguishable
207 from hydrolysis in distilled water. Data from both reactions of CH_3Cl follow first-order kinetics
208 (pseudo-first order reactions, Figure S6 and S7). The similar reaction rates obtained from both
209 experiments may indicate that halide exchange of CH_3Cl at ambient temperatures does not have
210 any measurable effect on the combined loss rate and hence hydrolysis should be the main abiotic
211 degradation mechanism in natural waters.

212 **Hydrolysis and associated isotope effects.** Isotopic enrichment factors caused by hydrolysis were
213 determined for stable carbon, hydrogen, and bromine isotopes of CH_3Br . At high concentrations
214 (10 mmol L^{-1}) additional equilibration with Br^- influenced the reaction rates and the Rayleigh
215 equation may only possess a limited validity for this experiment. Despite this limitation, the carbon
216 isotopic data followed a linear regression with an ϵ_C of $-49.6 \pm 5.6 \text{ mUr}$ (Figure S9). This value is
217 close to $-58.3 \pm 6.8 \text{ mUr}$ (Figure 1b) which was determined for the low-concentration experiment
218 (0.2 mmol L^{-1}) where no significant Br^- exchange occurred. Both ϵ_C are consistent with a published
219 carbon isotope enrichment factor of $-51.0 \pm 6.0 \text{ mUr}$ ⁵³. The same authors investigated the pH
220 independence of carbon isotope fractionation by carrying out experiments at different pH (4.6, 7.3,
221 and 8.8) and additionally in un-buffered solutions (pH 3.6 – 6.0). No significant difference was
222 observed in that study for isotopic enrichment factors obtained from unbuffered solutions
223 compared to those with a fixed pH confirming that hydrolysis primarily occurs via one reaction
224 (R1). Hence enrichment factors obtained in the current study should be valid for the conditions
225 found in relevant environmental compartments such as surface waters and soils.

226 Hydrogen isotope enrichment factors could only be measured for samples at high concentrations.
227 CH_3Br concentrations of 0.2 mmol L^{-1} were too low to meet the isotopic detection limit for
228 hydrogen isotope measurements. Despite the mentioned uncertainties regarding the rate law, the
229 enrichment factor of $+42 \pm 20 \text{ mUr}$ is consistent with a secondary isotope effect resulting from
230 reaction R1 (Figure 1a, Table 2). Secondary effects are usually smaller than primary isotope effects
231 and occur in elements located adjacent to a reactive position due to the changing structure of the
232 molecule or influences of bond vibrations, for example⁵⁴. Furthermore, the positive ϵ_{H} indicates an
233 inverse isotope effect. The remaining CH_3Br in water becomes successively depleted in deuterium
234 throughout the reaction. Secondary inverse isotope effects of hydrogen are in fact a common
235 feature for nucleophilic substitution reactions of methyl derivatives and this was investigated in
236 several experimental studies in the gas phase as well as in computational studies⁵⁵⁻⁵⁸. Accordingly,
237 the inverse isotope effects may be explained with transition state theory. During $\text{S}_{\text{N}}2$ reactions the
238 nucleophile (H_2O , Y^-) approaches the carbon atom from the side opposite to the halogen atom. In
239 the transition state both the nucleophile and the leaving halogen atom are partly bound to the
240 carbon atom. The tetrahedral geometry of the methyl halide molecule changes to a trigonal
241 bipyramidal geometry in the transition state where the hydrogen atoms are located in a single
242 plane⁵². This structural change is associated with an increase of the bending and stretching force
243 constants, the latter caused by a tightening of the C-H bonds⁵⁷. This increase is represented by a
244 symmetric excitation of the stretching vibration which increases the reaction probability of the
245 molecules containing a C-D bond to a larger extent than for molecules containing a C-H bond⁵⁸.
246 As a result, CH_3Br in the solution becomes enriched in ^{13}C and ^{81}Br (see below) but depleted in
247 ^2H . Even though our measured enrichment factor of $+42 \text{ mUr}$ was smaller than those in the cited
248 articles (up to $+200 \text{ mUr}$ in gas phase experiments), it qualitatively confirms these inverse effects

249 for different nucleophiles (see also discussion further below) reacting with methyl halides
250 dissolved in water.

