Point-by-point response to the issues raised by referee#1 (Matthew S. Johnson)

We thank the referee for the positive evaluation of our manuscript and for the helpful comments to improve the manuscript. Requested changes were taken into account.

Referee #1*(referee's comments are in italics)*

This is a solid paper that presents a convincing case, that earlier measurements of the isotope effects in methyl chloride oxidation should be revised. It should be published subject to technical corrections to address the points below.

Authors: We very much thank the referee for the positive evaluation of our manuscript. The technical corrections are addressed below.

1. The authors use the unit 'mUr' for milli-Urey. This is not an accepted/defined unit in the SI or IUPAC systems. It is an unnecessary unit, as we already have the per mil symbol, ‰ which can be found in for example the IUPAC green book. Science should avoid a situation where each sub-field has it's own obscure pet units or we shall soon see CO2 mixing ratios expressed in microKeeling.

Authors: Change applied. We have replaced mUr by ‰ throughout the entire manuscript.

2. In some places the grammar should be corrected e.g. Line 20 'but yet lacks'.

Authors: Changes applied.

3. Line 27, 'increasing stable hydrogen isotope values', unclear, does it mean 1H or2H, concentration, atom ratio, molecular ratio?

Authors: To avoid confusion we have removed "increasing" from the sentence.

4. Line 37 change 'named' to 'called'

Authors: Change applied.

5. Line 119, Agilent has made a lot of different GC-MS systems. Please specify which one.

Authors: We have added the requested information to the text (Hewlett Packard HP 6890 gas chromatograph coupled to a MSD 5973 mass spectrometer).

6. Lines 217, 225, etc. 'f' and 'c' and other variables for physical quantities should be italicised.

Authors: Changes applied.

7. Line 309, 'differences in the experimental smog chamber set-up', the phrase seems to be saying that the smog chamber was different from itself? Simply saying that FTIR is different from IRMS seems too obvious to be worth mentioning. Please give a specific cause or, leave it out.

Authors: We have appropriately modified the sentence.

I am wondering if there might be a better way to present the information in Figure 5, perhaps as a table, or a plot that would show both the fractionation of a given source and it's magnitude. The argument should not simply be the fractionation of each process, but it's effect on the atmospheric composition: isotopic mass balance.

Authors: All available information regarding known source and sink strengths of chloromethane and the related stable isotope data have been provided in Tables 2 & 3. However, in addition to these Tables we would like to keep Figure 5 in the manuscript as it schematically summarizes the global chloromethane budget and the application of stable hydrogen isotopes and thus gives the reader a quick overview of the results and their relationship to the isotopic mass balance. We have slightly modified the text of this section.

Point-by-point response to the issues raised by referee#2

We thank the referee for the helpful comments and suggestions which have improved the manuscript.

Referee #2 *(referee's comments are in italics)*

General comment

CH3Cl is the most abundant chlorine containing gas in the atmosphere, but it is not the target species of the Montreal protocol since emission regulation is not effective for stratospheric ozone recovery, given that its main sources are natural. An improved global budget estimate for CH3Cl is important for reducing uncertainties of future ozone prediction. In particular, the globally largest source, vegetation, is unknown in many aspects, emitting plant species, processes, mechanisms and global emission magnitude etc. As examined for relatively "major" trace gases such as CO2, CH4 and CO, isotopic mass balance is a powerful tool to separate different source categories and sink processes in the global budget. General approach is that atmospheric isotope ratio is considered to equal to sum of isotopic fluxes from all sources corrected for kinetic isotopic fractionations that happen in sink processes. For this purpose, accurate values for the all terms of the mass balance equation are required. Measurement of isotopic composition of CH3Cl is a difficult technical challenge and thus many of necessary terms in the isotopic mass balance are lacking. In this context, this study addresses the sink terms and it indeed gives an important contribution. New data presented in this study is significant and overall the paper is well organized and concise. I would recommend publication of this manuscript in ACP after some of concerns and questions below are considered.

Authors: We very much thank the referee for the positive evaluation of our manuscript. The concerns and questions of the referee are addressed below.

1. One earlier study Sellevåg et al. (2006) reported more 2H enrichments for the all reactions addressed in this study e.g. CH3Cl + OH, CH3Cl + Cl and CH4 + OH. Although the authors avoid deeper discussion and it may be difficult to identify the dominant cause now, maybe can they specify potential sources that could systematically bias either experiment? Any difference in smog chamber settings or production of OH/Cl radical? Use of different measurement method (FTIR versus IRMS)? In particular, spectroscopy measurements (FTIR) do not require chemical conversion of sample gas, but IRMS measurements need chemical conversion from CH3Cl or CH4 to H2 which could cause isotope fractionation.

Authors: One potential source of error is incomplete mixing inside the chamber. Incomplete mixing may result in an underestimation of the KIE due to transport limitation. The experiments of Sellevåg et al. (2006) were carried out in 250L electropolished stainless steel chamber, whereas our experiments were carried out in a 3500L Teflon-FEP chamber. Hence incomplete mixing might be an issue for our set up. However, the lifetime of CH_3Cl under the experimental conditions employed in our studies was in the order of 6 to 10h, whereas the turnover of air inside the chamber occurred on time scales of a few minutes, thus making incomplete mixing an unlikely source of error. Furthermore we would also highlight that incomplete mixing would also have affected the determination of the respective KIEs for methane. Since our reported values are in reasonable agreement with previously reported KIEs we consider incomplete mixing as a potential source of error in our experiments highly unlikely.

The chlorine radical generation scheme appears to be quite similar for both studies. Sellevåg et al. (2006) photolyzed molecular chlorine at 340 (310) nm whereas we used broadband photolysis (300 to 700 nm). Both are well-established methods.

In our study, OH was generated by UV-photolysis of ozone in the presence of water vapour and H_2 (2000 ppm). This is an established efficient method for OH radical generation (DeMore 1992, Cantrell et al. 1990). In the Sellevåg et al. (2006) study OH was generated under dry conditions from the UV-photolysis of ozone (300 to 500 ppm) in the presence of 2000 ppm H_2. In our study, ozone was photolyzed at a level of typically 0.5-10 ppm in the presence of water vapour (RH of 70%; 2.5% v/v) and 2000 ppm of H_2 to generate OH. The

reaction rate constants of O(1D) with H_2 and H_2O at 298 K are $1.1*10^{-10}$ and $2.2*10^{-10}$ cm^3 s^{-1} molecules^{-1}, respectively. At a relative humidity of 70% (corresponding to 25000 ppm), the reaction with H2O is by far the main pathway to form OH (with the H_2 pathway contributing less than 1% to the OH yield). Thus, in the absence of water vapour, the half-life can be estimated to be about 600h. This is consistent with previous studies, where ozone levels of 500 to 600 ppmv were required for a sufficient OH production from H_2 (Gola et al. 2005, Sellevåg et al. 2006). In our study, photolysis of 2 ppmv ozone in the absence of water vapour (RH<1%) but with 2000 ppm H_2 resulted in a CH_3Cl degradation of less than 3% over 10 hours because of the insufficient OH yield. With this, we can safely exclude any measurable effect from potential side reactions on the determination of the KIEs.

Additionally, we monitored the ratio of CH_3Cl and PFH for at least 2h prior to each experiment in order to assess potential side reactions. For the experiments with chlorine, this was done under dark conditions in the presence of 10 ppmv Cl_2. For the OH experiments, this was either done in the absence of light or ozone. None of these tests revealed any indication of a measurable degradation of CH_3Cl and thus we excluded any bias due to side reactions.

Cantrell et al. (1990) who used UV-photolysis in the presence of water as an OH source, estimated that the reaction of methane with O(1D) may contribute about 3% to the overall degradation. The higher ozone levels and the less efficient conversion of O(1D) to OH in the Sellevåg et al. (2006) study suggest an overall higher transient O(1D) concentration as compared to our experiments. However the KIE for the reaction of CH_4 with O(1D) is1.060 and thus substantially smaller than the respective KIE for the reaction with OH. When assuming a similar trend for the reactions of CH_3Cl, one would expect a small underestimation of the KIE for the reaction of CH_3Cl with OH. Since the KIE reported by Sellevåg et al. (2006) was larger than that determined in our study any side effect from this reaction is unlikely.

Any judgement on the different methods (FTIR versus IRMS) would be very speculative without directly comparing both methods during the same degradation experiment. We thus limit the discussion to our IRMS measurements. The thermolytic conversion of methane to H_2 is a well-established method for measuring δ2H values with IRMS and numerous studies have shown that these methods are reliable when correctly conducted. We have added a sentence to the discussion section of the revised manuscript where we refer the reader to Supplementary information where considerations on the differences between differences between the experimental and analytical design and protocols of the study by Sellevåg et al. (2006) and this study are provided.

2. Estimation of the kinetic isotope effect in this study relies on simple regression of the data (Figure 2–4). Lower remaining fraction f at the end of the experiment would cover wider range of the X axis and more frequent sample collection would increase the number of data, both might change the regression result. What is the limitation factor in the experiment? Beside this, the regression in principle should start from the point of origin (X=0 and Y=0), but the authors do not taken into this account. Why?

Authors: We agree that a more frequent sample collection particularly towards the end of the experiments would have increased the number of data and changed/improved the regression results. However, the number of samples collected during the experiments was limited by the number of available canisters (2 L stainless steel, electropolished, evacuated <10^{-4} mbar). We have modified the Figures so that the regression starts at X=0 and Y=0.

3. Section 2.4 is an important introduction. I would move this section into section 1 with some reformulation. Section 1 could be enriched so that readers could better understand overview of the global isotopic mass balance for CH3Cl and importance of KIE to close the budget. I would reformulate P3 L65–L89. The authors might present mass balance equations (mass balances for mixing ratio, _13C and _2H) and then

readers could clearly find the key role of the KIE in estimating the budget using isotopes. This would also help the authors for discussions in section 5.

Authors: As requested we have reformulated and restructured this section.

4. I am not sure how the new unit "mUr" would be accepted in the research community, because people are used to see the conventional unit ‰. In reality, I was very confused throughout the manuscript. The authors might want to share the newly suggested unit in the manuscript, but in my opinion the authors should choose one that would advance scientific discussion more smoothly under the current situation. It might be too early to use the new unit in a scientific paper even if it alters the conventional one in the future (I am not sure for this though).

Authors: Change applied. We have replaced mUr by ‰ throughout the entire manuscript.

Specific comments

P3 L65–L89: As in the earlier comment, I would like to suggest to reformulate the paragraphs so that readers could get the principle framework of the global isotope budget and how determination of the KIEs contributes to it.

Authors: We have revised this section of the introduction. Please refer to the response above.

P3 L81: "in view of the unexpected isotope fractionation" Please elaborate what this phrase means. What is expected and what is unexpected? Do you expect that FTIR measurements could be somehow biased?

Authors: The term "unexpected" refers to the large carbon isotope effects previously reported by this group for the reaction of CH_3Cl with OH. These are 5to 10 times larger than the respective KIEs for the reaction of methane and other hydrocarbons with OH. However, in order to avoid any confusion we have reworded the sentence.

Sections 2.1 and 2.2: Please describe traceability of mixing ratio measurements (both CH3Cl and CH4). Samples are measured against the working gases, but those working standards were calibrated ultimately to what type of standards or scales?

