

Reply to M. Johnson: We would like to thank M. Johnson for the positive evaluation of our manuscript and for the helpful comments to improve the manuscript. Requested changes were taken into account.

- 5 General Comments. This paper presents convincing experimental evidence and arguments supporting the view that earlier measurements of the KIE of the $\text{CH}_3\text{Cl} + \text{OH}/\text{Cl}$ were in error, the true value being 5 to 6 times smaller. This is based on experiments carried out in a 3500 L smog chamber coupled with offline IRMS analysis of canister samples. The analysis was further verified using GC-IRMS in two different
10 laboratories. The conclusion is supported by the lack of a significant seasonal covariation in tropospheric $\delta^{13}\text{C}(\text{CH}_3\text{Cl})$ values. Further, comparisons are made with KIE's determined by experiment and theory in chemically similar systems, which would also seem to indicate a revision in the accepted KIE. The revised KIE triggers an interesting and timely reanalysis of the atmospheric chloromethane budget.
- 15 Specific Comments. Accepting that other small molecules react with a smaller KIE, as argued at the bottom of page 6/top of page 7, this still does not account for the large KIE determined in the transition state theory study: As written in Sellevåg 2006, there will be a higher barrier to internal rotation in $\text{CH}_3\text{Cl} + \text{OH}$ than in $\text{CH}_4 + \text{OH}$. The authors note that they cannot find a flaw in these studies by Sellevåg and Gola;
20 Sellevåg may have agreed with the experimental work of Gola 2005 by a kind of perverse luck. In which case we should thank the authors of this work for their careful re-analysis. I would feel better though if there was a corresponding theoretical reanalysis; the question remains unanswered. $\text{CH}_3\text{Cl} + \text{OH}$ certainly will have a more constrained transition state than $\text{CH}_4 + \text{OH}$.

25 **Authors reply:** We fully agree with M. Johnson that a theoretical reanalysis of the isotope effects for the reaction of small molecules (c1 to c3) with OH and Cl is highly desirable for improving our understanding of these isotope effects. Our approach was clearly an experimental one and unfortunately such a reanalysis cannot be done within
30 our group.

Technical Corrections. I must complain a little bit about the use of units. 'micromole / mole' is fine, and I am often reading about 'ppm', but why use them both in the same paper? If you are going all in with IUPAC and SI notation then apply it consistently
35 and use only the former and it's related forms, never the latter. (e.g. page 4 line 32, page 6 lines 11 and 12, etc.) Always put a space between number and unit (e.g. (page 1 line 22 = p1ln22), p4ln25, p4ln345, p11ln4, etc.) Are you using 'L' for the liter p1ln22 or 'l' p5ln33? Be consistent. p3ln2, 'CMC Instruments' Check p3ln23, p5ln6, p6ln9.

40 **Authors reply:** We will use the IUPAC and SI notation throughout the manuscript, thoroughly check all units in the manuscript and use dm^3 for litre.

Reply to J. Rudolph: *We would like to thank the referee for the positive and very constructive evaluation of our manuscript and for the helpful comments to improve the manuscript. Requested changes were taken into account.*

5 The paper presents measurements of the carbon kinetic isotope effects (KIE) for reactions of chloromethane OH-radicals and Cl-atoms. These reactions are the dominant loss processes for chloromethane in the atmosphere and knowledge of their KIE is essential for understanding the carbon isotope budget of atmospheric chloromethane. Measurements of the carbon KIE for reactions of chloromethane have been published
10 before, but the measurements presented here hugely differ from those previously reported. This has a substantial impact on the use of chloromethane carbon isotope ratio measurements to constrain the sources of atmospheric chloromethane. The authors also present a budget estimate for chloromethane based on their new KIE using a two box model. They conclude that there should be a major unknown source for atmospheric
15 chloromethane in order to explain the atmospheric concentration and isotope ratio of chloromethane. Since chloromethane is the dominant natural source for stratospheric Cl it plays a major role in the budget of stratospheric ozone. Therefore, the subject of the paper is highly relevant for ACP. Overall the experimental data are well presented and sound. The two box model clearly demonstrates that, using the revised KIE, previously
20 published chloromethane budgets no longer are consistent with the known atmospheric isotope ratios of chloromethane. Consequently the paper should be published with some minor revisions. The authors argue that the low seasonal variability of the chloromethane carbon isotope ratio supports the finding of a much lower KIE for the atmospheric loss reactions of chloromethane than previously reported. To some extent I agree and it is
25 indeed difficult to reconcile a huge isotope effect for chloromethane loss reactions with a strong seasonal variability of the concentration, but a small seasonal change of the atmospheric chloromethane carbon isotope ratio. The authors argue that based on the revised KIE a substantial unidentified source for chloromethane must exist. Since by definition the seasonal variability of the carbon isotope ratio for an unknown source is not
30 known, there is some risk of circular reasoning resulting from assumptions of the strength of seasonal variability of emissions. For most sources there is very little direct information about the seasonality of the carbon isotope ratios of chloromethane emissions and for quite a few sources even magnitude and seasonality of emissions have large