251 For bromine isotopes in CH_3Br an ϵ_{Br} of -1.2 ± 0.4 mUr was measured for the experiment carried
252 out at 0.2 mmol L^{-1} (Figure 1c). At high concentrations (10 mmol L^{-1}) a nonlinear behavior of the
253 $\delta^{81}\text{Br}$ values could be observed which was not in agreement with the Rayleigh equation (Figure
254 S8). At first, the $\delta^{81}\text{Br}$ of the substrate became more enriched but then started to converge toward
255 the starting value again. Apparently, the rising concentrations of bromine ions released into the
256 solution started to equilibrate with the CH_3Br substrate. At low concentrations no such effect was
257 observed because Br^- concentrations in solution were too low to compete with H_2O as a
258 nucleophile (Supporting Information 4). Hence, this equilibration is unlikely to occur in most
259 freshwaters and soils, environments where CH_3Br and Br^- concentrations are low and where
260 hydrolysis may contribute to degradation. Even in ocean waters the Br^- content only reaches 25%
261 of the concentration required to compete with H_2O (Supporting Information 4) which might
262 explain why no indications of such an equilibration effect were observed in experiments with
263 brines, as discussed further below.

264 For hydrolysis of CH_3Cl , stable hydrogen, carbon, and chlorine isotope enrichment factors were
265 determined. The degradation experiment of CH_3Cl in distilled water (hydrolysis) was carried out
266 over 232 days and sampling occurred in time steps of 1-3 months. Isotopic enrichment factors of
267 $+25 \pm 6$ mUr (^2H), -41.7 ± 10.2 mUr (^{13}C), and -5.3 ± 1.3 mUr (^{37}Cl) were derived from the
268 Rayleigh plots (Figure 2a-c). No equivalent data is available in the literature for comparison.
269 Compared to hydrolysis of CH_3Br , enrichment factors for hydrogen and carbon showed a similar
270 magnitude and direction; that is, carbon isotope effects were relatively large and normal whereas
271 hydrogen isotope effects were small and inverse due to a secondary isotope effect caused by the

272 nucleophilic substitution reaction. The chlorine isotope enrichment factor is about 3 times larger
273 than the measured bromine isotope effect in CH₃Br which is consistent with a previous estimate
274 based on theoretical calculations for primary kinetic isotope effects for halogens⁵⁹.

275 **Isotope effects caused by halide exchange reactions.** The nucleophilic reaction of halide ions
276 was the second abiotic degradation process investigated in this study. The enrichment factors
277 obtained from experiments with CH₃Br dissolved in brine were $+22 \pm 13$ mUr, -63.3 ± 5.1 mUr,
278 and -1.2 ± 0.2 mUr for ²H, ¹³C, and ⁸¹Br, respectively (Figure 1d-f and Table 2). The measured
279 carbon isotope enrichment factor (-63.3 ± 5.1 mUr) agrees well with -57.0 ± 5.0 mUr reported by
280 Baesman and Miller⁵³. Another study published an ϵ_C of -41.2 mUr for this reaction which is by
281 about 20 mUr smaller⁶⁰. Compared to the hydrolysis experiments carried out in the current study,
282 enrichment factors for halide exchange are indistinguishable if the analytical uncertainty is taken
283 into account (Table 2). Chlorine ions dominated the exchange reaction with CH₃Br because Cl⁻
284 concentrations were about nine times higher than necessary to compete with water as a nucleophile
285 (Supporting Information 4). The product of this reaction was CH₃Cl which could be identified
286 during $\delta^{13}\text{C}$ -CH₃Br measurements (Supporting Information 5). The measured $\delta^{13}\text{C}$ values of the
287 generated CH₃Cl were indistinguishable from the $\delta^{13}\text{C}$ predicted by the Rayleigh equation for the
288 cumulative product (Table S3, Figure S10) and CH₃Cl is considered the major product of this
289 reaction.

290 Exchange of chlorine with bromine is a sink for CH₃Br but simultaneously constitutes a source for
291 CH₃Cl. Still, oceanic concentrations of CH₃Br are very low compared to CH₃Cl. Hu et al.⁶¹
292 reported average concentrations of 2 pM which is much lower than the 88 pM found for CH₃Cl
293 during the same cruise in the Atlantic Ocean. Thus the transformation of CH₃Br would only
294 marginally (< 2%) increase the total CH₃Cl concentration in sea water even if all CH₃Br were

295 completely transformed to CH₃Cl. Chlorine exchange in CH₃Br is therefore not a significant
296 source of CH₃Cl despite its importance as an abiotic sink for CH₃Br.