Authors: We used a Linde CH_3Cl standard 1006±12 ppmv in N_2. This standard was verified in-house by measurement against a Scott TOC 15/17 standard containing CH_3Cl among others at 1 ppmv each. This standard is traceable to NIST. PFH was added as a liquid (~0.7 μL) to the chamber. We used the abundance of CH_3Cl relative to PFH to calculate the remaining fraction of CH_3Cl (equation 4) hence traceability to an ultimate scale is not an issue in this case. The relative standard deviation of this procedure was determined prior to each experiment and during a blank experiment and ranged between 1.3% and 1.9%. We have added this information to the method section.

The CH_4 mixing ratios of the chamber were continuously measured with a Picarro G225i cavity ring down spectrometer. For quality control prior to the experiments pressurized air from a tank with a known CH_4 mixing ratio (provided by the MPI for Biogeochemistry in Jena) was measured.

P6 L141: What is "PFA"?

Authors: PFA should be PFH and is the abbreviation of perfluorohexane which is introduced on page 4.

P6 L157: "relative trueness" I am not familiar with this wording. Does it mean that a sample is measured against the working standard gas (H2) that were calibrated independently? Please reword. Otherwise please define "trueness" and "relative trueness".

Authors: We have appropriately reworded the sentence.

P6 L159: typo "LSVEC", but description about NBS22 and LSVEC is not necessary, because _13C measurement is out of scope.

Authors: Agreed. Change applied.

P6 L167: It appears to me that the SD magnitude is not in relation to the absolute _2H value but that it depends on the relative "distance" from the value of the working standard. In such a large range of _2H values determined by extrapolation, the IRMS

Authors: The magnitude of the SD depends (as correctly mentioned by the reviewer) on the relative "distance" from the value of the working standard and also on the sample amount transferred to the IRMS as lowest SD were observed for samples with highest mixing ratios and higher SD for samples with lowest mixing ratios. This is important for the samples with low remaining fraction (towards the end of the experiments).

P7 L170–174: Please refer to my general comment no 4.

Authors: We have removed this section from the manuscript

P7 L175: Please see my comment to P6 L167.

Authors: Please see response above.

P7 L194: Same comment as above (P6 L167). This sentence should be reworded as the authors also mention to the possible error in the IRMS calibration. The current sentence is misleading as in my earlier comment.

Authors: Please refer to comment answer above.

Section 2.4: I would move this to section 1 or at least before section 2.1 since the content is the principle of this study rather than measurement methods which constitute large part of section 2.P7 L175: Please see my comment to P6 L167.

Authors: We have moved a part of the section to the introduction.

P8 L218: might be more specific i.e. the heavier CH2DCl or CH3D.

Authors: Change applied.

Figure 2: See my general comment no 2. Also the authors should specify significant digits in the annotation of the graphs.

Authors: All Figures including Figure 2 have been revised.

Figures 2–4: "_10 (or 6) ppmv". How precisely/accurately was the CH3Cl mixing ratio measured? This relates to transparency of the error bars given in the figures.

Authors: The relative standard deviation ranged between 1.3% and 1.9%. We have added this information to the method section.

P10 L10: What is the "limited analytical resources"? The information might help following researchers.

Authors: As stated above the number of samples collected during one experiment and for repeating the same experiment several times was limited by the number of available canisters (2 L stainless steel, electropolished, evacuated $<10^{-4}$ mbar). Unfortunately, canisters could not directly be measured immediately after chamber experiments were performed and therefore had to be stored for a time period prior stable isotope measurements.

P14 L306–309: As in the earlier comment, I would like to see a bit deeper discussion. The authors might be able to specify possible or potential sources of the biases.

Authors: We have added a sentence to the discussion section of the revised manuscript where we refer the reader to Supplementary information where considerations on the differences between differences between the experimental and analytical design and protocols of the study by Sellevåg et al. (2006) and this study are provided.

P14 L310ff: The authors might want to validate their results by comparing to previous measurements and to indicate advantage over Sellevåg et al. (2006). Even supposing that the KIE of the $CH_4 + OH$ reaction are in good agreement, the fact might support validity of the chamber set-up (common in all the experiments in this study) but not of the IRMS measurement including preparation steps that are not identical for CH_3Cl and CH_4. Please clarify this point in the manuscript.

Authors: Please refer to comment answers above.

P14 L331: "cmu" capitalized?

Authors: No, but in italics. Change applied.

P15 L354: "excellent agreement" looks a bit exaggerated. This study's result agrees to some of previous measurements within the range of uncertainty. Skeptical eyes could see this study's result for $CH_4 + OH$ reaction being at less negative end among previous measurements (Table 1) and this possible trend is also the case for $CH_3Cl + OH/Cl$ reactions.

Authors: We have replaced "excellent" by "good".

Point-by-point response to the issues raised by referee#3

We thank the referee for the helpful comments and suggestions which have improved the manuscript.

Referee #3 *(referee's comments are in italics)*

The paper presents isotope fractionation measurements of CH3Cl for the reactions with hydroxyl and chlorine radicals and CH4+OH. This is a valuable contribution to the hitherto scarce information on hydrogen kinetic isotope effect of reactions significant for the atmosphere. Isotopes deliver valuable adjunct information which can, together with other data, increase the understanding of the atmospheric processes. Therefore the paper is highly suitable to be published in the journal. The paper contains yet some weak points which need to be improved before publishing.

Authors: We very much thank the referee for the positive evaluation of our manuscript. The comments of the referee are addressed below

Major comment

The major issue which should be made clearer to the reader is linked to the necessity of very accurate concentration and isotopic composition of the reactant during its degradation for delivering reliable epsilon values. Since during both oxidation reactions of CH4 and CH3Cl a similar temporal evolution of the concentration is observed, it should exist one order of magnitude difference in the produced OH concentration. For the former, this should be in the range of 10^{10} cm-3 range, which is very ambitious for the photooxidation of ozone method. The authors should give some more details about designing the experiments, for instance on ozone concentration, UV lamp intensity...To rule out any losses of the very small methane molecule (wall permeation, tightness), it would be helpful to add a figure (also as supplement) depicting a 'zero-run', i.e. the concentration evolution of methane in the FEP bag without reaction during the time of 10 h.

Authors: The reviewer is correct with his estimate of the OH concentration. In our study, OH was generated by UV-photolysis of ozone in the presence of water vapour. This is a well-established efficient method for OH radical generation (DeMore 1992, Cantrell et al. 1990). In order to perform the degradation experiments within a day, the experimental conditions were modified for the different experiments as indicated by the new Table S1 which has been added to the supplementary information file of the revised manuscript. Based on the high radiant efficiency of the TUV lamp at the absorption band of O_3 the photolysis of O_3 to O^1D and O_2 and the subsequent OH generation by O^1D+H_2O is favoured. One can estimate a photolysis rate of $J(O_3)$ in the range of 10^{-3} s^{-1} for the first experiment with CH_3Cl. For the CH4 experiments we even had 4 TUV lamps installed around the chamber, which increased the $J(O_3)$ value. This is represented by the reduced lifetime of O_3 when the lamps are on and no O_3 is injected (roughly 11 min for the CH_3Cl+OH experiment and 4 min for the CH_4+OH experiment). The reaction rate of OH for CH3Cl is roughly 6 times higher than for CH_4 (based on the higher O_3 concentrations 623 ppbv over 9h for CH_3Cl+OH and 3570 ppbv over 13h for CH_4+OH. These differences have been specified in the revised manuscript and related data has been provided in the Supplementary (Table S1). Furthermore, we have added data and a related discussion section to the Supplementary that rule out any unaccounted loss of methane during our experiments.

Finally, please note that we also have added a third degradation experiment of CH_3Cl+OH to the manuscript. These data have only recently become available and were included in the revised manuscript to improve statistical considerations. Thus the mean isotope fractionation for the reaction of CH_3Cl+OH has slightly changed from -242 to -263‰.

Other comments

Page2Line62: The authors might consider to add a short statement on the significance of CH3Cl losses into the stratosphere.

Authors: Added as requested.

Page3Lines83-84: reformulate, the authors give themselves enough literature sources

Authors: Change applied.

Page8Equation2: The authors should revise the consistency of this equation: they should keep 1000 also behind the second '='. This is dependent on the delta expression, and as it looks like (behind the first '='), this is in x10-3, permil, or the unusual murey.

Authors: Change applied. Furthermore, we have replaced mUr by ‰ throughout the whole manuscript.

Editorial revisions:

Page6Line 141: replace PFA by PFH

Authors: Change applied.

1 **Mass spectrometric measurement of hydrogen isotope fractionation for the**

2 **reactions of chloromethane with OH and Cl**

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19 **Abstract**

20 Chloromethane (CH_3Cl) is an important provider of chlorine to the stratosphere but ~~yet lacks~~

21 detailed knowledge of its budget is missing. Stable isotope analysis is potentially a powerful

22 tool to constrain CH_3Cl flux estimates. The largest degree of isotope fractionation is expected

23 to occur for deuterium in CH_3Cl in the hydrogen abstraction reactions with its main sink

24 reactant tropospheric OH and its minor sink reactant Cl atoms. We determined the isotope

25 fractionation by stable hydrogen isotope analysis of the fraction of CH_3Cl remaining after

26 reaction with hydroxyl and chlorine radicals in a 3.5 m^3 Teflon smog-chamber at 293 $\pm$ 1K.

27 We measured the ~~increasing~~ stable hydrogen isotope values of the unreacted CH_3Cl using

28 compound specific thermal conversion isotope ratio mass spectrometry. The isotope

29 fractionations of CH_3Cl for the reactions with hydroxyl and chlorine radicals were found to

30 be -2~~644~~2 $\pm$ ~~457 mUr (or ‰)~~ ‰ and -280 $\pm$ 11 ~~mUr~~‰, respectively. For comparison, we

31 performed similar experiments using methane (CH$_4$) as the target compound with OH and
32 obtained a fractionation constant of -205 ± 6 ‰mUr which is in good agreement with values
33 previously reported. The observed large kinetic isotope effects are helpful when employing
34 isotopic analyses of CH$_3$Cl in the atmosphere to improve our knowledge of its atmospheric
35 budget.

1 Introduction

38 Chloromethane (often namedcalled methyl chloride) is the most abundant chlorine containing
39 trace gas in the Earth's atmosphere, currently with a global mean mixing ratio of ~540 ± 5
40 parts per trillion by volume (pptv) and an atmospheric lifetime of 1.0–1.2 years (Carpenter et
41 al., 2014). The global emissions of CH$_3$Cl have been estimated to be in the range of 4 to 5 Tg
42 yr^{-1} (1 Tg = 10^{12} g) stemming from predominantly natural but also anthropogenic sources
43 (Montzka and Fraser, 2003; WMO, 2011; Carpenter et al., 2014). However, current estimates
44 of the CH$_3$Cl global budget and the apportionment between sources and sinks are still highly
45 uncertain. Known natural sources of CH$_3$Cl include tropical plants (Yokouchi et al., 2002;
46 Yokouchi et al., 2007; Umezawa et al., 2015), wood-rotting fungi (Harper, 1985), oceans
47 (Moore et al., 1996, Kolusu et al. 2017), plants of salt marshes (Rhew et al., 2003; Rhew et
48 al., 2000), aerated and flooded soil (Redeker et al., 2000; Keppler et al., 2000), senescent
49 leaves and leaf litter (Hamilton et al., 2003; Derendorp et al., 2011) and wild fires.
50 Anthropogenic CH$_3$Cl release to the atmosphere comes from the combustion of coal and
51 biomass with minor emissions from cattle (Williams et al., 1999) and humans (Keppler et al.,
52 2017). In addition, it has been reported that emissions from industrial sources, particularly in
53 China, might be much higher than previously assumed (Li et al., 2016).