uncertainties. The plausibility that the seasonal variability of the strength and isotope ratios of chloromethane emissions nearly exactly balances the otherwise expected high seasonal variability of the carbon isotope ratio of chloromethane is a matter of debate, but cannot be completely dismissed. It also has to be remembered that recent estimates
5 of the atmospheric chloromethane, including budgets which serve as basis for the two box models, budget have been influenced by the necessity to include a source for highly depleted chloromethane in order to reconcile atmospheric observations and the huge carbon KIE for atmospheric removal reactions reported previously. In summary, the authors make a very strong point that the currently existing atmospheric chloromethane
10 budgets are not consistent with the new carbon KIE for reactions of chloromethane. However, they should add some caveats that considering uncertainties in a budget without constraints from isotope ratio measurements will have extremely large uncertainties. In my opinion the strongest argument that the reported low KIEs are correct is the presented experimental evidence demonstrating the high quality of the
15 measurements. The indirect arguments about better agreement with atmospheric observations weakens the main point. Based on the strong evidence for measurements of high quality it is extremely probable that there is a serious gap in the current understanding of the atmospheric budget of chloromethane.

Authors reply: *Our conclusion “that based on the revised KIE a substantial unidentified
20 source for chloromethane must exist” is derived from yearly averaged emission and isotope data. Hence we don’t think that this is a circular reasoning. We agree with J. Rudolph, that seasonal variations in the isotopic composition of the CH₃Cl emissions are not known. For this reason, the isotopic source signatures of the CH₃Cl emissions were randomly varied. On global and hemispheric scales seasonal variations in the isotopic
25 source signatures have a surprisingly small effect on the tropospheric $\delta^{13}\text{C}(\text{CH}_3\text{Cl})$, mainly because of the strong dilution effect of the tropospheric background. In our simulations seasonal variations in the combined isotopic source signature of about $\pm 4\text{‰}$ induced seasonal fluctuations in the tropospheric $\delta^{13}\text{C}(\text{CH}_3\text{Cl})$ of less than 1.1 ‰. Seasonal variations in the range of ± 7 to $\pm 11\text{‰}$ in the combined source signature,
30 covering the reported uncertainty ranges of most source signatures result in seasonal variations of less than 3‰. Such variations still have a minor effect on the seasonality of the tropospheric $\delta^{13}\text{C}(\text{CH}_3\text{Cl})$ when applying a KIE of -59 ‰ to the OH sink. Masking such a large isotope effect for the losses would require variations by about 50 ‰ in northern*

hemispheric emissions and seasonal variations of 27 ‰ in the southern hemispheric emissions. Moreover these large variations in the source signatures have to be inversely correlated with OH loss in both hemispheres.

To our opinion this is an extremely unlikely scenario and the good agreement between the modeled seasonal variations of the tropospheric $\delta^{13}\text{C}(\text{CH}_3\text{Cl})$ with atmospheric observations hence strengthens our experimental results. As we could not detect any obvious flaws in the studies of Gola et al. (2005) and Sellevåg et al (2006) we found it important to provide this additional evidence for our smaller KIEs.

10

There are some minor details that need to be addressed:

1. KIE Measurements. Overall the description and presentation of the experiments and results are sound and demonstrate that the measurements are state of the art. I am aware that more details are presented in the cited paper by Keppler et al. (2018). However, given the fact that previously published measurements are very different from the results presented here, the authors should provide as much detail about the experiments and their results as possible. This could be done in a supplement to avoid adding length and material to the paper which would only be relevant for experts in laboratory studies of isotope effects.

20 **Authors reply:** A more detailed description has been added to the supplementary information (Supplement S1).

1.1: Some more information about the linear range of the carbon isotope ratio measurements. Does the linear range cover the range of concentrations in the experiments should be provided?

25 **Authors reply:** The sampled CH_3Cl amounts varied between 0.8 and 15 nmole. The Hamburg method has been shown to be linear from 0.01 to 20 nmole but with a decreasing reproducibility below 0.1 nmole (Bahlmann et al., 2011). The Heidelberg method was linear within the whole range of measured sample amounts. We will add this to the method section.

30

1.2: Is there some explanation why the GC-IRMS measurements of the carbon isotope ratio of chloromethane in the artificial test mixture differs by 1.1 ‰ from the DI measurements? Could this be a linearity problem? The difference seems to be larger than the uncertainty of the measurements and larger than discrepancies reported previously in similar studies, including chloromethane.

Authors reply: *Indeed the difference between the DI and GC-C-IRMS is at the upper end of those reported in previous studies. The reason for this has not been exploited. As outlined above this has no effect on the linear range of the Hamburg method.*

1.3: The use of orthogonal regression to determine the KIE implies that the error of both variables have identical variances. How realistic is this. Does a conventional linear regression result in identical KIEs?

Authors reply: *For each experiment the KIEs obtained with an orthogonal regression agreed well with those obtained with a linear regression. For the reaction of CH₃Cl with OH the orthogonal regression results in a KIE of (-11.2 ± 0.8) ‰ and the linear regression results in a KIE of (-11.0 ± 0.7) ‰. For the reaction CH₃Cl with Cl the respective KIEs were (-10.2 ± 0.5) ‰ and (-10.1 ± 0.5) ‰.*

1.4 Based on the relative rates for the CH₃Cl and CH₄ reactions it should be possible to calculate a limit for contributions from other possible reactions contributing to loss reactions of CH₃Cl.