297 The degradation of CH₃Cl dissolved in brine generated similar enrichment factors as for hydrolysis
298 of CH₃Cl in distilled water: +24 ± 19 mUr for hydrogen, -40.6 ± 13.9 mUr for carbon and -
299 5.2 ± 1.0 mUr for chlorine (Figure 2d-f, Table 1). In contrast to CH₃Br, the addition of sea salt did
300 not increase the reaction rates of CH₃Cl (see discussion above) and it can be assumed that only
301 hydrolysis took place. Furthermore, chlorine isotope measurements did not deliver any evidence
302 for equilibrium exchange of Cl⁻ with CH₃Cl. The CH₃Cl dissolved in the brine had a starting δ³⁷Cl
303 of +6.02 mUr SMOC⁴⁰ whereas Cl⁻ in the added sea salt should be close to 0.0 mUr SMOC⁶². In
304 our experiments we observed a shift of δ³⁷Cl toward more enriched values following clearly first-
305 order kinetics (Figure S7). In contrast, exchange of CH₃Cl with Cl⁻, if occurring at ambient
306 temperatures, should have caused a shift of δ³⁷Cl in the direction of the lighter values of the added
307 sea salt. Thus, halide exchange in CH₃Cl may be considered negligible at ambient temperatures
308 and should not affect the δ³⁷Cl of methyl chloride in most environments.

309 Overall, the results of the current study give further insights into the importance of these two
310 reactions for degradation of CH₃X in water and provide first isotopic enrichment factors for
311 hydrogen and halogens. For CH₃Br, halide exchange should be the dominant abiotic degradation
312 mechanism in seawater which confirms the findings of previous studies^{15, 53, 63}. Hydrolysis may
313 have a rather minor role in degrading CH₃Br in freshwaters and soils. Hydrolysis of CH₃Br also
314 occurs in oceans at a ten times slower rate and isotopic enrichment factors are similar to those
315 obtained from halide exchange reactions due to the same reaction mechanism (S_N2 reaction).
316 Consequently, the two processes cannot be individually characterized and quantified with isotopic
317 methods and both processes may be included as a combined abiotic sink in future isotope-based

318 budget estimates. Still, if necessary, degradation by the individual processes can be estimated from
319 the relative rate difference of these abiotic processes which should be constant at relevant
320 temperatures in seawater. For CH₃Cl, only hydrolysis may occur as an abiotic mechanism in most
321 environments with reaction rates being one order of magnitude lower than for hydrolysis of CH₃Br.
322 Consequently, hydrolysis should only marginally contribute to degradation of CH₃Cl in oceans,
323 freshwater, and soils as confirmed by previous studies^{51, 64}.

324 **Dual-element isotope ratios.** Λ -values provide a more precise parameter than ϵ values to
325 characterize and compare reaction mechanisms because these ratios are insensitive to masking and
326 rate limitation by additional processes⁶⁵. For the current study, lambda values were derived from
327 dual-element isotope plots provided in Figure S11–S14. The resulting $\Lambda_{H/C}$, $\Lambda_{C/Cl}$, and $\Lambda_{C/Br}$ are
328 given in Table 2. $\Lambda_{H/C}$ values ranged from -0.3 to -0.7 for both compounds and both reaction
329 pathways. The $\Lambda_{C/Cl}$ for CH₃Cl ranged from 6.9 to 7.3 and the $\Lambda_{C/Br}$ of CH₃Br ranged from 46.1 to
330 48.2. No other lambda values have been reported yet for both CH₃Cl and CH₃Br. Some $\Lambda_{H/C}$ for
331 reactions of CH₃Cl could be calculated from published ϵ_H and ϵ_C according to Equation 3 because
332 these enrichment factors were derived from the same experiment. The resulting $\Lambda_{H/C}$ are given in
333 Table S4. For CH₃Br no dual-element isotope studies are available yet and therefore lambda values
334 of other reaction pathways could not be calculated.

335 The $\Lambda_{H/C}$ of -0.6 for hydrolysis of CH₃Cl shows a similarly small absolute value as degradation
336 by methylotrophic bacteria²⁷ ($\Lambda_{H/C} = 0.7$, Table S4), differing by the algebraic sign due to an
337 inverse ϵ_H for hydrolysis. Consortia of soil microbes showed slightly larger $\Lambda_{H/C}$ which ranged
338 from 1.3 up to 4.6 due to a decreasing ϵ_C with decreasing CH₃Cl concentrations⁶⁶. These small
339 lambdas for abiotic and biotic reactions in water are the result of relatively small secondary

340 hydrogen isotope effects (<-50 mUr) due to rupture of the C-X bond. Abiotic and biotic reactions
341 in water are, however, still distinguishable by opposing positive and negative $\Lambda_{H/C}$.

