Point by point reply to J. Kaiser (Co-Editor comment are in italics): We would like to thank the Co-Editor for the very constructive evaluation of our manuscript and for the helpful comments to improve the manuscript. In addition to the requested changes some minor changes have been applied and the figures 4s and 5s in the supplement have been reformatted.

Co-Editor Decision: Publish subject to minor revisions (review by editor) *(29 Dec 2018) by Jan Kaiser*
Comments to the Author (pdf): acp-2018-855-comments-to-author.pdf
Comments to the Author:
Gola et al. (2005) and Sellevåg et al. (2006) have neglected the influence of the reaction of CH3Cl with O(1D) in their experiments. It is also missing from their FACSIMILE-based kinetic reaction modelling (supplement to the Gola et al. paper). This reaction is likely to have biased their results for the isotope effect of the CH3Cl + OH sink. In the present set of experiments, the influence of the O(1D) reaction is likely to be small (assuming the difference between the measured CH4 + OH isotopic fractionation and the literature value of Saueressig et al. 2001 is due to the presence of O(1D)). See also comments below. You should make a stronger statement (around 7/24; "unresolved" doesn't really capture the potential experimental error of the Gola et al. experiments).

Authors response: Referring to the Co-Editors comment on possible spectral interferenes we added the following sentence on page 7/39 "However it appears that the authors have not tested the accuracy of their isotope ratio measurements as a function of the isotopologue mole fraction in the presence of other species with overlapping spectra (HCl, H_2O, O_3, etc.), e.g. by using a dilution series."

It would be interesting (and straightforward) to measure the isotope effect of the reaction of O(1D) with CH3Cl. You do not appear to have done a corresponding control experiment (O3 photolysis without water vapour). Please mention the absence of this control experiment in your discussion.
Use decimal points, not commas, throughout the manuscript (incl. figures and tables).

Authors response: We indeed did not carry out a control experiment to measure the isotope effect of the reaction with O(1D), but our control experiment in the absence of water vapour but with 2000 $\mu mol\ mol^{-1}$ H_2 comes close to such a control experiment. We clarified this on page 5/21:

" Potential side reactions with $O(^1D)$ were not explicitly investigated in our study but because of the reduced OH yield, this experiment allows to constrain potential losses of CH_3Cl due to reaction with $(O(^1D)$."

You sometime refer to control and sometimes to "blank" experiments. Please use the term control experiment throughout the paper.

Authors response: Change applied.

1/22: For clarity, please write "13C/12C carbon isotope effect (ε = k(13C)/k(12C) – 1)" (or "carbon isotope fractionation").

Authors response: Change applied.

1/23 & 1/24: Please write either "we found an ε value of (x±y) ‰" or "we found ε = (x±y) ‰."

Authors response: Change applied.

1/27: Replace "fractionation factors" with "values for the carbon isotope effect" or "carbon isotope fractionations".

Authors response: Change applied.
2/18: Change to "KIEs of the main tropospheric sink reactions (CH3Cl + OH, CH3Cl + Cl)".

Authors response: Change applied.
3/37: Brackets missign around (-26.8±0.2) ‰.

Authors response: Change applied.
4/1: Measurements against the machine working as do not follow the "identical treatment principle", so the value of –37.2 ‰ should be provided for anecdotal purposes only. This is NOT an offset between DI and GC-IRMS method. The offline method represents the calibration of the CH3Cl standard, which should be used as anchor point to report all subsequent measurements of CH3Cl by GC-IRMS.

Authors response: To clarify that this was a calibration, this section has been changed to: "In order to assure compliance with VPDB scale, a single component standard of CH_3Cl (100 µmol mol^{-1} in nitrogen, Linde Germany) was calibrated against a certified CO_2 reference standard (Air Liquide, Germany, -26.8± 0.2 ‰ and a solid standard (NIST NBS 18, RM 8543) after offline combustion and analysis via a dual inlet (DI). The results from the DI (n=6) were (-37.2 ±0.1) ‰ for CH_3Cl. The respective $\delta^{13}C$ values from the GC-GC/IRMS, measured against the machine working gas (Air Liquide, Germany, ((-26.8± 0.2) ‰) were (-36.1±0.2) ‰ resulting in an offset (DI – 2D-GC-IRMS) of -1.1 ‰ for CH_3Cl."

Was the same CH3Cl/N2 reference standard used in Hamburg and Heidelberg?

Authors response: No the Heidelberg group used a different standard. There may be indeed be a difference in absolute scales as stated on page 4/16.

4/15 & elsewhere: Please change to "the kinetic isotope effect (KIE, symbol ε)". To avoid ambiguity, whenever you refer to the value of the KIE in the manuscript, please use the quantity symbol ε rather than the abbreviation KIE, including in the supplement.

Authors response: Change applied.

4/15 & 19 (3 times): Delete the square brackets around ‰.