Authors reply: *The relative rate CH₄/CH₃Cl in experiment 4 of 5.8 is 4.4 % larger than the recommended rate constants of 5.6 (Burkholder et al., 2015). The difference of 4.4 % might indicate small contributions from other loss processes but is within the stated uncertainties of the relative rate constants of 10% for CH₄ and CH₃Cl, respectively. The control experiment in the absence of water vapor revealed a loss of less than 3% over 10 h that can most likely be attributed to the reaction with OH originating from the reaction of O¹D with H₂. In any case this experiment provides an upper limit of 3% for contributions from other possible reactions to the observed loss of CH₃Cl.*

30

2. Uncertainty estimates (Page 10, lines 21-31, Figure 5):

2.1. Monte Carlo type calculations are very useful to estimate uncertainty ranges, but the results are not always easy to interpret in terms of the probability for a given value being within or outside of a given probability range. Does the scatter shown in Figure 5 represent a $\pm 1 \sigma$ uncertainty range, a given percentile, or even a firm boundary (which would be difficult to interpret)? Some more explanations are needed.

Authors reply: *The scatter represents a $\pm 1 \sigma$ uncertainty range with $\pm 1 \sigma$ uncertainties of 7 ‰ for biomass burning, 6 ‰ for ocean net emissions and other known sources and 10‰ for the tropical rainforest source. We have added this information to the revised manuscript in table 4 and figure 5.*

2.2. Figure 5 presents uncertainties stemming from uncertainty in carbon isotope ratios of emissions. However, the magnitude of emissions from known sources also has substantial errors. Figure 5 only considers errors of isotope ratios of emissions. I understand that a “missing source” in principle is to some extent equivalent to underestimating identified sources. Still, some more explanation is needed to which extent uncertainties in the magnitude of identified sources may reduce the gap between identified sources and the unknown source.

Authors reply: *With respect to the modelling uncertainties in the carbon isotope ratio of emissions are to some extent equivalent to uncertainties in their source strengths.*

At the current level of uncertainty in the isotopic source signatures all emissions except those from higher plants can be scaled to the upper limits of source strength within the stated uncertainties. We indicated this on page 10, line 29. On page 12 line 36 we further stated that increasing the emissions from these other known sources within the stated uncertainties could reduce the missing emissions from $(1530 \pm 190) \text{ Gg a}^{-1}$ to $(1100 \pm 200) \text{ Gg a}^{-1}$. We will clarify this issue in the revised manuscript. :

3. Since current thinking seems to be that the tropical chloromethane emissions are from higher plants, the very simple extrapolations using biomass or rainforest areas may have extremely large uncertainties. For isoprene and terpenes many very detailed studies with the purpose of developing emission algorithms have been conducted and it has been clearly demonstrated that using biomass or forest area alone is clearly insufficient.

Authors reply: We fully agree with the referee, that using biomass or forest area alone has its limitations regarding a global upscaling. Nevertheless, any upscaling can only be made on the basis of available information. Currently there is no information about how physiological and environmental drivers might affect CH₃Cl emissions from tropical rainforests. Apart from the observation that some members of the Dipterocarpaceae family are particular strong emitters of CH₃Cl, this also holds true with respect to species composition.

It should further be noted that the area bases on the previous bottom-up estimates are not consistent. Furthermore, Blei et al. (2008) and Saito et al. (2008; 2013) used an unrealistic high leaf biomass of 900 g m² in their flux conversion from leaf biomass to m². Given this, we found a simplified biomass based upscaling approach more reliable than an area based upscaling. However, we will mention the limitations of this approach and further suggest the need for more detailed CH₃Cl flux studies in the tropics.

15 Technical details:
Page, line 1,21: remove e.g.

Authors reply: Change applied.

1,23 (and other locations): 3500 dm³

20 **Authors reply:** We now use dm³ instead of litre throughout the whole manuscript.

1, 28 (and other locations): Avoid inconsistencies in use of isotope fractionation, fractionation factor, kinetic isotope effect (definitions page 4, lines10-14).

Authors reply: We checked the terminology for consistency.

25 1,30: remove tropical, I am not sure how well a two box model can support a specific unknown “tropical” source.

Authors reply: The support for an unknown tropical source mainly comes from previous 2- and 3-D model studies. However, “tropical” is an unnecessary restriction and will be removed.

30

3, 27: 2 dm³

Authors reply: We now use dm³ instead of litre throughout the whole manuscript.

3, 27: baked out at which temperature?

Authors reply: *The stainless steel canisters were heated at 250°C. The information has been added to the revised manuscript*

5 3, 28: packing and dimensions of adsorption tubes should be provided.

Authors reply: *The requested information has been added to the revised manuscript.*

3,35-37: Significant digits are inconsistent. Based on the 3 significant digits given for the working gas and reference standard, 4 significant digits for the results cannot be
10 justified.

