Gola et al. (2005) and Sellevåg et al. (2006) have neglected the influence of the reaction of CH_3Cl 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 CH_3Cl + 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 CH_4 + OH isotopic fractionation and the literature value of Saueressig et al. 2001 is due to the presence of $O(^1D)$). See also comments below. I suggest you make a stronger statement on this around 7/24; "unresolved" doesn't really capture the potential experimental error of the Gola et al. experiments.

It would be interesting (and straightforward) to measure the isotope effect of the reaction of $O(^1D)$ with CH_3Cl. You do not appear to have done a corresponding control experiment (O_3 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).

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

1/22: For clarity, please write "$^{13}C/^{12}C$ carbon isotope effect ($\varepsilon = k(^{13}C)/k(^{12}C) - 1$)" (or "carbon isotope fractionation").

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

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

2/18: Change to "KIEs of the main tropospheric sink reactions (CH_3Cl + OH, CH_3Cl + Cl)".

3/37: Brackets missign around (-26.8±0.2) ‰.

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 CH_3Cl standard, which should be used as anchor point to report all subsequent measurements of CH_3Cl by GC-IRMS.

How often was the CH_3Cl/N_2 reference standard analysed?

Was the same CH_3Cl/N_2 reference standard used in Hamburg and Heidelberg?

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.

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

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

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

Change to "residual CH_3Cl fraction".

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

5/12: Delete "$molecule^{-1}$". There is no such unit.

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

5/16: Please change to "the partial lifetime of CH_3Cl with respect to OH" (the OH lifetime is much shorter).

5/20: "stable carbon isotope delta values"

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

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

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 CH_3Cl loss in your experiment is 2.3 % - still small, but not <1 % as you claim. It is less than for CH_4 because the relative reaction rate coefficients favour the reaction with OH over $O(^1D)$ in case of CH_3Cl compared with CH_4.

8/15: Komatsu is misspelled.

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

9/19: Without an estimate of the degree of CH_3Cl 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 $\delta(^{13}C)$ value alone. E.g. if only 5 % got broken down, the 2.4 ‰ difference between soil and atmospheric $^{13}C/^{12}C$ ratio would correspond to an kinetic isotope effect of –48.5 ‰.

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.

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.

Supplement

Please provide consecutive line numbers for the supplement.

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.

Page 1

- Teflon FEP (not Felon FEP)
- Replace "ppb" with "nmol mol^{-1}".
- <1 nmol mol^{-1} O_3 (see page 6)
- <500 pmol mol^{-1} NO_x (or <0.5 nmol mol^{-1}, which helps avoid using another unit)
- "for at least 4 µmol mol-1 8 h" does not make sense
- "typically cleaned for 6 to 8 h" (delete h after 6)

- What was the make and model of the Teflon fan?
- Teflon is written with uppercase initial T because it is a proper name.
- O_2 and NO_x should be written with subscript "2" and "x". "x" in NO_x should be written in italics.
- Delete "ppm" in "1ppm".
- 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.
- helium is written with lower-case "h" (or use the chemical symbol "He")
- Valco – capital V

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".
- Please state the temperature at which the experiments were carried out.
- Delete ")" after 5 %.
- Replace "*" multiplication signs with "×".
- 25000 mmol mol^{-1} should be 25000 µmol mol^{-1}. However, even that corresponds to a temperature of 27 ºC. Is this correct?
- Delete "molecule^{-1}". There is no such unit.
- Delete "molecules" after 2.9×10^9 and after 2.0×10^{10}.

Page 3:

- H_2
- Replace "µmole mole-1" with "µmol mol^{-1}" (2 times).

Page 4

- "an unknown source" (not: emissions)
- "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.
- How many model runs did you carry out?

Page 6:

- Replace ppb with nmol mol^{-1} and ppt with pmol mol^{-1}.

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 $y(CH_3Cl)/(\mu mol\ mol^{-1})$ and $y(PFH)/(\mu mol\ mol^{-1})$, to designate that you have plotted mole fractions (the square bracket symbol means "concentration").

The right axis should be labelled "residual fraction f_t" (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

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].

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 $y(CH_3Cl)/(\mu mol\ mol^{-1}) = 133.5\ e^{-0.004t/h}$. Please provide another decimal for the coefficient in the exponent.

Fig. S4: The axis labels should be amended as per the comments on Fig. S2 above.

The equations should be written as

$y(CO_2\ measured)/(\mu mol\ mol^{-1}) = 469.5\ e^{-0.00118t/h}$ and

$y(CH_4\ measured)/(\mu mol\ mol^{-1}) = 3.52\ e^{-0.00117t/h}$

to be dimensionally correct.

Fig. S5: Again, axis labels should be "time t/h", "$y(CH_4)/(\mu mol\ mol^{-1})$", "$y(CO_2)/(\mu mol\ mol^{-1})$" and "$y(O_3)/(\mu mol\ mol^{-1})$".