342 In contrast, the main abiotic degradation pathways of CH_3Cl in the gas phase ($\text{OH}\cdot$, $\text{Cl}\cdot$ radical
343 reactions) are characterized by larger $\Lambda_{H/C}$ of 23.6 to 27.5 (Table S4) based on the enrichment
344 factors published by two recent studies^{28, 67}. Radical reactions cleave the C-H bond and therefore
345 primary isotope effects for both C and H can be observed causing an overall larger $\Lambda_{H/C}$ which is
346 clearly distinguishable from reactions in water, even though only two isotopic systems are used.

347 **Implications for future isotope-based studies of CH_3X .** The results presented in this paper
348 provide a first glimpse of the capabilities of triple-element isotope analysis of CH_3X for
349 identification and characterization of sinks of methyl halides. Specifically, the pattern of isotopic
350 shifts defined by enrichment factors and lambda values will be a useful tool to distinguish abiotic
351 degradation processes from other sinks of CH_3X . A comparison of isotope effects measured for
352 degradation mechanisms of CH_3Cl demonstrates that basically all known relevant abiotic and
353 biotic degradation mechanisms in water (and soils) are due to a C-Cl bond cleavage in CH_3Cl
354 (Figure 3). Resulting $\Lambda_{C/Cl}$ are relatively similar for all these reactions but $\Lambda_{H/C}$ may still be used
355 to distinguish abiotic from biotic degradation due to opposing inverse and normal hydrogen
356 fractionation, respectively (Table 2, Table S4). Methylotrophic bacteria, for instance, were
357 identified as the main biotic sink in water and soils because these organisms are capable of
358 degrading large amounts of methyl halides⁶⁸. Large carbon isotope enrichment factors (-38 to $-$
359 41 mUr) were reported for this biotic sink but rather small secondary hydrogen isotope enrichment
360 factors (-27 to -29 mUr) due to cleavage of the C-Cl bond²⁷. Halogen isotope effects for aerobic
361 microbial degradation of CH_3Cl (or CH_3Br) have not been measured yet but it is conceivable that
362 they show a similarly large isotopic fractionation as reported for other halogenated alkanes.

363 Aerobic microbial degradation of 1,2-dichloroethane, for instance, caused an ϵ_{Cl} of at least -3.8
364 mUr^{69} which was similar to the ϵ_{Cl} reported for anaerobic microbial degradation (-4.2 mUr)²⁶.

365 In contrast, CH_3X in the troposphere mainly degrades *via* OH and Cl radical reactions¹ which
366 cause a C-H bond dissociation. Consequently, reported hydrogen isotope effects for CH_3Cl were
367 large²⁸ (>-264 to -280 mUr) and carbon isotope effects were moderate (-10.2 to -11.2 mUr)⁶⁷.
368 Halogens present in CH_3X should only show small secondary isotope effects because they are not
369 involved in radical reactions⁵⁴. Consequently, gas phase reactions of CH_3Cl show a completely
370 different pattern of isotopic shifts compared to reactions in water and soils (Figure 3). This
371 separation of fractionation patterns of aqueous and gas phase reactions may also be conceivable
372 for CH_3Br because biotic and abiotic degradation mechanisms are largely the same¹. The
373 possibility to clearly distinguish degradation in water from degradation in the gas phase may
374 considerably simplify the characterization and quantification of sinks of methyl halides when
375 triple-element isotope analysis is applied.

376 In order to fully benefit from the advantages of triple-element isotope analysis in the future,
377 however, it will be necessary to determine three-dimensional isotopic fingerprints of atmospheric
378 samples and of the largest sources (macroalgae, salt marshes, biomass burning, plants, soils).
379 Moreover, full sets of isotopic enrichment factors and lambda values for the main sinks (OH radical
380 reactions, microbial degradation in oceans and soils) must be determined. Once these tasks are
381 completed, the isotopic data can be fed into models. Previous models relied on upscaled emission
382 data, atmospheric concentrations and corresponding stable carbon isotopic signatures to create
383 isotopic mass balances for both CH_3Cl and $\text{CH}_3\text{Br}^{24, 67, 70}$. The future use of two additional isotopic
384 systems for each compound may substantially improve this mass balance approach because of the
385 different sensitivity of hydrogen and halogen isotopes for radical reactions in the atmosphere and