54 The dominant sink for atmospheric CH$_3$Cl results from the reaction with photochemically-
55 produced hydroxyl radicals (OH), currently estimated at about 2.8 Tg yr^{-1} (Carpenter et al.,
56 2014). Furthermore, in the marine boundary layer the reaction of CH$_3$Cl with chlorine
57 radicals (Cl) represents another sink estimated to account for up to 0.4 Tg yr^{-1} (Khalil et al.,
58 1999; Montzka and Fraser, 2003). Microbial CH$_3$Cl degradation in soils may be a relevant
59 additional global sink (McAnulla et al., 2001; Harper et al., 2003; Miller et al., 2004; Jaeger
60 et al., 2018a) but its impact on the global CH$_3$Cl budget is still highly uncertain. The
61 microbial CH$_3$Cl soil sink strength has been estimated to range from 0.1 to 1.6 Tg yr^{-1}
62 (Harper et al., 2003; Keppler et al., 2005; Carpenter et al., 2014). Moreover, small
63 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). Loss of tropospheric CH_3Cl to the stratosphere is a result of turbulent mixing and the transport process itself is not thought to cause a substantial isotope fractionation (Thompson et al. 2002).

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). The general approach is that the atmospheric isotope ratio of a compound (e.g. CH_3Cl) is considered to equal the sum of isotopic fluxes from all sources corrected for kinetic isotopic fractionations that happen in sink processes:

$$\delta^2 H^{atm} = \sum_{i=l}^{n} \Phi_i^{source} \times \delta^2 H_i^{source} + \sum_{j=l}^{n} \Phi_j^{\sin k} \times \varepsilon_j^{\sin k} \qquad (1)$$

where $\delta^2 H^{atm}$ and $\delta^2 H_i^{source}$ are the hydrogen isotope values of CH_3Cl in the atmosphere and of the different sources i in per mil. Φ_i and Φ_j are the CH_3Cl flux fraction for each source and sink. ε_j is the isotope fractionation of each sink j in per mil.

Stable isotope analysis, when used in combination with CH_3Cl flux measurements, has the potential to better constrain the atmospheric CH_3Cl budget as suggested by Keppler et al. (2005) and Saito & Yokouchi (2008). The isotopic composition of tropospheric CH_3Cl 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 CH_3Cl 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 CH_3Cl 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 CH_3Cl 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).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:

$$KIE = \frac{k_1}{k_2} \tag{2}$$

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 ε (also termed isotope enrichment constant) or isotope fractionation constant α.

First approaches of an isotope mass balance regarding stable carbon isotopes of CH_3Cl have been provided by Keppler et al. (2005) and Saito & Yokouchi (2008). Several studies have investigated the stable carbon isotope source signature of CH_3Cl produced via biotic and abiotic processes, however, for a more detailed overview we refer readers to the studies of Keppler et al. (2005) and Saito & Yokouchi (2008). Moreover, researchers have measured the KIE of stable carbon isotopes of CH_3Cl 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 CH_3Cl with OH has been reported by Gola et al. (2005) and this 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, we consider it important to confirm this result using another measurement technique such as stable isotope ratio mass spectrometry (IRMS).

So far most isotopic investigations of CH_3Cl have ~~predominantly~~ focused on stable carbon isotope measurements~~.~~ but s~~S~~table hydrogen isotope measurements including both sources and sinks of CH_3Cl have also recently 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 CH_3Cl and their reactions with Cl and OH. The OH and Cl reaction rates of CH_2DCl were measured by long-path FTIR spectroscopy relative to CH_3Cl at 298 ± 2 K and 1 atm (Sellevåg et al., 2006) (Table 1).

In this manuscript, using a 3.5 m^3 Teflon smog chamber and IRMS measurements, we present results from kinetic studies of the hydrogen isotope fractionation in the atmospheric

124 OH and Cl loss processes of CH$_3$Cl. Furthermore, we also measured the isotope fractionation
125 for the reaction between methane (CH$_4$) and OH using a similar experimental design and
126 compared this value with those from previous studies.

2 Materials and Methods

2.1 Smog chamber experiments with chloromethane

129 The isotope fractionation experiments were performed in a 3.5 m^3 Teflon smog-chamber
130 (fluorinated ethylene propylene, FEP 200A, DuPont, Wilmington, DE, USA) with initial
131 CH$_3$Cl mixing ratio of 5 to~~about~~ 10 parts per million by volume (ppmv). Atomic chlorine
132 were generated via photolysis of molecular chlorine (Cl$_2$) (Rießner Gase, 0.971% Cl$_2$ in N$_2$)
133 by a solar simulator with an actinic flux comparable to the sun in mid-summer in Germany
134 (Bleicher et al., 2014). Hydroxyl radicals were generated via the photolysis of ozone (O$_3$) at
135 253.7 nm in the presence of water vapor (RH = 70%) (produced by double-distilled water in a
136 three-neck bottle humidifier) and/or H$_2$. To obtain efficient OH formation, a Philips TUV
137 lamp T8 (55 W) was welded in Teflon film (FEP 200) and mounted inside the smog chamber.
138 O$_3$ was monitored by a chemiluminescence analyzer (UPK 8001). The chamber was
139 continuously flushed with purified, hydrocarbon-free zero air (zero-air-generator, cmc
140 instruments, <1 ppbv of O$_3$, <500 pptv NO$_X$, <100 ppbv of CH$_4$) at a rate of 4 L min^{-1} to
141 maintain a slight overpressure of 0.5-1 Pa logged with a differential pressure sensor
142 (Kalinsky Elektronik DS1). The quality of the air inside the chamber in terms of possible
143 contamination was controlled by monitoring NO and NO$_X$ (EcoPhysics CLD 88p, coupled
144 with a photolytic converter, EcoPhysics PLC 860). Perfluorohexane (PFH) with an initial
145 mixing ratio of ~25 parts per billion by volume (ppbv) was used as an internal standard to
146 correct the resulting concentrations for dilution. The temperature was set to 20±1°C and
147 monitored, together with the relative humidity, by a Teflon-cased sensor (Rotronic, HC2-
148 IC102). To guarantee constant mixing and small temperature gradients, a Teflon fan was
149 mounted and operated inside the chamber. More detailed specification of the smog chamber
150 can be found elsewhere (e.g. Wittmer et al., 2015). The mixing ratios of CH$_3$Cl and PFH
151 were ~~monitored~~ quantified by a Hewlett Packard HP 6890 gas chromatograph coupled to a
152 MSD 5973 mass spectrometer ~~by gas chromatography-mass spectrometry~~ (GC-MS, Agilent
153 Technologies, Palo Alto, CA) with a time resolution of 15 minutes throughout the
154 experiments. Two CH$_3$Cl reference gases from Linde (1006±12 ppmv diluted in N$_2$) and
155 Scott (1 ppmv) were used for calibration. The abundance of CH$_3$Cl relative to PFH was used
156 to calculate the remaining fraction of CH$_3$Cl (equation 4). The relative standard deviation of

157 this procedure was determined prior to each experiment and also during control experiment
158 and ranged between 1.3 and 1.9%. Aliquots (5 ml) were withdrawn from the chamber with a
159 gas tight syringe, injected into a stream of He (30 ml min$^-$1) and directed to a pre-
160 concentration unit that was attached to the GC-MS. The pre-concentration unit consisted of a
161 simple 8 port valve (VICI Valco) equipped with two cryotraps made of fused silica, which
162 were immersed in liquid nitrogen for trapping the analytes. Prior to each sample
163 measurement, a gaseous standard (5 ml of 100 ppmv CH_3Cl in N_2) was measured. Figure 1
164 shows the design of the smog chamber used in our experiments.

165 In the CH_3Cl and OH experiments (1 to~~and~~ 3~~2~~) 2000 ppmv H_2 was used to scavenge chlorine
166 atoms originating from the photolysis or oxidation of formyl chloride (HCOCl), which forms
167 as an intermediate in the reaction cascade. Under the experimental conditions typically more
168 than 70% of the CH_3Cl was degraded within 6~~7~~ to 10 h. From each experiment (CH_3Cl + OH
169 and CH_3Cl + Cl) 10 to 15 canister samples (2 L stainless steel, evacuated <10^{-4} mbar) were
170 collected at regular time intervals for subsequent stable hydrogen isotope measurements at
171 Heidelberg University. An overview of the experimental details (Table S1) and control
172 measurements is provided in the Supplementary.

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175

176 **Figure 1:** Scheme of the experimental smog chamber

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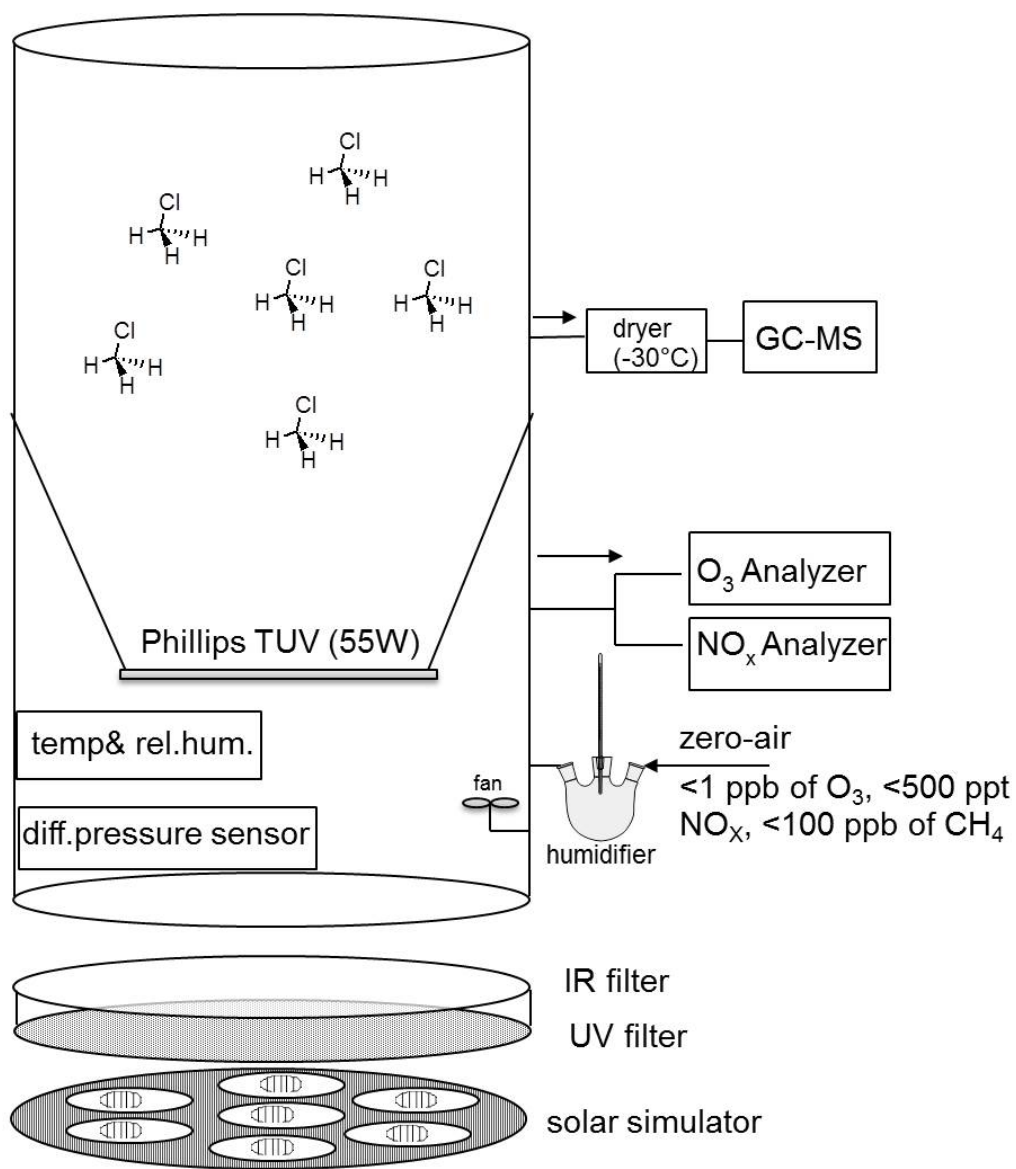
2.2 Smog chamber degradation experiments with methane

The CH_4 degradation experiments were carried under the same conditions as the CH_3Cl
degradation experiments but without PFAH 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_4 mixing ratio was 6 ppmv. Throughout these experiments CH_4 and CO_2 mixing ratios
were monitored with a Picarro G225i cavity ring down spectrometer directly connected to the
chamber. For more details see information provided in the Supplementary.