Authors response: Change applied.

4/17: Replace "1000" with "1" (two occasions).

Authors response: Change applied.

4/18: Replace "enrichment factor" with "kinetic isotope fractionation" or "kinetic isotope effect".

Authors response: Change applied.

Change to "residual CH3Cl fraction".

Authors response: Change applied.

5/4: Negative sign missing before "0.00117". +6

Authors response: Change applied.

5/12: Delete "molecule–1". There is no such unit.

Authors response: Change applied.

5/12: Replace "" multiplication signs with "×".*

Authors response: Change applied.
5/16: Please change to "the partial lifetime of CH3Cl with respect to OH" (the OH lifetime is much shorter).

Authors response: Change applied.

5/20: "stable carbon isotope delta values"

Authors response: Change applied.

5/20 to end of page: Replace "KIEs" with "isotope effects" or "isotopic fractionations" or "ε = …", as appropriate.

Authors response: Change applied.

5/30: Insert "(in terms of absolute magnitude)" after "upper end".

Authors response: Change applied.

5/37: A 3 % contribution from O(1D)-related loss would have only changed the epsilon value by about 0.3 ‰. This cannot explain the difference to the result reported by Saueressig et al.
In fact, a contribution of 9 % (= (4.7–3.9) / (13–3.9)) from O(1D)-related loss is required to explain the higher (in terms of magnitude) ε value found here.
7/1: Based on the value of 9 %, the potential contribution of O(1D)-related loss to the overall CH3Cl loss in your experiment is 2.3 % - still small, but not <1 % as you claim. It is less than for CH4 because the relative reaction rate coefficients favour the reaction with OH over O(1D) in case of CH3Cl compared with CH4.

Authors response: We picked this up and clarified the potential contributions from O(1D)-related losses. On page 5/6 the following sentence was added: “Saueressig et al. (2001) reported an ε value of -3.9 ‰ for the reaction of CH_4 with OH. With respect to this value, a contribution of 9% from the reaction with $O(^1D)$ is required to explain the difference in terms of $O(^1D)$ loss.” and on page we added: ”Assuming a contribution of 9% from the reaction with O^1D in the CH_4 experiment, the reaction with O^1D should contribute less than 2.3 % to the observed CH_3Cl loss”

8/15: Komatsu is misspelled.

Authors response: Change applied.

8/26: Please give the "other" NH and SH source strengths also in Gg a–1, for consistency and ease of comparison.

Authors response: Change applied.

9/19: Without an estimate of the degree of CH3Cl break-down (e.g. soil mole fraction / atmospheric mole fraction), nothing can be said about the magnitude of the isotope effect based on the soil δ(13C) value alone. E.g. if only 5 % got broken down, the 2.4 ‰ difference between soil and atmospheric 13C/12C ratio would correspond to an kinetic isotope effect of –48.5 ‰.

Authors response: We agree with this and have deleted the respective statement on page 9/38

10/9: Your statement "In this case, increasing the soil sink could even lead to a depletion in the tropospheric δ13C once the apparent KIE of the soil sink becomes smaller than the KIE of the OH sink." does not make sense because the tropospheric δ13C is "fixed" (by observations). Presumably, you want to say that "increasing the soil sink" leads to a decrease in the overall sink isotope effect, which must be balanced by an overall increase (i.e. becoming less negative) in the average source δ13C value.

Authors response: We changed the statement to: **"**The isolated effect of the soil sink would result in a maximum enrichment of 3.8‰ in the tropospheric δ^{13}C that reduces to 2.1‰ when accounting for the concurrent reduction in the OH sink. In this case, increasing the soil sink could even lead to a decrease in the overall sink isotope effect once the apparent isotope effect of the soil sink becomes smaller than the isotope effect of the OH sink."

10/23 & 10/34: The atmospheric measurements impose a strong constraint on the model and should be discussed in their own section (new section number 3.2), immediately following the model description (section 3.1) and before section 3.1.1.
Sections 3.1.1 and 3.1.2 should be renumbered 3.3 and 3.4.
Section 3.2 and 3.3 should be renumbered 3.5 and 3.6.

Authors response: The sections have not been renumbered so far and we would like the numbering as it is. The sections 3.11. and 3.1.2 are part of the model description and the discussion in section 3.2 refers to this model description. To our opinion the discussion of the atmospheric measurements should be done in the context with the model results However, we are open to further discussions.

Supplement
Please provide consecutive line numbers for the supplement.

Authors response: Change applied.

Some of the information in the supplement duplicates the methods section. Please remove anything from the supplement that is already included in the methods section.

Authors response: We removed duplicates as far as possible but with respect to the readability of the supplement, some repetitions were necessary.

Page 1

- *Teflon FEP (not Felon FEP)*

Authors response: Change applied.

- *Replace "ppb" with "nmol mol–1".*

Authors response: Change applied.