Authors reply: *Change applied.*

4,2: Notwithstanding?

Authors reply: *The sentence has been changed to read “A combustion reactor filled
15 with copper (II) oxide at 850°C was used to convert CH₃Cl and CH₄ into CO₂.”*

4, 5: Based on error propagation the 1 σ error of measurements the difference should be $\pm 0.8 \%$ at the 1 σ level, which is somewhat lower than the observed value. This is not surprising, but still some comment should be added.

20 **Authors reply:** *This larger difference may result from small additional error of scales adding to the measurement uncertainties. For the purpose of this study we made no efforts to compare the working standards used in both labs. We have added a short comment to the revised manuscript.*

25 4, lines 10-15, eq. 1 and 2: no need to introduce α , it is not used anywhere else in the paper.

Authors reply: *We removed “ α ” from eq. 1 and 2 in the revised manuscript.*

4, 24: Table 1 4, 30: Prior to 4, 13 and 5, 6: Provide value for limit of “measurable
30 loss”

Authors reply: *The limit for a measurable loss was between 1.4 and 2% in our experiments. This information has been added to the manuscript.*

5 5,22: ... measured KIE.

Authors reply: *Change applied.*

5,24: replace “reasonably well” by “within”, the possibility of bias due to impact from other reactions should be briefly discussed (see above, 1.4) either here or in 2.3.

10 A higher OH-KIE may be due to interference from Cl-atom reactions.

Authors reply: “reasonably well” has been replaced by “within”. *We added a brief discussion on potential interferences from side reactions to the revised manuscript. to the revised manuscript: “Prior to the methane degradation experiment (exp. 6 in table 1) we made the methane blank experiment (exp 5 in table 1) with no ozone but the UV-light*
15 *being switched on. This experiment revealed no methane loss over 10 h. With this we can exclude any interferences from reactive chlorine during the CH₄-OH experiment. The higher KIE found here might result from the reaction of methane with O¹D. Cantrell et al. (1990), who also used UV-photolysis in the presence of water as an OH source, found an even higher KIE of (-5.4 ±0.9) ‰ and estimated that the reaction of CH₄ with O(¹D)*
20 *showing a KIE of -13 ‰ (Saueressig et al., 2001) may have contributed about 3% to the overall degradation.”*

5,33:.. whereas we used..

Authors reply: *Change applied.*

25

6,1: “agree well” is subjective, the strongest argument against problems with mixing would be a presentation of the measured dilution factor combined with a comparison with a theoretical (volume and volume flow based), maybe in a supplement.

Authors reply: *The effect of mixing on the observed KIE can be approximated from the*
30 *time scales of mixing and reaction according to the following equation (Morgan et al., 2004; Kaiser et al., 2006) :*

$$\epsilon_{obs} \approx \frac{1}{2} \epsilon_i \times \left(1 + \sqrt{\frac{1}{1+Q}} \right)$$

Here ϵ_i is the intrinsic fractionation factor, ϵ_{obs} is the observed fractionation factor and Q is the ratio of the mixing time and reaction time scale ($1/k$). With a reaction time scale of at least 300 minutes and a mixing time scale of 10 minutes we obtain

5
$$\epsilon_{obs} \approx 0.99 \times \epsilon_i$$

This clearly shows that mixing problems are no issue in our study. We have added this information to the revised manuscript.

6,24: prior to 7, 33-34: Keppler et al. (2005) give (Table 1) a value of -38 ‰ with an
10 uncertainty range of 4 ‰

Authors reply: We apologize for this shortened description. The value given in Keppler et al. (2005) served as a starting point in our study. It refers to Kommatsu (2004) reporting a mean $\delta^{13}\text{C}$ of -38‰ for CH_3Cl in coastally influenced waters off Japan and more enriched $\delta^{13}\text{C}$ values in the range of -12‰ to -30‰ from the open North-East Pacific. We
15 obtained average $\delta^{13}\text{C}$ values of -43 ± 3 ‰ from a productive lagoon in southern Portugal (Weinberg et al. 2014). Taking the biotic and abiotic degradation of CH_3Cl into account we estimate the mean isotopic source signature of the ocean source to -36 ± 6 ‰. We have added this information to the revised manuscript.

8, 22-23: Needs more discussion. In a unidirectional emission the isotope ratio of the
20 emissions is independent of atmospheric concentration and isotope ratio. In a bidirectional exchange atmospheric concentration and isotope ratio will influence the isotope ratio as well as the source strength of the net emissions.

Authors reply: Saito et al. (2013) proposed a bidirectional exchange. However, a
25 detailed discussion of the exchange processes and their implications on the isotopic source signature is clearly beyond the scope of this paper.

In this study the authors used the same incubation method to determine the stable carbon isotope ratios of CH_3Cl emitted from tropical plants (Saito et al., 2008; Saito & Yokouchi, 2008). Moreover the site and most of the sampled plant species were the same in Saito
30 et al. (2013) and in (Saito et al., 2008). Hence, regardless of the nature of the exchange

process, we can safely assume that any potential effect of the bidirectional exchange reported in 2013 is already included in the isotopic source signatures reported in 2008 and that there is no need for a correction of these values as stated in our manuscript.