2.3 Stable hydrogen isotope analysis using isotope ratio mass spectrometry

2.3.1 Chloromethane

Stable hydrogen isotope ratios of CH_3Cl 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_2 (Alphagaz 2, hydrogen 6.0, Air Liquide, Düsseldorf, Germany) with a δ^2H value of ~-250 ~~mUr‰ (milliurey = 0.001 = 1‰, cf. section below)~~ versus VSMOV was used as the working gas. The conventional delta notation, expressing the isotopic composition of the sample relative to that of VSMOW standard (Vienna Standard Mean Ocean Water) in per mil is used. All ~~measured~~ sample δ^2H values were measured relative to ~~monitored for their relative trueness by analyzing~~ an in-house working standard of known δ^2H value. The CH_3Cl 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 δ^2H value of -140.1 ± 1.0 ~~mUr‰~~ vs. VSMOW (n = 10, 1σ). 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_3Cl 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 δ^2H values (~-140 ~~mUr‰~~) and highest mixing ratios and higher SD for samples with highest δ^2H 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 (Coplen, 2011) value unit. Thus, an isotope delta value expressed traditionally as −50 ‰ can be written −50 mUr. Similarly as for the δ^2H 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 δ^2H data might be affected by an additional error ("scale compression") and particularly might affect the uncertainties of the very positive δ^2H values. Unfortunately CH_3Cl working standards with distinct isotopic

signatures spanning the full range of measured δ^2H 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 CH_4 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 δ^2H analysis of CH_3Cl (c.f. section 2.3.1.).

All δ^2H values obtained from analysis of CH_4 were corrected using two CH_4 working standards (isometric instruments, Victoria, Canada) calibrated against IAEA and NIST reference substances (not specified by the company). The calibrated δ^2H values of the working standard in ~~mUr~~‰ vs. V-SMOW were -144 ± 4 ~~mUr~~‰ and -138 ± 4 ~~mUr~~‰.

The H_3^+ 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 CH_4 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 δ^2H values (~-140 ~~mUr~~‰) and highest mixing ratios and higher SD for samples with highest δ^2H values (~+800 ~~mUr~~‰) and lowest mixing ratios.

2.4 Kinetic isotope effect, fractionation constant α and the isotope enrichment constant ε

~~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 ε (also termed isotope enrichment constant) or isotope fractionation constant α.~~

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

$$\ln \frac{R_t}{R_0} = \ln \left(\frac{\delta^2 H_t + 1000}{\delta^2 H_0 + 1000} \right) = \ln \frac{(\delta^2 H_0 + \Delta \delta^2 H + 1)}{(\delta^2 H_0 + 1)} \cong (\alpha - 1) \cdot \ln f = \varepsilon \cdot \ln f \qquad (32)$$

Where R_t and R_0 are the $^2H/^1H$ ratios in CH_3Cl or CH_4 at the different time points and time zero, respectively, and f is the remaining CH_3Cl or CH_4 fraction at the different time points. Negative values of ε indicates that the remaining CH_3Cl or CH_4 is enriched in the heavier isotope and corresponds to a $\alpha < 1$, meaning that over the entire experiment, the heavier $CH_{32}DCl$ or CH_4-D react by this factor more slowly than the lighter CH_3Cl or CH_4.

The kinetic isotope effect is then calculated as:

$$KIE = \frac{1}{\alpha} \qquad (43)$$

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

$$f = c_{xT} * c_{i0} / (c_{x0} * c_{iT}) \qquad (54)$$

where c_{x0} and c_{xT} are the mixing ratios of CH_3Cl at time zero and time t and c_{iO} and c_{iT} are the respective concentrations of the internal standard PFH.

3 Results

Three ~~he first~~ experiments of CH_3Cl degradation with OH w~~ere~~as performed between ~~on the~~ 25/02/2014 and ~~repeated under similar conditions on~~ the 03/02/2015. Under the experimental conditions (see methods section and Supplementary) more than 70% of the CH_3Cl was degraded within 6~~7~~ to 10 h. The results from these ~~two~~ experiments are shown in Figure 2.

Both the trend of changes in δ^2H values of CH_3Cl as well as the remaining fraction of CH_3Cl observed in the three~~wo~~ independent experiments are in good agreement (Figure 2a). The calculated ε values for experiments 1 to ~~and~~3 ~~2~~ are -264 ± 78 ~~mUr‰, and~~ -21920 ± 6 ~~mUr‰~~ and ~~,~~ -308 ± 8 ‰ respectively (Figure 2b), with a correlation coefficient R^2 of the slope of the regression line of 0.99 for all three~~both~~ experiments.

Figure 2: Reaction of CH_3Cl and OH. Three~~wo~~ independent experiments (triangles, ~~and~~ dots and squares) were carried out using an initial mixing ratio of 5 to~~~~ 10 ppmv CH_3Cl. More than 70% of the CH_3Cl was degraded within 68 to 10 h. (a) Measured δ^2H values (filled circles, ~~and~~ triangles and squares) of CH_3Cl versus residual fraction (open circles ~~and,~~ triangles and squares) of CH_3Cl (calculated from changes of CH_3Cl and PFH). Error bars of δ^2H value of CH_3Cl 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 δ^2H values of CH_3Cl and the remaining fraction. Dashed lines represent 95% confidence intervals of the linear regressions (bold lines).

2a)

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2b)