386 degradation in water/ soil respectively. Hence, three different isotopic mass balances may be
387 created which have to yield matching results for emissions and degradation rates thus providing a
388 tool for verification of this mass balance approach. Apart from these bottom-up approaches,
389 inverse top-down models using isotopic data might be appropriate methods for source
390 apportionment of atmospheric compounds⁷¹. These inverse models estimate source and sink terms
391 from variations in the atmospheric composition but require long-term monitoring using a relatively
392 dense network of sampling stations⁷². Inverse models may, however, provide an alternative route
393 to calculate the atmospheric budget but for CH₃X the application of these models is currently still
394 out of reach because of the challenges to regularly measure the isotopic composition of
395 atmospheric CH₃X. Once these challenges are overcome triple-element isotope analysis may
396 provide a realistic chance to better quantify the unbalanced atmospheric budgets of CH₃X and to
397 identify the putatively missing sources.

398

399 **Associated content**

400 The Supporting Information is available free of charge on the ACS publications website:

401 Additional information on analytical methods (isotope analysis, quantification), cross-calibration
402 of standards for bromine isotope analysis, relative nucleophilicities of halogens and water,
403 graphical determination of the rate laws of the different reactions, isotopic measurements of carbon
404 and bromine for hydrolysis of CH₃Br at high concentrations, determination of lambda values from
405 the current and previous studies, and isotopic information of product-CH₃Cl

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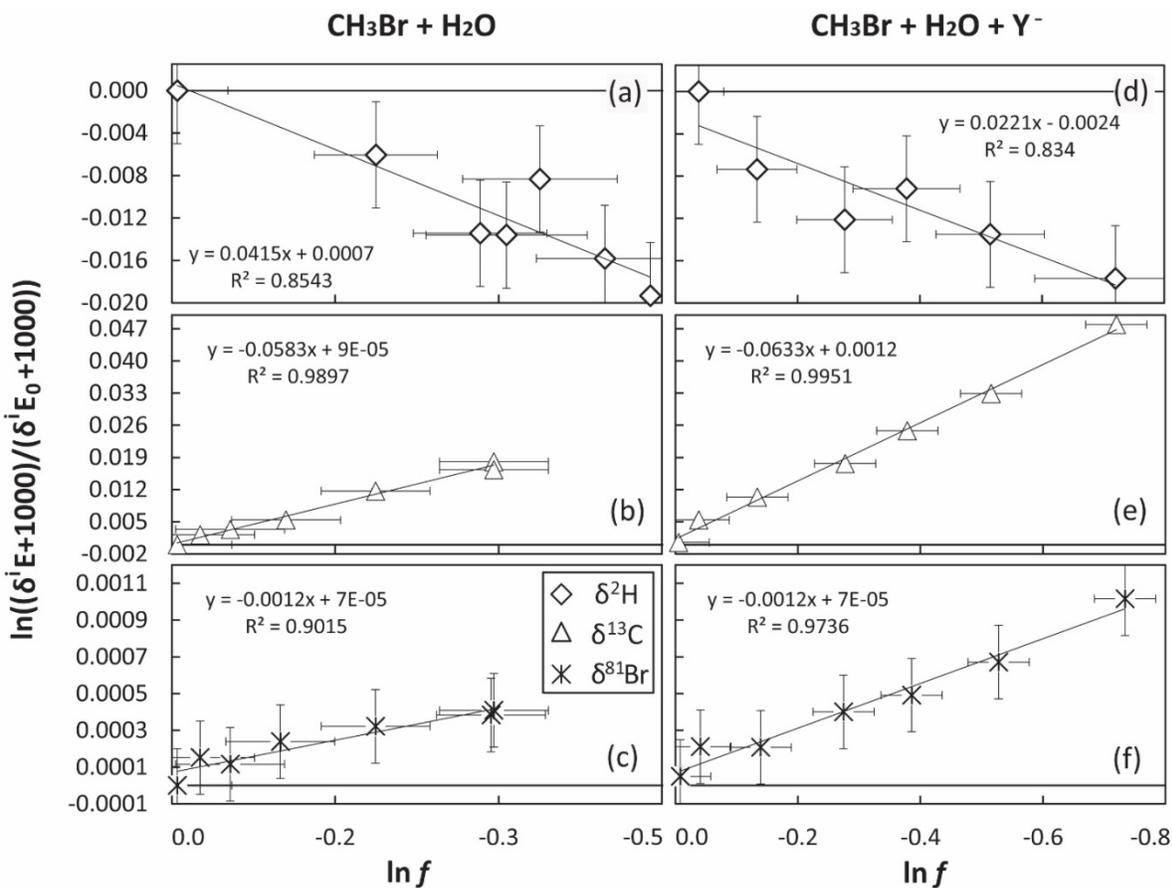
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620