5 8,25-30: “The lifetimes were then forced to ... ” is unclear and, if taken literally, questionable. In order to “force the lifetime” to reproduce the seasonal variations at Mace Head assumptions about the seasonality of emission rates are needed. Apart from the very limited a priori information on known sources, this would create circular reasoning about the seasonality of the “unknown source”.

10

Authors reply: We apologize for the confusion. More precisely the loss rates were forced to reproduce the seasonal variations at Mace Head. This forcing accounts for the spatio-temporal variabilities in the OH and CH₃Cl concentration fields, which cannot be adequately represented in a two box model.

15 Several 2- and 3-D model studies (Lee Taylor et al., 2001; Yoshida et al., 2006; Xiao et al., 2010) provide a quite consistent picture of the seasonal and spatial variations in the overall emissions that serves as a base for this forcing. It should be noted that the seasonality of the unknown source is not discussed in our manuscript. Further, as outlined before tropospheric $\delta^{13}\text{C}(\text{CH}_3\text{Cl})$ against seasonal and random variations in the isotopic
20 source signatures.

9,11: spore space

Authors reply: This should be pore space and has been corrected.

25 9,31: “nicely resembles”?

Authors reply: We removed “nicely”

10,11: This conclusion depends strongly on assumption about the seasonal variation of the isotopic signature of emissions.

30 **Authors reply:** This conclusion is based on yearly averaged source signatures. As outlined in our response above seasonal variations of the isotopic source signatures have only a minor effect on seasonal variations in the tropospheric $\delta^{13}\text{C}(\text{CH}_3\text{Cl})$

because of the strong dilution effect of the tropospheric background. A more detailed discussion regarding this issue has been added to the supplementary information.

References should be checked carefully, I noticed that some cited publications are
5 not included in the references.

Authors reply: *We thoroughly checked all references included in the revised manuscript.*

Table 4: The meaning of range should be explained ($a \pm n \cdot \sigma$ probability range, a
10 percentile, a firm limit based on a given probability?)

Authors reply: *Please refer to response of comment above.*

List of major changes:

p. 3, l. 23 has been changed to:

Further information on the smog chamber setup is provided in the supplementary information and has recently been published elsewhere (Wittmer et al., 2015; Keppler et al., 2018).

On p. 3, l. 28 we added the following sentence:

The adsorption tubes were made of stainless steel (1/4 inch outer diameter, 7 inch length) and filled with 77 mg Carboxen 1016®, 215 mg Carboxen X 569®, 80 mg Carboxen® 1003 and 9 mg Tenax® TA in order of the sampling flow direction.

p. 4, l. 7 has been changed to:

The $\delta^{13}\text{C}$ values measured in both laboratories generally agreed within ± 1.3 ‰ on the 1σ level. This range is somewhat larger than expectable from error propagation and may result from small additional errors of scale adding to the uncertainty. For the purpose of this study no attempts were made to adjust differences of scale in between both laboratories. Methane carbon isotope ratios were only analyzed at the University of Heidelberg. On p. 5, l. 35 we added the following paragraph:

Prior to the CH_4 degradation experiment with OH we performed a blank experiment (exp. 5 in table 1) that revealed no CH_4 loss over 10 h. With this we can exclude any interferences from reactive chlorine during the CH_4 -OH experiment. The higher KIE for the reaction with OH found here might result from the reaction of methane with $\text{O}(^1\text{D})$. Cantrell et al. (1990), who also used UV-photolysis in the presence of water as an OH source, reported an even higher KIE of (-5.4 ± 0.9) ‰ and estimated that the reaction of CH_4 with $\text{O}(^1\text{D})$ showing a KIE of -13 ‰ (Saueressig et al., 2001) may have contributed about 3% to the overall degradation.

p. 6, l. 11 has been changed to:

The effect of mixing on the observed KIE can be approximated from the time scales of mixing and reaction according to the following equation (Morgan et al., 2004; Kaiser et al., 2006):

$$\epsilon_{obs} \approx \frac{1}{2} \epsilon_i \times \left(1 + \sqrt{\frac{1}{1+Q}} \right)$$

Here ϵ_i is the intrinsic fractionation factor, ϵ_{obs} is the observed fractionation factor and Q is the ratio of the mixing time and reaction time scale ($1/k$). The chemical lifetime of CH_3Cl under the experimental conditions was in the order of 6 to 8 h and the turnover of air inside the chamber occurred on time scales of a few minutes. With a reaction time scale of 300 minutes and a mixing time scale of 10 minutes we obtain $\epsilon_{obs} \approx 0.99 \times \epsilon_i$.

p. 8, l. 22 has been changed to:

Keppler et al. (2005) estimated average isotopic composition of dissolved CH_3Cl to (-36 ± 4) ‰. This value refers to Kommatsu (2004), who reported a mean $\delta^{13}\text{C}$ of -38 ‰ for CH_3Cl in coastally influenced waters off Japan and more enriched $\delta^{13}\text{C}$ values in the range of -12 ‰ to -30 ‰ from the open North-East Pacific. We obtained average $\delta^{13}\text{C}$ values of -43 ± 3 ‰ from a productive lagoon in southern Portugal (Weinberg et al. 2014). Taking the biotic and abiotic degradation of CH_3Cl into account we estimate the mean isotopic source signature of the ocean source to (-36 ± 6) ‰.

p. 9, l. 9 has been changed to:

This uptake might affect the isotopic composition of CH₃Cl from tropical rainforests. However, because the incubation
5 methods used in this study were the same as that previously used to determine the isotopic composition of CH₃Cl
emitted from tropical plants (Saito & Yokouchi, 2008; Saito et al., 2008) we can reasonably assume that any potential
isotopic effect of this bidirectional exchange is included in the previously reported carbon isotope ratios.

p. 11, l. 20 has been changed to:

10 Increasing the emissions from all other known sources within the given ranges might reduce the missing emissions by
about 500 Gg a⁻¹.

On p. 13, l. 14 we added the following paragraph:

Using error propagation, we estimate the uncertainty of our approach to ±30.4 % with respect to the available data.
15 However, we note an urgent need for more detailed flux studies. Currently there is no information about how
physiological and environmental drivers might affect CH₃Cl emissions from tropical rainforests. Apart from the
observation that some members of the Dipterocarpaceae family are particular strong emitters of CH₃Cl, this also holds
true with respect to species composition.

The following references were added:

20 Anderson, R. S., Huang, L., Iannone, R., Thompson, A. E., and Rudolph, J.: Carbon Kinetic Isotope Effects in the
Gas Phase Reactions of Light Alkanes and Ethene with the OH Radical at 296 ± 4 K, *The Journal of Physical
Chemistry A*, 108, 11537-11544, 10.1021/jp0472008, 2004.

Anderson, R. S., Huang, L., Iannone, R. & Rudolph, J. Measurements of the 12C/13C Kinetic Isotope Effects in the
Gas-Phase Reactions of Light Alkanes with Chlorine Atoms. *The Journal of Physical Chemistry A* 111, 495-504,
25 doi:10.1021/jp064634p, 2007.

Global Forest Resource Assessment 2012, Food and Agriculture Organization of the United Nations, Rome, ISBN
978-92-5-107292-9, 2012

Global Forest Resources Assessment 2015, Food and Agriculture Organization of the United Nations, Rome, Desk
Reference, ISBN 978-92-5-108826-5, 2015

30 Kaiser, J., Engel, A., Borchers, R., and Röckmann, T.: Probing stratospheric transport and chemistry with new balloon
and aircraft observations of the meridional and vertical N₂O isotope distribution, *Atmos. Chem. Phys.*, 6, 3535–3556,
doi:10.5194/acp-6-3535-2006, 2006.

Komatsu, D. D., Tsunogai, U., Yamaguchi, J., et al.: The budget of atmospheric methyl chloride using stable carbon
isotopic mass- balance, Poster A51C-0784, AGU Fall Meeting, San Francisco, 2004.

35 Lee-Taylor, J. M., Brasseur, G. P., and Yokouchi, Y.: A preliminary three-dimensional global model study of
atmospheric methyl chloride distributions, *J. Geophys. Res.*, 106(D24), 34221–34233, 2001.

Morgan, C. G., Allen, M., Liang, M. C., Shia, R. L., Blake, G. A., and Yung, Y. L.: Isotopic fractionation of nitrous
oxide in the stratosphere: Comparison between model and observations, *J. Geophys. Res.*, 109, D04305,
doi:10.1029/2003JD003402, 2004.

Weinberg, I., Bahlmann, E., Eckhardt, T., Michaelis, W., and Seifert, R.: A halocarbon survey from a seagrass dominated subtropical lagoon, Ria Formosa (Portugal): flux pattern and isotopic composition, *Biogeosciences*, 12, 1697-1711, 10.5194/bg-12-1697-2015, 2015.

5 Yokouchi, Y., Ikeda, M., Inuzuka, Y., and Yukawa, T.: Strong emission of methyl chloride from tropical plants, *Nature*, 416, 163–165, 2002.

Table 4: The ranges were corrected.

Figure 5, figure caption: The uncertainty interval (1σ) has been specified.

| 10

Evidence for a major missing source in the global chloromethane budget from stable carbon isotopes

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Abstract. Chloromethane (CH₃Cl) is the most important natural input of reactive chlorine to the stratosphere, contributing about 16% to stratospheric ozone depletion. Due to the phase out of anthropogenic emissions of chlorofluorocarbons, CH₃Cl will largely control future levels of stratospheric chlorine.