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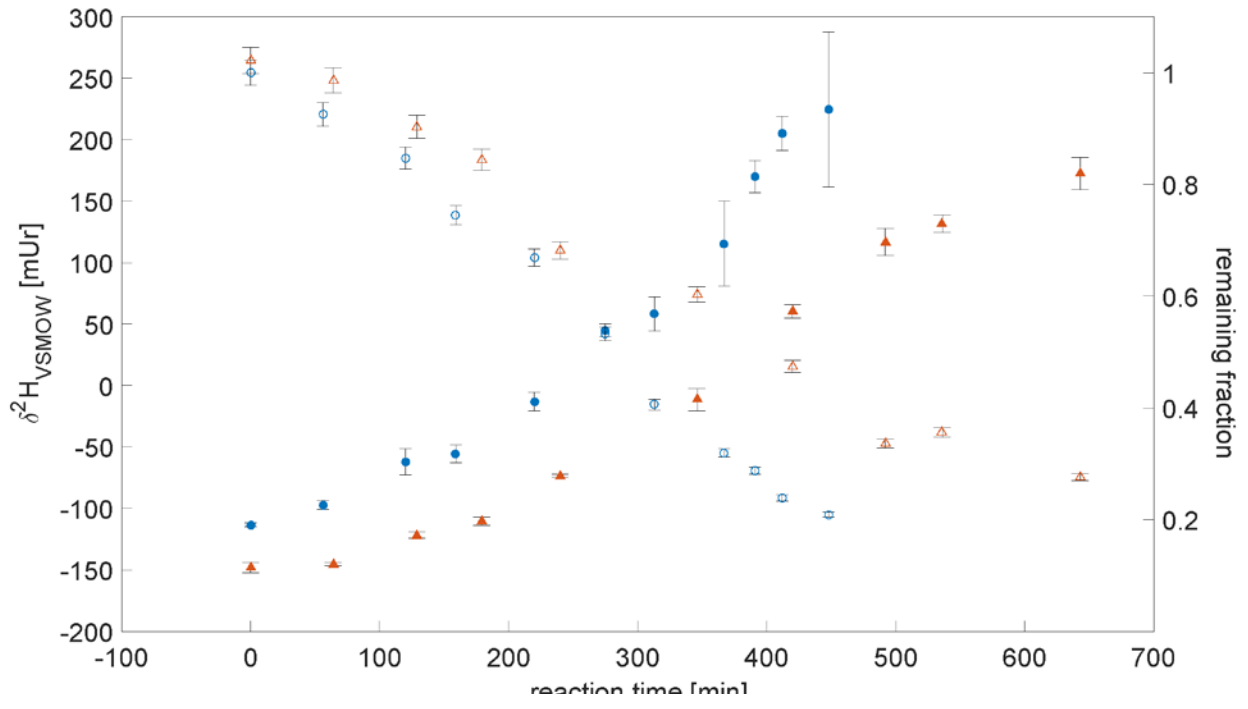
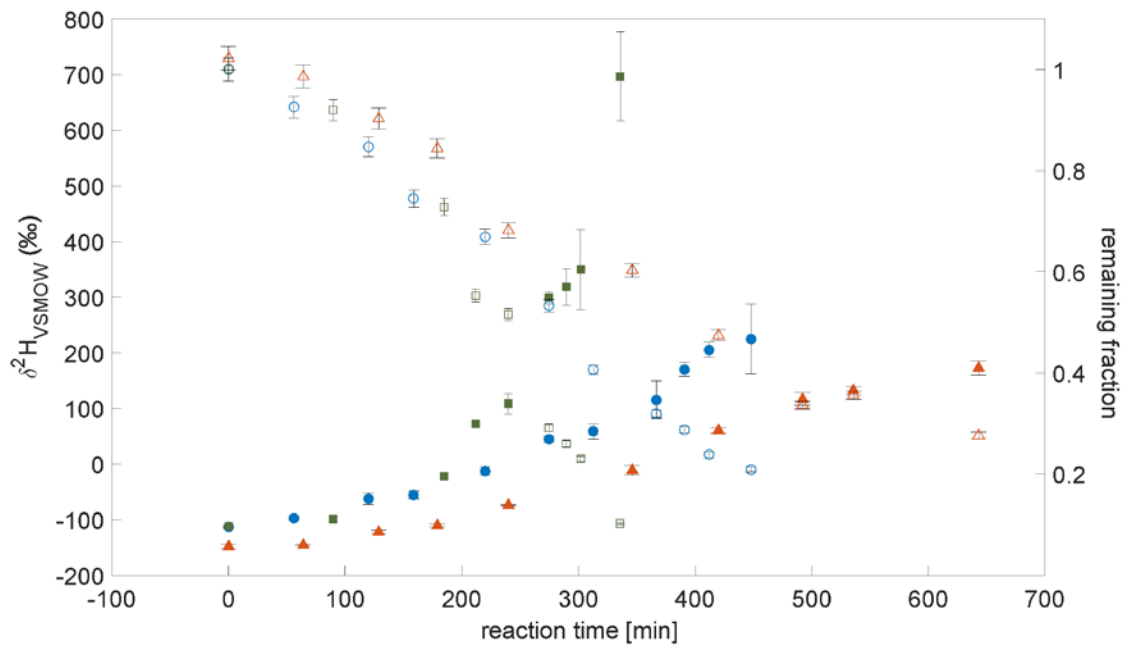
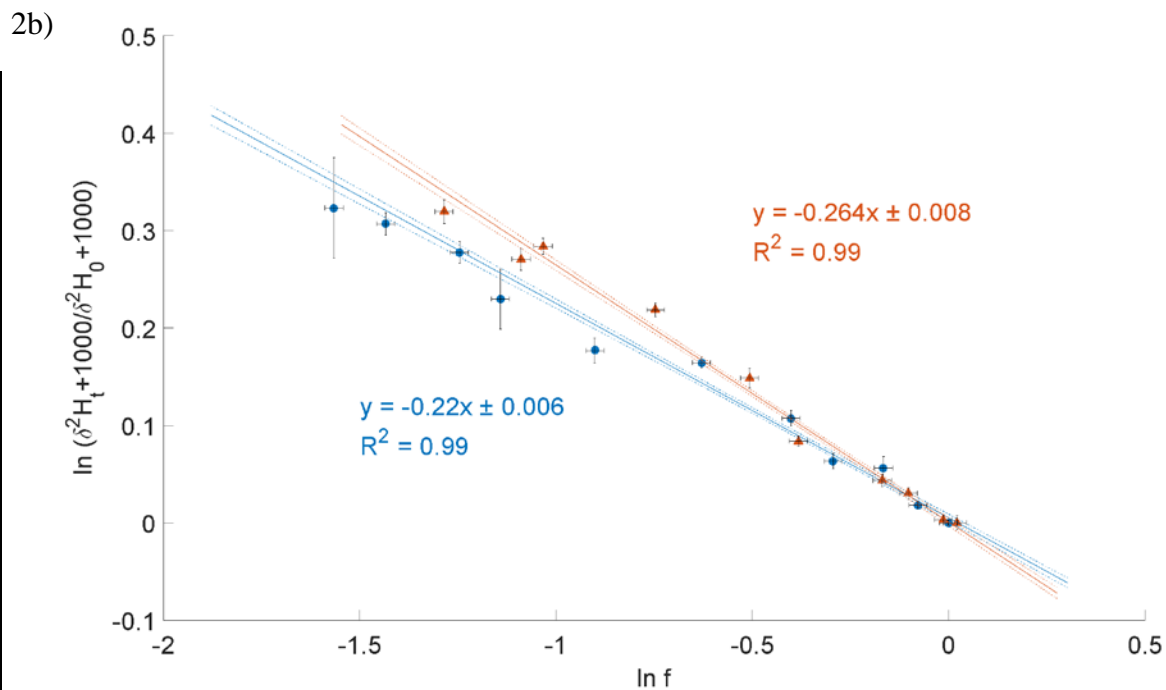
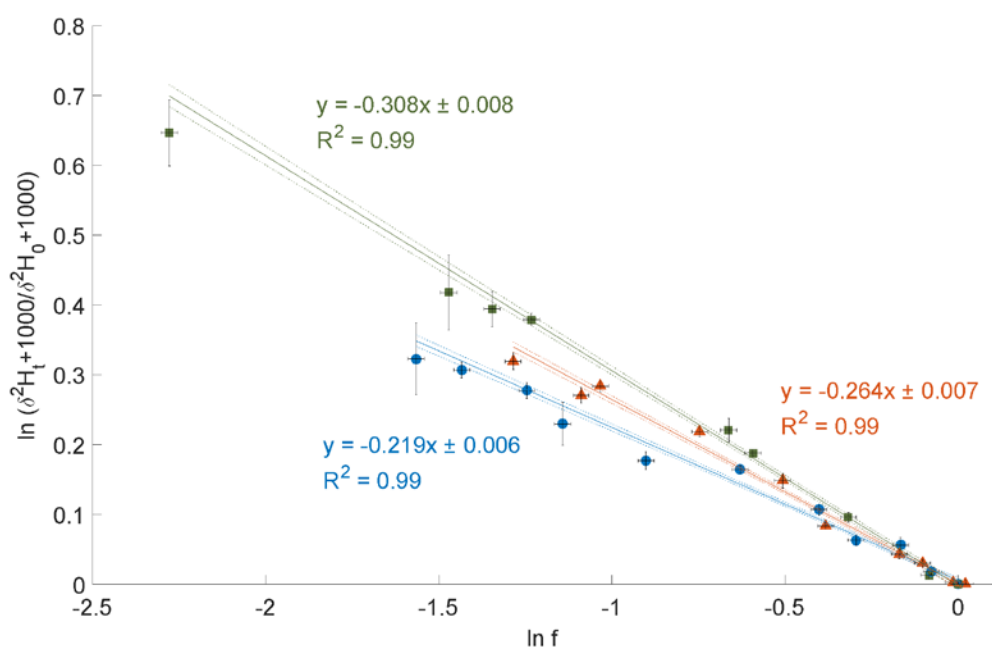

The CH₃Cl degradation with Cl experiment was conducted on the 18/02/2014. Here, over 90% of CH₃Cl was degraded during reaction with Cl radicals within 7 to 8 hours (Figure 3a). The calculated ε of experiment 3 is -280 ± 11 ~~mUr~~‰ (Figure 3b) with a correlation coefficient of the slope of the regression line of 0.99. Due to limited analytical resources it was not possible to repeat this experiment.

309

310   **Figure 3:** Reaction of CH_3Cl and Cl. Initial mixing ratio of CH_3Cl was ~10 ppmv. More than

311   90% of the CH_3Cl was degraded within 7 to 8 h. (a) Measured δ^2H values (filled circles) of

312   CH_3Cl versus residual fraction (open diamonds) CH_3Cl. Error bars of δ^2H values of CH_3Cl

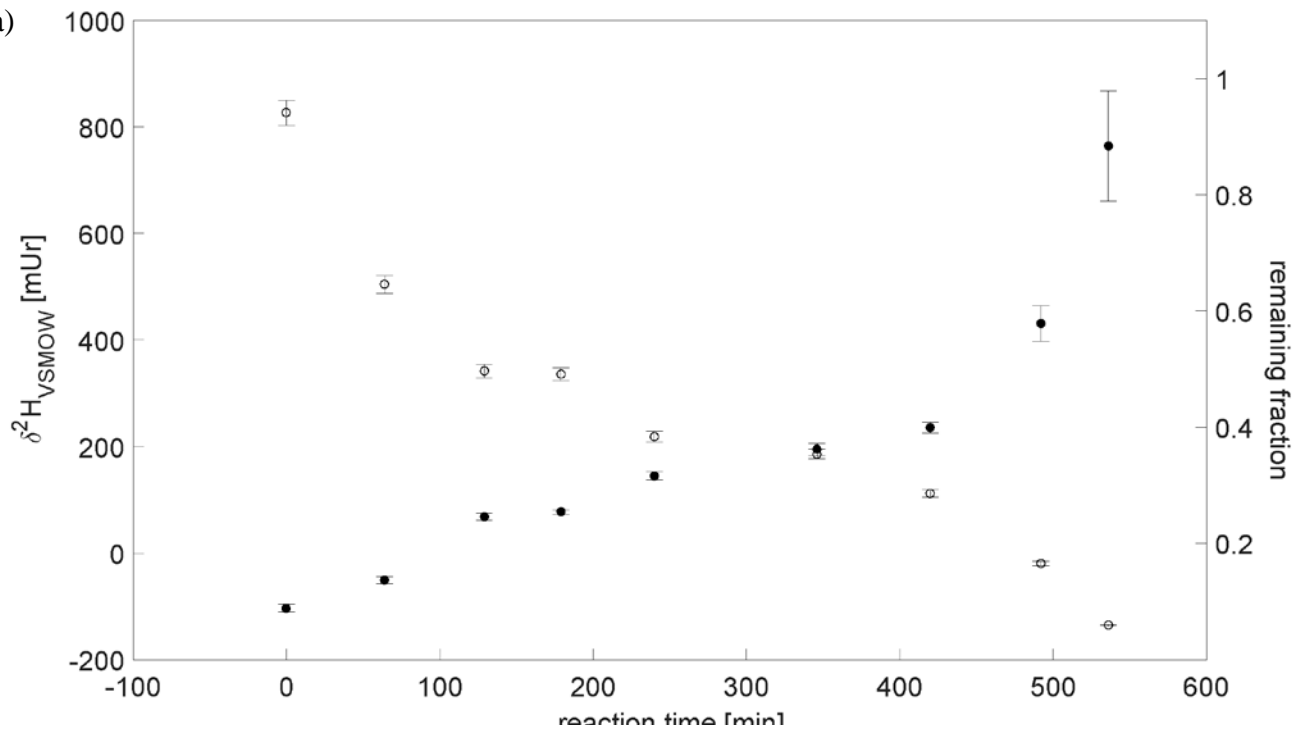
313   indicate the standard deviation (SD) of the mean of three replicate measurements. Some error

314   bars lie within the symbol. (b) Rayleigh plot (equation 2). Data are expressed as the

315   mean $\pm$ standard error of the mean, $n = 3$. Error bars were calculated by error propagation

316   including uncertainties in δ^2H values of CH_3Cl. Dashed lines represent 95% confidence

317   intervals of the linear regressions (bold line).