621 Figure 1. Rayleigh plots for abiotic reactions of CH_3Br in water. Panel (a), (b), and (c) show results

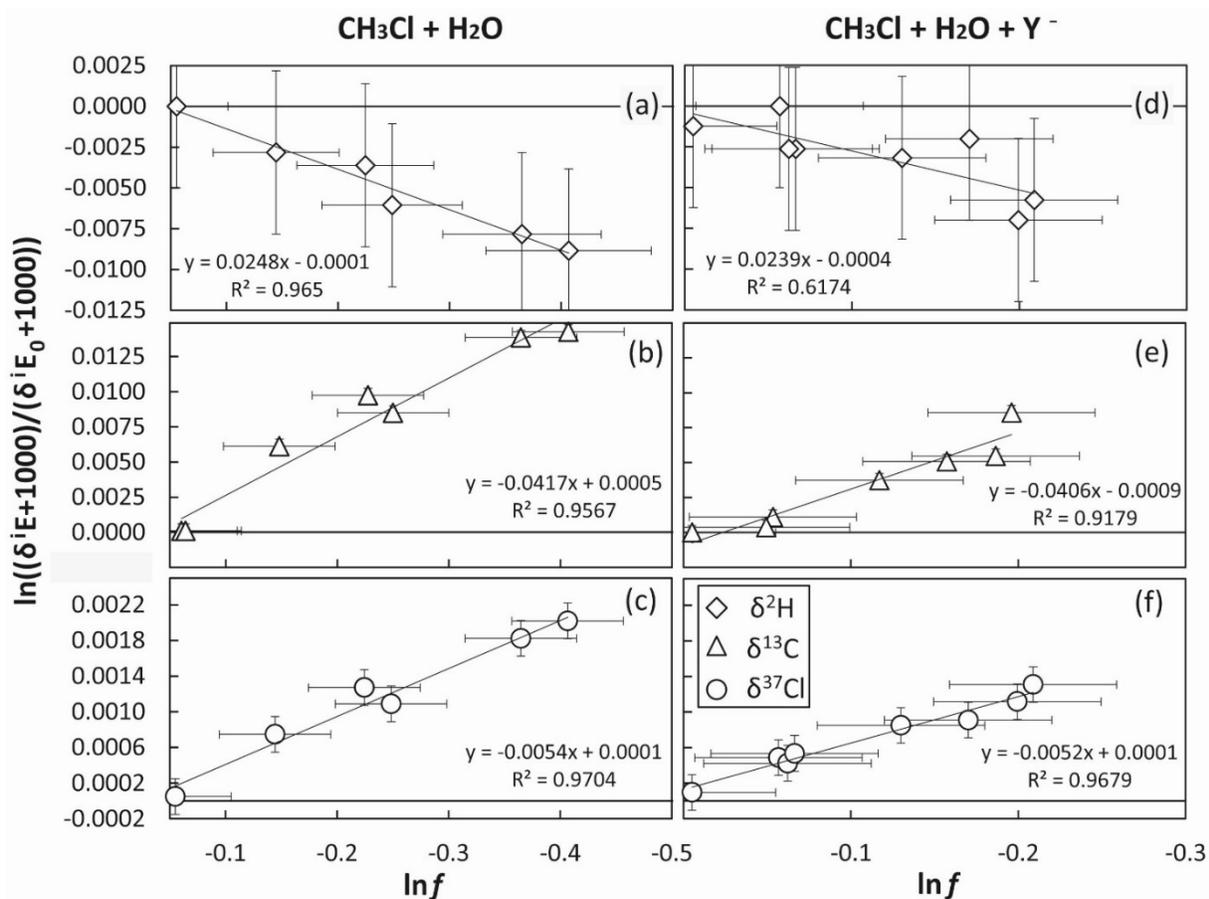
622 of the reaction $\text{CH}_3\text{Br} + \text{H}_2\text{O}$ (hydrolysis). Panel (d), (e), and (f) demonstrate isotope effects due

623 to $\text{CH}_3\text{Br} + \text{H}_2\text{O} + \text{Y}^-$ (hydrolysis and halide exchange combined). The slope of the regression