The tropical rainforest is commonly assumed to be the strongest single CH₃Cl source, contributing over half of the global annual emissions of about 4000 to 5000 Gg (1 Gg = 10⁹ g). This source shows a characteristic carbon isotope fingerprint, making isotopic investigations a promising tool for improving its atmospheric budget. Applying carbon isotopes to better constrain the atmospheric budget of CH₃Cl requires sound information on the kinetic isotope effects for the main sink processes—e.g. the reaction with OH and Cl in the troposphere. We conducted photochemical CH₃Cl degradation experiments in a 3500 dm³ smog chamber to determine the carbon isotope fractionation effect (ε) for the reaction of CH₃Cl with OH and Cl. For the reaction of CH₃Cl with OH, we determined a ε of (-11.2±0.8) ‰ (n=3) and for the reaction with Cl we found a ε of (-10.2±0.5) ‰ (n=1) being five to six times smaller than previously reported. Our smaller isotope effects are strongly supported by the lack of any significant seasonal covariation in previously reported tropospheric δ¹³C(CH₃Cl) values with the OH driven seasonal cycle in tropospheric mixing ratios. Applying these new fractionation factors to the global CH₃Cl budget using a simple two hemispheric box model, we derive a tropical rainforest CH₃Cl source of (670±200) Gg a⁻¹, which is considerably smaller than previous estimates. A revision of previous bottom up estimates, using above ground biomass instead of rainforest area, strongly supports this lower estimate. Finally, our results suggest a large unknown tropical CH₃Cl source of (15230±200) Gg a⁻¹.

1 Introduction

In the mid-90s, the recognition that the known CH₃Cl sources, mainly biomass burning and marine emissions, are insufficient to balance the known atmospheric sinks (Butler, 2000) motivated intense research on potential terrestrial sources. Today, it is common thinking that large emissions from tropical rainforests (Monzka et al., 2010; Xiao et al., 2010; Carpenter et al., 2014) can close this gap. Several model studies revealed a strong tropical CH₃Cl source in the range of 2000 Gg a⁻¹ (Xiao et al. 2010, Yoshida et al., 2004, Lee Taylor et al. 1998). Particular support for a strong tropical rainforest source arose from observations of elevated CH₃Cl concentrations in the vicinity of tropical rainforests (Yokouchi et al., 2000), greenhouse experiments (Yokouchi et al., 2002), several field measurements in

tropical rainforests (Saito et al. 2008; Gebhardt et al. 2008; Blei et al., 2010; Saito et al., 2013 and from carbon stable isotope mass balances (Keppler et al. 2005; Saito & Yokouchi, 2008). The majority of CH₃Cl in tropical rain forests ((2000±600) Gg a⁻¹) is thought to originate from higher plants (Monzka et al., 2010; Xiao et al, 2010; Yokouchi et al. 2000; Saito & Yokouchi, 2008). A minor fraction of about 150 Gg a⁻¹ may be emitted from wood rotting fungi (Monzka et al., 2010; Xiao et al, 2010; Carpenter et al., 2014). Further emissions from senescent leaf litter (Keppler et al. 2005) may substantially contribute to this source, but this has not yet been confirmed in field studies (Blei et al. 2010). On a global scale, biomass burning ((400 to 1100) Gg a⁻¹) and surface ocean net emissions (140 to 640 Gg a⁻¹) are further important sources (Monzka et al., 2010; Xiao et al, 2010; Carpenter et al., 2014). Chloromethane from higher plants has an average stable isotope signature (¹³C/¹²C ratio, δ¹³C value) of (-83±15) ‰ (Saito et al., 2008; Saito & Yokouchi, 2008). Compared to the other known sources with δ¹³C values in the range from -36 ‰ to -62 ‰ (Keppler et al. 2005; Saito & Yokouchi, 2008), the tropical rainforest source is exceptionally depleted in ¹³C making stable isotope approaches particularly useful to better constrain CH₃Cl flux estimates.

The isotopic composition of tropospheric CH₃Cl links the isotopic source signatures to the kinetic isotope effects (KIEs) of the sinks. The primary CH₃Cl sink is its oxidation in the troposphere by OH and Cl, accounting for about 80% of total losses (Monzka et al., 2010; Xiao et al, 2010; Carpenter et al., 2014). Further sinks comprise soil uptake and loss to the stratosphere (Monzka et al., 2010; Xiao et al, 2010; Carpenter et al., 2014). An accurate determination of the KIEs of the bulk tropospheric sink (OH + Cl) is crucial for constraining the tropical rainforest source from an isotopic perspective. A previous study (Gola et al. 2005) revealed large KIEs of (-59±8) ‰ and (-70±10) ‰ for the reaction of CH₃Cl with OH and Cl, respectively, which supported the hypothesis of large emissions from tropical rainforests (Keppler et al., 2005; Saito & Yokouchi, 2008). In particular, the KIE for the reaction with OH is much larger in comparison to previously reported KIEs for the reaction of OH with methane (Saueressig et al., 2001) and other hydrocarbons (Rudolph et al., 2000; Anderson et al., 2004). We thus performed photochemical degradation experiments of CH₃Cl in a 3500 L-dm³ Teflon smog chamber using established radical generation schemes (see method section for details) to reassess the KIEs for the reaction of CH₃Cl with OH and Cl. For validation purposes, we further determined the known KIEs for the same reactions of methane.