3a)

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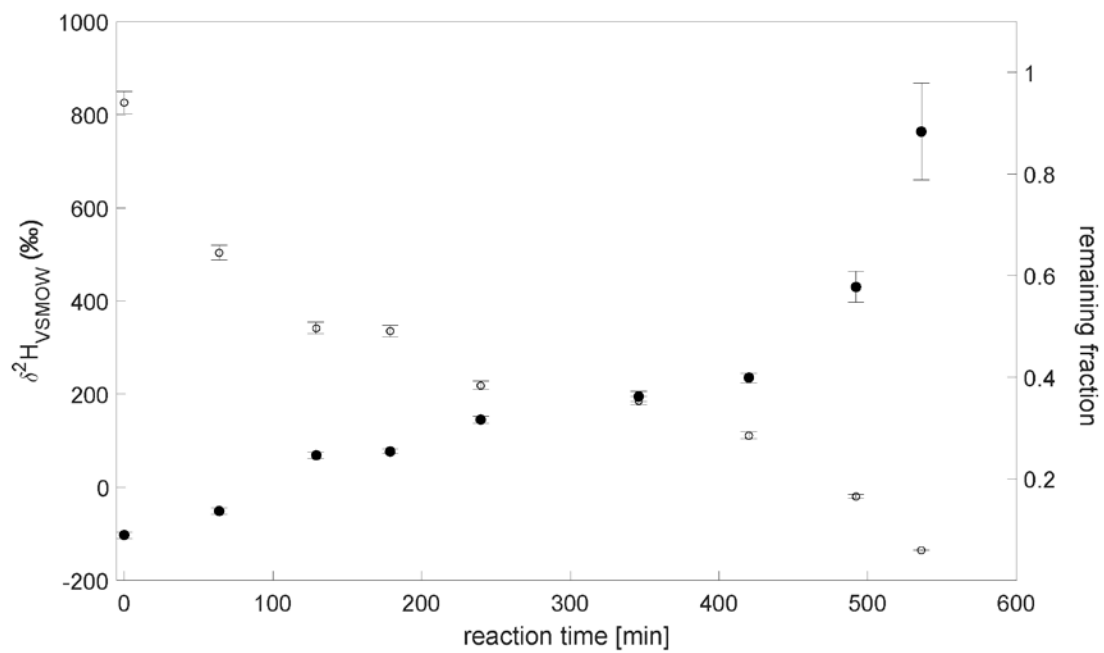
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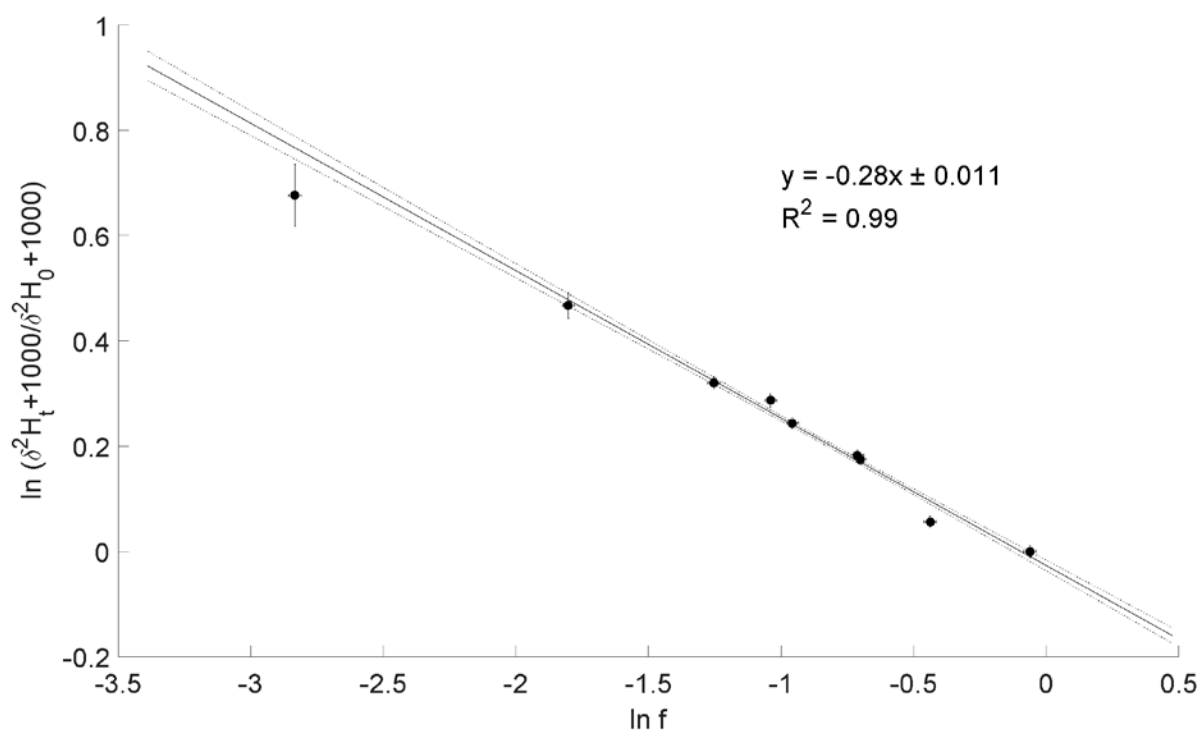
3b

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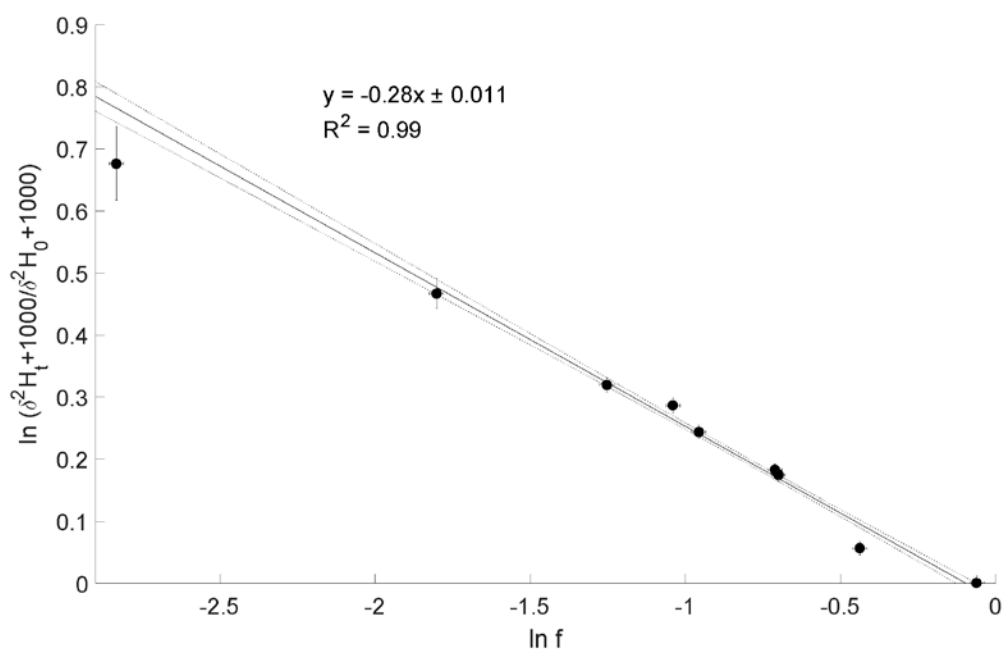
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325 The experiment to determine the isotope enrichment constant of the degradation of CH_4 by

326 hydroxyl radicals was conducted on the 02/02/2015. Over 80% of CH_4 was degraded during

327 reaction with OH radicals within 7 hours (Figure 4a). The calculated ε of experiment 4 is -

328   205 ± 6 ~~mUr~~‰ (Figure 4b) with a correlation coefficient of the slope of the regression line of

329   0.99.

330

331

332   **Figure 4:** Reaction of CH_4 and OH. Initial mixing ratio of CH_4 was ~6 ppmv. More than 80%

333   of the CH_4 was degraded within 7 h. (a) Measured δ^2H values of CH_4 versus residual fraction

334   of CH_4. Error bars of δ^2H values of CH_4 indicate the standard deviation (SD) of the mean of

335   three replicate measurements. Some error bars lie within the symbol. (b) Rayleigh plot