624 indicates the enrichment factor in Ur . Error bars represent the analytical uncertainty of 5 mUr

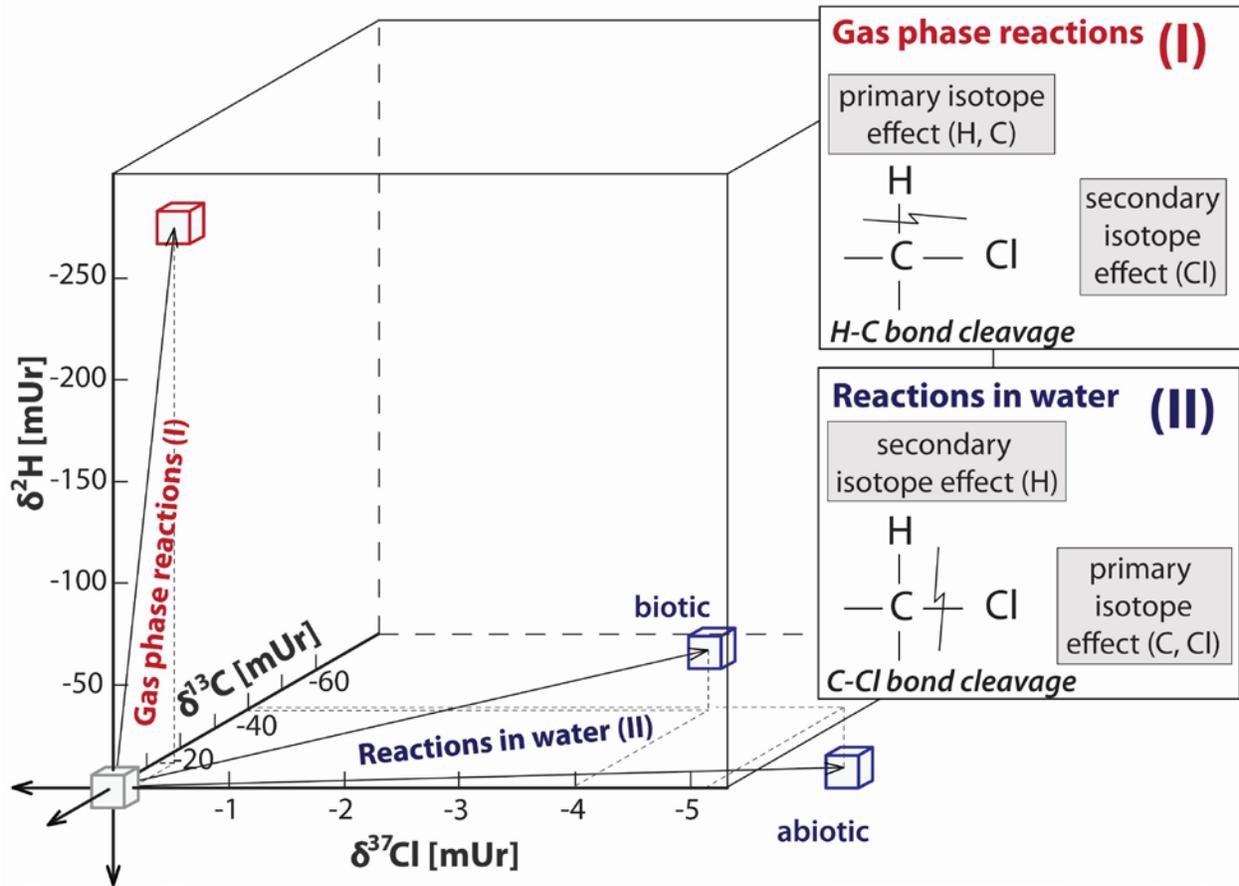
625 ($\delta^2\text{H}$), 0.5 mUr ($\delta^{13}\text{C}$), and 0.1 mUr ($\delta^{81}\text{Br}$). For carbon isotopes, error bars are smaller than the

626 used symbols. The quantification was carried out with an uncertainty of usually better than 5 %.



627

628 Figure 2. Rayleigh plots for reactions of CH₃Cl. Panel (a), (b), and (c) show results of the reaction
 629 CH₃Cl + H₂O (hydrolysis). Panel (d), (e), and (f) represent isotope effects due to CH₃Cl + H₂O +
 630 Y⁻ (combined hydrolysis and halide exchange). The slope of the regression indicates the
 631 enrichment factor in Ur. Error bars represent the analytical uncertainty of 5 mUr ($\delta^2\text{H}$), 0.5 mUr
 632 ($\delta^{13}\text{C}$), and 0.2 mUr ($\delta^{37}\text{Cl}$). For carbon isotopes, error bars are smaller than the used symbols. The
 633 quantification was carried out with an uncertainty of usually better than 5 %.