- *<1 nmol mol–1 O3 (see page 6)*

Authors response: Change applied.

- *<500 pmol mol–1 NOx (or <0.5 nmol mol–1, which helps avoid using another unit)*

Authors response: Change applied.

- *"for at least 4 µmol mol-1 8 h" does not make sense*

Authors response: “4 µmol mol-1” has been removed.

- *"typically cleaned for 6 to 8 h" (delete h after 6)*

Authors response: Change applied.

- *What was the make and model of the Teflon fan?*

Authors response: The Teflon fan was made in-house from PTFE

- *Teflon is written with uppercase initial T because it is a proper name.*

Authors response: Change applied.

- *O2 and NOx should be written with subscript "2" and "x". "x" in NOx should be written in italics.*

Authors response: Change applied.

- *Delete "ppm" in "1ppm".*

Authors response: Change applied.

- *Should this be "between and 1 and 10 µmol mol–1"?*
- *Delete "~" sign before 25 µmol mol–1 and replaced with an actual estimate of the uncertainty of this quantity.*

Authors response: Change applied.

- *helium is written with lower-case "h" (or use the chemical symbol "He")*

Authors response: Change applied.

- *Valco – capital V*

Authors response: Change applied.

Page 2

- *(also 3/23) Please state the actual actinic flux (in photons per area and time or energy per area and time) as well as the make and model of the solar simulator, in addition to "actinic flux comparable to the sun in mid-summer in Germany".*

Authors response: A figure and appropriate references have been added to the supplement.

- *Please state the temperature at which the experiments were carried out.*

Authors response: The information has been added on page 1/21.

- *Delete ")" after 5 %.*

Authors response: Change applied.

- *Replace "*" multiplication signs with "×".*

Authors response: Change applied.

- *25000 mmol mol–1 should be 25000 µmol mol–1. However, even that corresponds to a temperature of 27 ºC. Is this correct?*

Authors response: This was a miscalculation, we apologize for. The true mixing ratio was 16000 µmol mol^{-1}.

- *Delete "molecule–1". There is no such unit.*

Authors response: Change applied.

- *Delete "molecules" after 2.9 × 109 and after 2.0 × 1010.*

Authors response: Change applied.

Page 3:

- *H2*

Authors response: Change applied.

- *Replace "µmole mole-1" with "µmol mol–1" (2 times).*

Authors response: Change applied.

Page 4

- *"an unknown source" (not: emissions)*

Authors response: Change applied.

- *"were randomly" varied? What do you mean by random? What underlying probability density function did you use? Gaussian? Uniform? Triangular? Beta? Please be more specific.*

Authors response: We used a Gaussian probability density function have specified this.

- *How many model runs did you carry out?*

Authors response: In total 100 seasons were modelled with i: no fractionation assigned to the sinks showing the imprint of the combined source signature on the tropospheric $\delta^{13}C(CH_3Cl)$, ii: an ε value of -11.2 ‰ for the tropospheric loss and an ε value a KIE of -59‰ for the tropospheric loss. We added this information to the supplement.

Page 6:

- *Replace ppb with nmol mol–1 and ppt with pmol mol–1.*

Authors response: Change applied.

Figure S2: Please add a figure legend to identify the three different colours/symbols (or label the curves as in Fig. S5 below). Use decimal points, not commas. The axis labels should be y(CH3Cl)/(µmol mol–1) and y(PFH)/(µmol mol–1), to designate that you have plotted mole fractions (the square bracket symbol means "concentration").

The right axis should be labelled "residual fraction ft" (see Eq. 3; you might want to add a cross-reference to this equation in the figure caption). Use the same scale for both mole fractions (the scaling by 0.5 doesn't seem to be correct anyway based on the information on p. 3/8

Authors response: The scaling was indeed not correct. Requested changes were applied.

The x-axis should be labelled with integer numbers (0, 2, 4, …) to avoid confusion with clock time. The axis label should be "time t/h" [this means time divided by hours].

Authors response: The x-axis has been labelled with integer numbers.

Figure S3: Again, a figure legend is needed and the axis labels should be amended as per the comments on Fig. S2 above. The equation in the caption should be written as y(CH3Cl)/(µmol mol–1) = 133.5 e–0.004t/h. Please provide another decimal for the coefficient in the exponent.

Authors response: The x-axis has been labelled with integer numbers.

Fig. S4: The slope is -0.004t/h. Requested changes were applied.

The equations should be written as

y(CO2 measured)/(µmol mol–1) = 469.5 e–0.00118t/h and

y(CH4 measured)/(µmol mol–1) = 3.52 e–0.00117t/h

to be dimensionally correct.

Authors response: Change applied.

Fig. S5: Again, axis labels should be "time t/h", "y(CH4)/(µmol mol–1)", "y(CO2)/(µmol mol–1)" and "y(O3)/(µmol mol–1).

Authors response: Change applied.