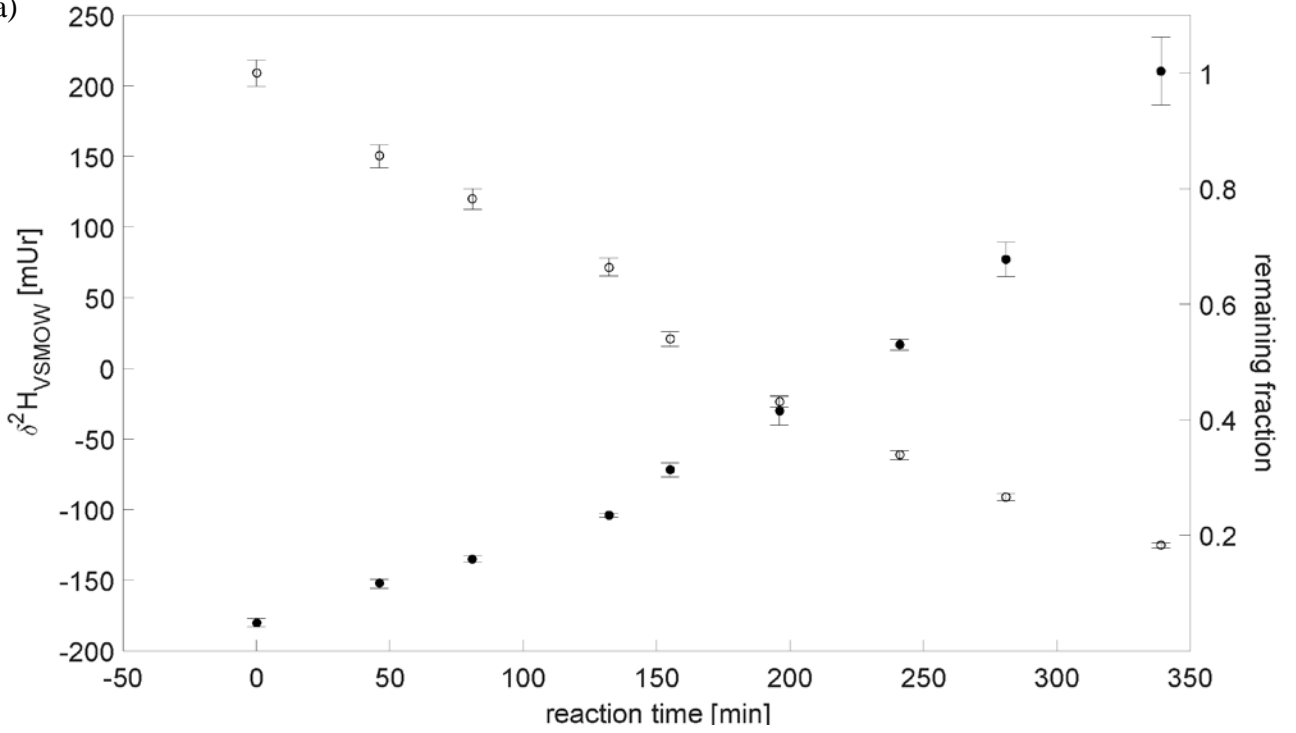
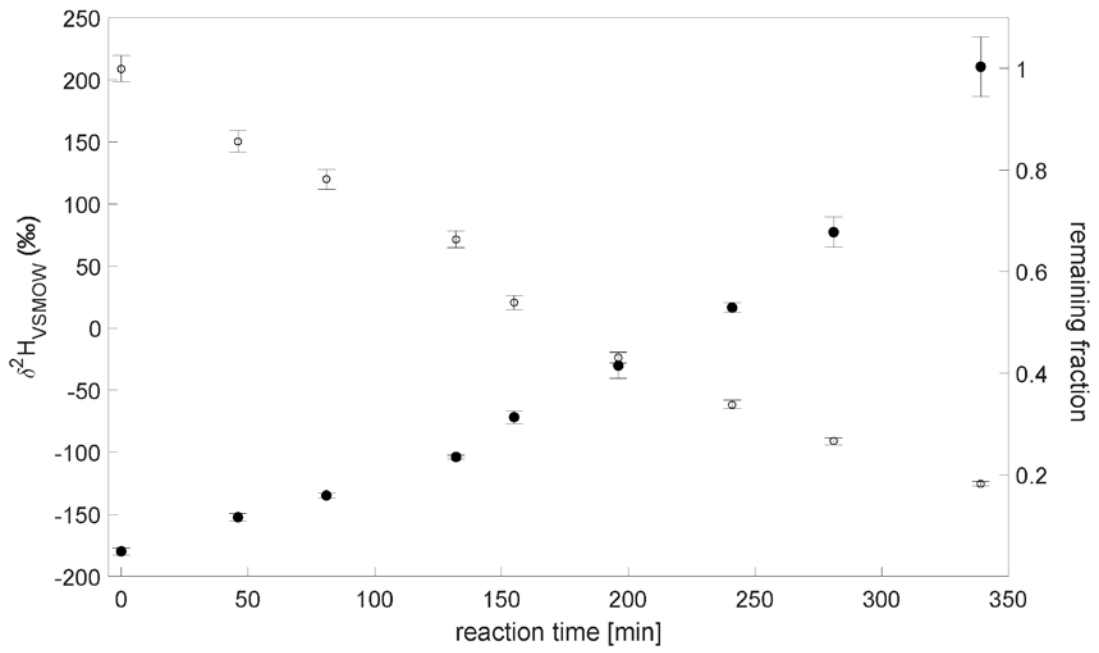
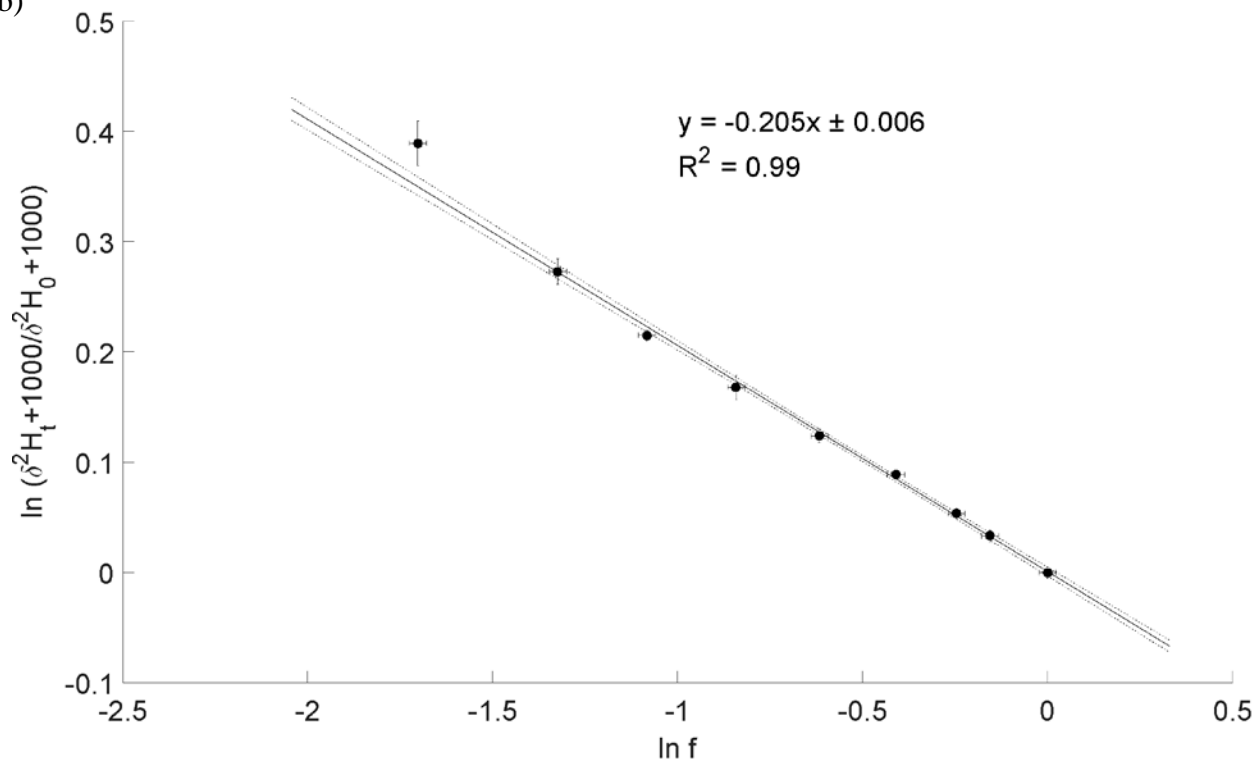
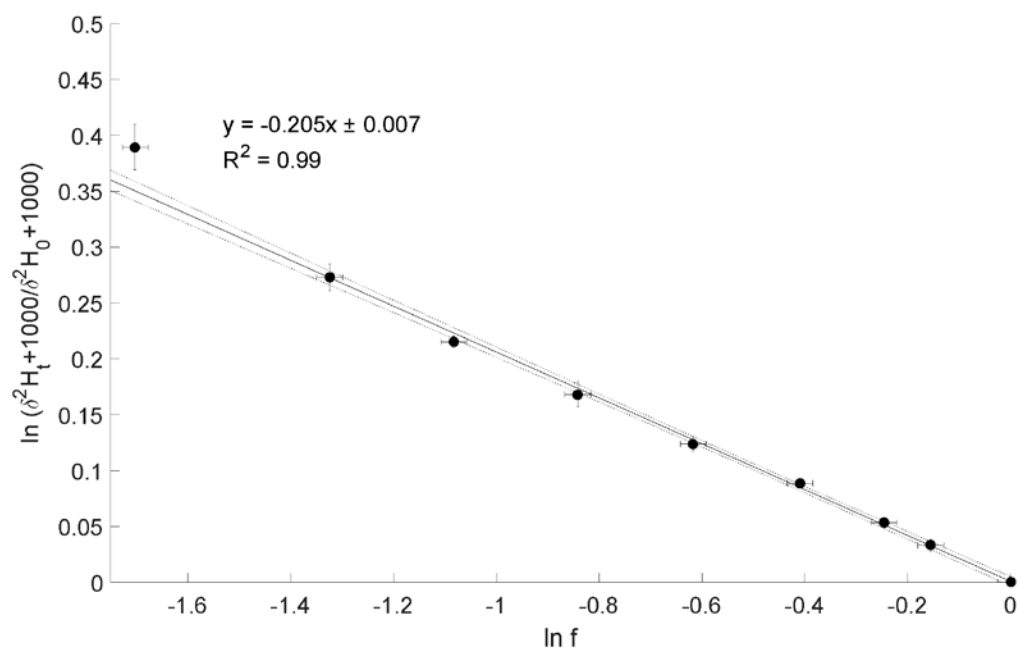
336   (equation 2). Error bars were calculated by error propagation including uncertainties in δ^2H

337   values of CH_4 and the remaining fraction. Dashed lines represent 95% confidence intervals of

338   the linear regressions (bold line).

339

4a)

4b)

4 Discussion

Chloromethane reacts with both hydroxyl and chlorine radicals in the atmosphere. The first degradation step of CH_3Cl in both reactions is the abstraction of a hydrogen atom to yield CH_2Cl and H_2O 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

350 so-called primary isotope effect (Elsner et al., 2005). Particularly for hydrogen these primary
351 kinetic isotope effects are in general large as they involve a large change in relative mass of
352 the atoms being abstracted. In the following we would like to discuss and compare our results
353 with (i) previous work conducted by (Sellevåg et al., 2006), (ii) with OH degradation
354 experiments of CH_4 and (iii) with the very recent report of biochemical degradation of CH_3Cl
355 in soils and plants (Jaeger et al., 2018b; Jaeger et al., 2018a).

356 Although our experimental results show relatively large hydrogen isotope fractionations with
357 ε values of -2~~64~~42 ± 45 (mean result from ~~three~~two independent experiments ± SD) and -280
358 ± 11 ‰ ~~mUr,~~(mean result from three replicate analytical measurements of the same sample ±
359 SD) ~~-~~for reaction of CH_3Cl with OH and Cl radicals, respectively, ~~-~~they are smaller than the
360 isotope fractionations previously measured and theoretically calculated by (Sellevåg et al.,
361 2006) (Table 1). These researchers employed smog chamber experiments at 298 K and used
362 FTIR measurements to determine the stable hydrogen isotope fractionation of CH_3Cl and
363 reported ε values of -410 and -420 ~~mUr~~‰ for the reaction of CH_3Cl with OH and Cl radicals,
364 respectively. They also performed theoretical calculations of ε for the reactions of CH_2DCl
365 with OH and Cl radicals and reported ε values in the range of -330 to -430 and -540 to -590
366 ~~mUr~~‰, respectively (Table 1). Whilst we do not know the reasons for the ~~large~~ discrepancies
367 in the experimental ε values observed here and those reported by Sellevåg et al. (2006), we
368 suggest that they may be due to ~~differences in the experimental smog chamber set up or the~~
369 different measurement techniques employed in each of the studies. For further discussion
370 regarding differences of the experimental and analytical design and protocols of the two
371 studies we ~~-~~would refer the reader to the Supplementary. However, we also conducted similar
372 smog chamber experiments for the degradation of CH_4 with hydroxyl radicals (see methods
373 section and Figure 4) and calculated an ε value of -205 ± 6 ~~mUr~~‰ for the reaction of CH_4
374 with OH radicals at a temperature of 293 ± 1 K. In Table 1 we compare our results with those
375 from a number of previous studies (Saueressig et al., 2001; Sellevåg et al., 2006; DeMore,
376 1993; Gierczak et al., 1997; Xiao et al., 1993), which were conducted at temperatures ranging
377 from 277 to 298 K (Table 1). The ε values for the reaction of CH_4 with OH radicals from all
378 studies ranged from -145 to -294 ~~mUr~~‰ with a mean value of -229 ± 44 ~~mUr~~‰ with the
379 most negative ε value of -294 ± 18 ~~mUr~~‰ reported by Sell~~ae~~va~~å~~g and coworkers (2006). The
380 ε value found in this study (-205 ± 6 ~~mUr~~‰) was in good agreement with previous
381 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_3Cl 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_3Cl the methyl group is transferred to a corrinoid cofactor by the protein CmuA. In this case the carbon-chlorine bond of CH_3Cl 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 CH_3Cl 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 CH_3Cl by OH and Cl radicals measured in either this study or reported by Sellevåg et al. (2006).

5 Conclusions and future perspectives

We have performed experiments to measure the hydrogen isotope fractionation of the remaining unreacted CH_3Cl following its degradation by hydroxyl and chlorine radicals in a 3.5 m^3 Teflon smog-chamber at 293 ± 1K. δ^2H values of CH_3Cl were measured using GC-IRMS. The calculated isotope fractionations of CH_3Cl 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 CH_4 using the same smog-chamber facilities yielding an isotope enrichment constant for the reaction of CH_4 with hydroxyl radicals of -205 ± 6 ~~mUr~~‰ which is in ~~excellent~~good agreement with previous reported results. Although stable hydrogen isotope measurements of CH_3Cl sources are still scarce, some recent studies have reported first data on δ^2H values of CH_3Cl 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 δ^2H values of environmental CH_3Cl sources and their estimated fluxes in Table 2. Furthermore, the strengths of known CH_3Cl sinks and their associated isotope enrichment constants are presented in Table 3. Eventually Figure 5 displays the global CH_3Cl 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 CH_3Cl cycle (modified after Keppler et al., 2005) with known (experimentally determined) corresponding δ^2H values and isotope enrichment constants, respectively. Red straight and dashed lines of arrows indicate sources and sinks of CH_3Cl, respectively. Size/thickness of arrows indicate strength of fluxes in the environment. Questions marks indicate where currently no data exist. All values are given in ~~mUr~~‰.

