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 5 to 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.

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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 CH4 + 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 CH3Cl and CH4. 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 CH4 +OH reaction being at less negative end among previous measurements (Table 1) and this possible trend is also the case for CH3Cl +OH/Cl reactions.

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