634

635 Figure 3. Illustration of fractionation effects of CH₃Cl in water and in the gas phase (troposphere).

636 The $\delta^2\text{H}$, $\delta^{13}\text{C}$, and $\delta^{37}\text{Cl}$ are expressed as the relative difference from $\delta^2\text{H}_0$, $\delta^{13}\text{C}_0$, and $\delta^{37}\text{Cl}_0$ of

637 the undegraded sample. All isotopic values for abiotic reactions in water are taken from the current

638 study whereas carbon and hydrogen isotope values are taken from the literature (Table S4).

639 Fractionation for chlorine isotopes in biotic reactions has been estimated assuming a minimum

640 isotope effect of -4 mUr based on previous studies on chlorinated alkanes as described in the text

641 (average of aerobic/ anaerobic reactions). For gas phase reactions an insignificant secondary

642 chlorine isotope effect was assumed being smaller than analytical uncertainty of 0.2 mUr. The

643 figure demonstrates a clear distinction between isotopic fractionation in the gas phase

644 (troposphere) and fractionation in water.

645 Table 1: Loss rates for hydrolysis and halide exchange of CH₃Br and CH₃Cl

	loss rates ¹ [%·d ⁻¹]	loss rates (previous studies) [%·d ⁻¹]
CH ₃ Br + H ₂ O	1.3 ± 0.2	2.1 ± 0.2 ^a
CH ₃ Br + H ₂ O + Y ⁻	11.5 ± 2.3	15.4 ± 6.0 ^b
CH ₃ Cl + H ₂ O	0.15 ± 0.05	0.14 ± 0.02 ^c
CH ₃ Cl + H ₂ O + Y ⁻	0.12 ± 0.03	-

646 ¹ Loss rates were determined graphically from plots of ln[f] versus time and indicate the loss rate
 647 at 23±1°C (296 K). The errors are given as the 95% confidence interval. Literature values are
 648 taken from ^a Jeffers and Wolfe¹⁶, ^b King and Saltzman¹⁷, ^c Elliot and Rowland⁵¹;

649 Table 2: Isotopic enrichment factors (ϵ) and lambda values (Λ) of abiotic reactions in water

	ϵ_{H} mUr	ϵ_{C} mUr	ϵ_{Cl} mUr	ϵ_{Br} mUr	$\Lambda_{\text{H/C}}$	$\Lambda_{\text{C/Cl}}$	$\Lambda_{\text{C/Br}}$
$\text{CH}_3\text{Br} + \text{H}_2\text{O}$ (10 mmolL ⁻¹)	+42 ± 20	-49.6 ± 5.6	-	<i>n.d.</i>			
$\text{CH}_3\text{Br} + \text{H}_2\text{O}$ (0.2 mmol L ⁻¹)	n.d.	-58.3 ± 6.8	-	-1.16 ± 0.42	-0.7 ± 0.2*		46.1 ± 16.1
$\text{CH}_3\text{Br} + \text{H}_2\text{O} + \text{Y}^-$	+22 ± 13	-63.3 ± 5.1	-	-1.22 ± 0.23	-0.3 ± 0.2		48.2 ± 6.5
$\text{CH}_3\text{Cl} + \text{H}_2\text{O}$	+25 ± 6	-41.7 ± 10.2	-5.3 ± 1.3	-	-0.6 ± 0.3	7.3 ± 0.9	
$\text{CH}_3\text{Cl} + \text{H}_2\text{O} + \text{Y}^-$	+24 ± 19	-40.6 ± 13.9	-5.2 ± 1.0	-	-0.6 ± 0.2	6.9 ± 2.3	

650 Enrichment factors are derived from the Rayleigh plots in Figure 1 and Figure 2. Lambda values are determined graphically from
651 dual-elemental isotope plots (Figure S11-S14, Supporting Information). Errors are given as the 95% confidence interval of the
652 regressions. Values in italics indicate that these reactions might not strictly follow first-order kinetics and epsilons only serve as an
653 approximation despite acceptable correlation coefficients; n.d. means “not determined”; * indicates that this value was calculated
654 using Equation 3.

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