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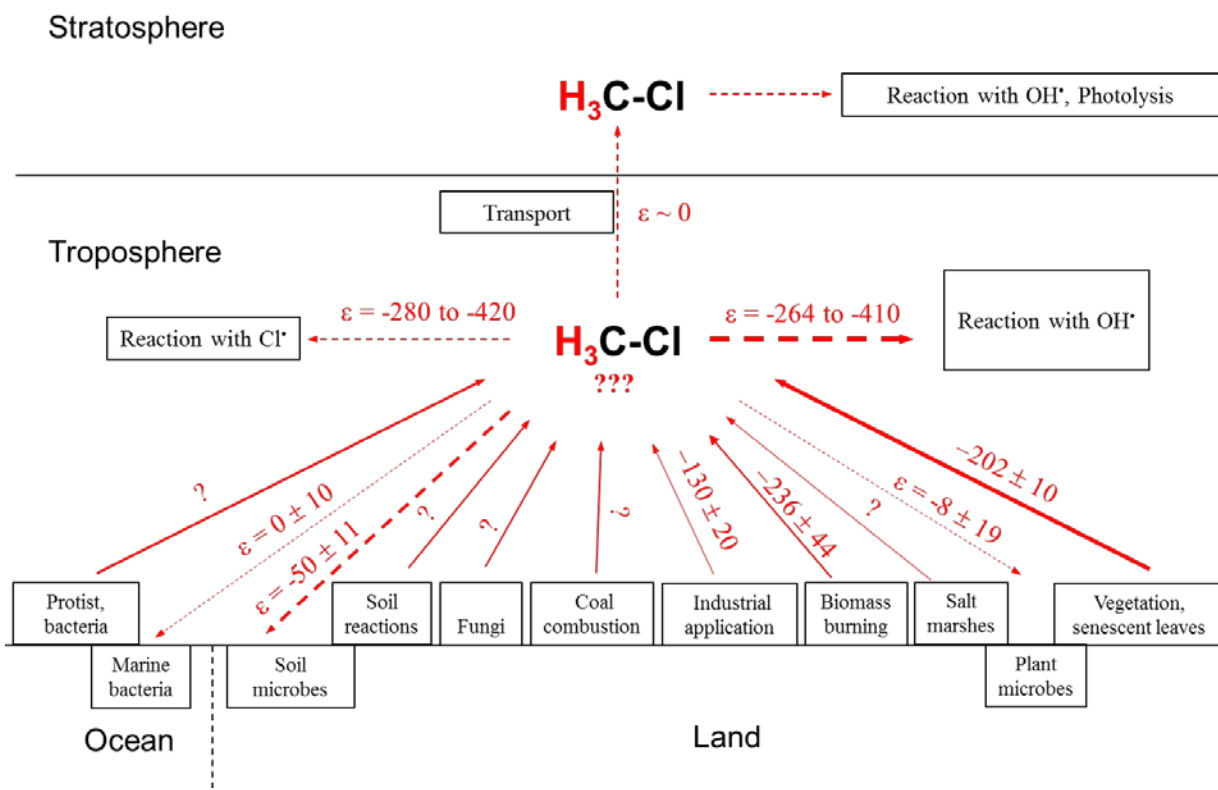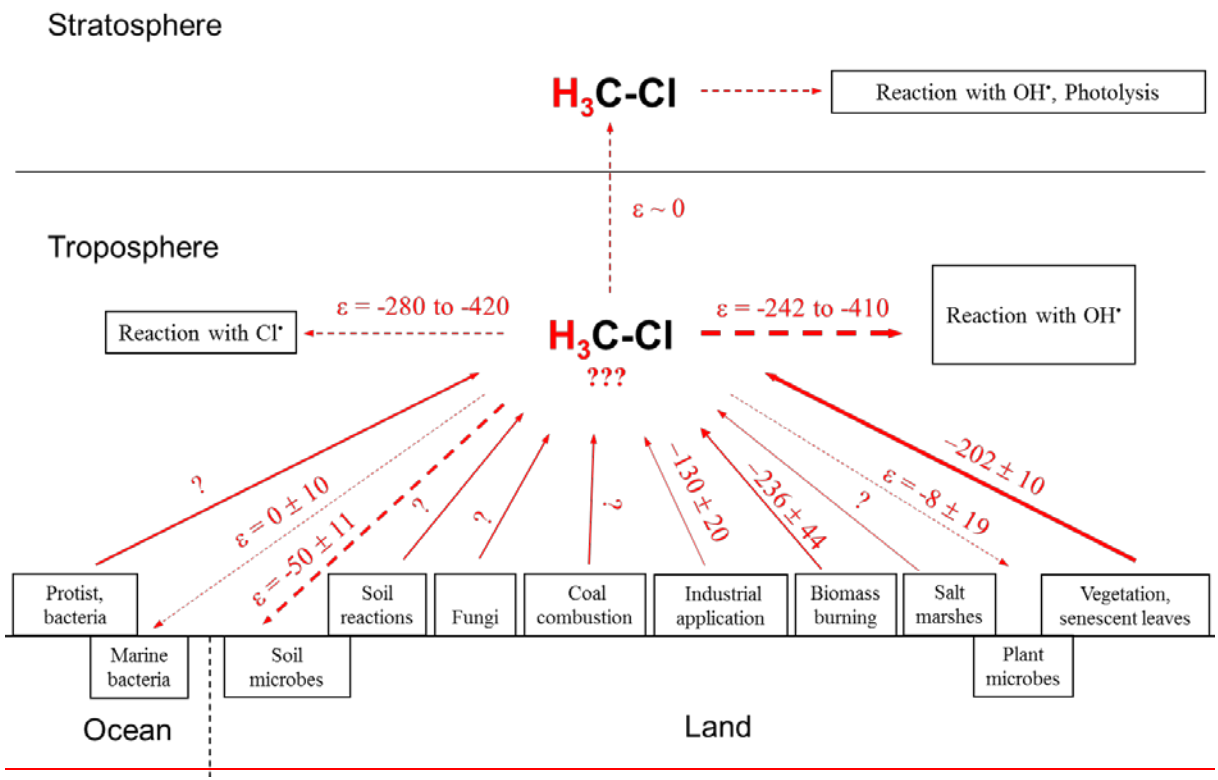
Our results suggest that stable hydrogen isotope measurements of both sources and sinks of CH₃Cl and particularly the observed large kinetic isotope effect of the atmospheric CH₃Cl sinks might strongly assist with the refinement of current models of the global atmospheric CH₃Cl budget. In contrast to the large hydrogen fractionation of CH₃Cl by chemical

439   degradation of OH and Cl radicals, the isotope fractionation of CH_3Cl biodegradation are in

440   the range of an order of magnitude lower. This therefore holds the opportunity to improve our

441   understanding of the global CH_3Cl budget once the δ^2H value of atmospheric CH_3Cl has been

442   measured. The stable hydrogen isotopic composition of tropospheric CH_3Cl depends on the

443   isotopic source signatures and the kinetic isotope effects of the sinks, primarily the reaction

444   with OH and consumption by soils and potentially plants.

445   Several attempts at modelling the global CH_3Cl budget using stable carbon isotope ratios

446   have already been made (Harper et al., 2001; Harper et al., 2003; Thompson et al., 2002;

447   Keppler et al., 2005; Saito and Yokouchi, 2008) but there are still major uncertainties

448   regarding source and sink strengths as well as the respective stable isotope signatures.

449   Therefore, we now suggest combining our knowledge of stable carbon and hydrogen isotopes

450   of CH_3Cl in the environment. Such a two dimensional (2D) stable isotope approach of

451   hydrogen and carbon can be used to better understand the processes of CH_3Cl biodegradation

452   and formation. Furthermore, when this approach is combined with CH_3Cl flux estimates it

453   could help to better constrain the strength of CH_3Cl sinks and sources within the global

454   CH_3Cl budget (Nadalig et al., 2014; Jaeger et al. 2018b)

455   We would highlight that currently no data is available for the δ^2H value of atmospheric

456   CH_3Cl. Although it will be a massive analytical challenge to obtain this value, we strongly

457   consider that it would likely lead to a better refined isotopic mass balance for atmospheric

458   CH_3Cl and thus to our better understanding of the global CH_3Cl budget.

459

460   **Acknowledgements**

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465   Ocean Processes in the Anthropocene (grants 03F0611E and 03F0662E). We thank John

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468

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628 Table 1: Reported hydrogen isotope enrichment constants for the reaction of CH_3Cl with OH

629 radicals and with Cl atoms and the reaction of CH_4 with OH radicals.

Reaction	ε / ~~mUr~~‰	Method and remarks	Reference
CH_3Cl + OH	-2~~2~~644 ± ~~mean~~ 45	experimental: 3.5 m^3 smog-chamber at 293 ± 1 K; IRMS	Exp. 1 ~~&~~to 3~~2~~, this study
CH_3Cl + OH	-410 ± 50	experimental: smog-chamber, long-path FTIR spectroscopy relative to CH_3Cl at 298 ± 2 K	Sellevåg et al. 2006
CH_3Cl + OH	-330 to -430	theoretical calculations	Sell~~ae~~våg et al. 2006
CH_3Cl + Cl	-280 ± 11	experimental: 3.5 m^3 smog-chamber at 293 ± 1 K; IRMS	Exp. 4~~3~~, this study
CH_3Cl + Cl	-420 ± 40	experimental: smog-chamber, long-path FTIR spectroscopy relative to CH_3Cl at 298 ± 2 K	Sell~~ae~~våg et al. 2006
CH_3Cl + Cl	-540 to -590	theoretical calculations	Sell~~ae~~våg et al. 2006
CH_4 + OH	-205 ± 6	experimental: 3.5 m^3 smog-chamber at 293 ± 1 K; IRMS	Exp. 5~~4~~, this study
CH_4 + OH	-227 ± 11	experimental: at 296 K, IRMS and tunable diode laser absorption spectroscopy	Saueressig et al. 2001
CH_4 + OH	-231 ± 45	experimental: at 277 K	Gierczak et al., 1997
CH_4 + OH	-251 ± 10	ab initio at 298 K	Xiao et al., 1993
CH_4 + OH	-145 ± 30	experimental: at 298 K	DeMore et al., 1993
CH_4 + OH	-294 ± 18	experimental: smog-chamber, long-path FTIR spectroscopy relative to CH_3Cl at 298 ± 2 K	Sell~~ae~~våg et al. 2006
CH_4 + OH	-60 to -270	theoretical at 298 K	Sell~~ae~~våg et al. 2006

Table 2. Known sources and strengths of tropospheric CH$_3$Cl and corresponding δ^2H values.

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

[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_3Cl and the mean isotope enrichment constant ε reported for each.

Sinks	Sink (best estimate)[a] (Gg yr^{-1})	Sink (full range)[a] (Gg yr^{-1})	Isotope enrichment constant ε / ~~mUr‰~~	Uncertainty ε ± ~~mUr‰~~
Reaction with OH in troposphere	2832	2470 to 3420	-2~~644~~2[b] -410[c]	45~~7~~[b] 50[c]
Loss to stratosphere	146	?	0[~~de~~][d]	?
Reaction with Cl in marine boundary layer	370[d]	180 to 550[d]	-280[b] -420[c]	11[b] 40[c]
Microbial degradation in soil	1058	664 to 1482	-50[e]	13[e]
Loss in ocean	370	296 to 445	0[f]	10[f]
Microbial degradation in plants[g]	?	?	-8[g]	19[g]
Total sinks	4406 (4776)			

[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 t~~wo~~ three 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)

[~~f~~][g] Jaeger et al. (2018b)

? denotes that no value has been provided