In the next step, we used the seasonal variations in the mixing ratios (Prinn et al., 2000) and isotopic composition (Thompson et al., 2002; Redeker et al., 2007) of tropospheric CH₃Cl to further assess the reliability of the obtained KIEs. This was done with a simple two-box model, dividing the atmosphere into a northern and a southern hemisphere and using a simplified emission scheme. The same model was then used to constrain the tropical rainforest source from an isotopic perspective. We finally improved previous bottom up estimates of the tropical rainforest source using carbon density maps of the tropical rainforest instead of coverage area.

2 The kinetic isotope effect (ε) for the reaction of CH₃Cl with OH and Cl

2.1 Materials and methods

2.1.1 Smog chamber

The smog chamber set up and the experimental conditions are the same as recently described in Keppler et al. (2018). The samples for the carbon isotope analysis were taken from the same experiments described therein. Briefly, the isotope fractionation experiments were performed in a (3500±100)-L-dm³ Teflon smog-chamber. The chamber was

continuously flushed with purified, hydrocarbon-free zero air (zero-air-generator, cmc instruments, <1 nmol mol⁻¹ of O₃, <500 pmol mol⁻¹ NO_x, <100 nmol mol⁻¹ of CH₄) at a rate of 0.6 - 4 dm³ min⁻¹ to maintain a slight overpressure of 0.5-1 Pa logged with a differential pressure sensor (Kalinsky Elektronik DS1). A Teflon fan inside the chamber ensured constant mixing throughout the experiments. NO and NO_x were monitored on a routine basis with an EcoPhysics, CLD 88p chemiluminescence analyzer coupled with an EcoPhysics photolytic converter, PLC 860. Ozone was monitored by a chemiluminescence analyzer (UPK 8001). Initial CH₃Cl mixing ratios were between 5 μmol mol⁻¹ and 14 μmol mol⁻¹. Perfluorohexane (PFH) was used as an internal standard with initial mixing ratios of (25±3) μmol mol⁻¹ to correct the resulting concentrations for dilution. The mixing ratios of CH₃Cl and PFH were monitored by GC-MS (Agilent Technologies, Palo Alto, CA) with a time resolution of 15 minutes throughout the experiments. The stability of the instrument was regularly checked using a gaseous standard (5 ml of 100 μmol mol⁻¹ CH₃Cl in N₂). Mixing ratios of methane and CO₂, used as internal standard in the methane degradation experiments, were measured with a Picarro G221i cavity ring down spectrometer. Prior to the experiments, the instrument was calibrated with pressurized ambient air from a tank obtained from the Max-Planck-Institute for Biogeochemistry in Jena/Germany (CO₂ mixing ratio of (394.6±0.5) μmol mol⁻¹, methane mixing of (1.752±0.002) μmol mol⁻¹). OH radicals were generated via the photolysis of ozone (about 2000 μmol mol⁻¹ for CH₃Cl and about 10000 μmol mol⁻¹ for CH₄) at 253.7 nm in the presence of water vapor (Relative humidity = 70%). This is a well-established efficient method for OH radical generation (Cantrell et al. 1990, DeMore 1992). In the CH₃Cl + OH experiments initially 2000 μmol mol⁻¹ of H₂ was added for scavenging chlorine radicals originating from the photolysis or oxidation of formyl chloride (HCOCl) occurring as an intermediate in the reaction cascade (Gola et al., 2005). To obtain an efficient OH formation, Philips TUV lamps (1x55 W for CH₃Cl, 4x55 W for CH₄) were welded in Teflon film and mounted inside the smog chamber. Atomic chlorine (Cl) was generated via photolysis of molecular chlorine (Cl₂) at a relative humidity of less than 1% by a solar simulator with an actinic flux comparable to the sun in mid-summer in Germany. ~~A more~~ Further information-detailed description on the experimental smog chamber setup-setup is provided in the supplementary information and has recently been published elsewhere (Wittmer et al., 2015; Keppler et al., 2018).

2.1.2 Sampling and carbon isotope determination

From each experiment 10 to 15 canister samples (2 dm³ stainless steel, evacuated <1.3x10⁻³ Pa and baked out at 250°C for 2 h) and 10 to 15 adsorption tube samples were taken at regular time intervals for subsequent analysis of carbon isotope ratios. The adsorption tubes were made of stainless steel (1/4 inch outer diameter, 7 inch length) and filled with 77 mg Carboxen 1016®, 215 mg Carbopack X 569®, 80 mg Carboxen® 1003 and 9 mg Tenax® TA in order of the sampling flow direction. The adsorption tube samples and one set of canister samples from the CH₃Cl degradation experiments were analyzed by 2D-GC-IRMS/MS at the University of Hamburg using the method of Bahlmann et al. (2011). This method has been shown to be free of interferences from other compounds. The precision and reproducibility of the δ¹³C measurements based on standards were ± 0.6‰ (n = 18) on the 1σ level. In order to assure compliance with VPDB scale, a single component standard of CH₃Cl (100 μmol mol⁻¹ in nitrogen, Linde Germany) was analyzed via the 2D-GC-IRMS. The results were compared to those after offline combustion and analysis via a dual inlet (DI) against a certified CO₂ reference standard (Air Liquide, Germany, -26.8± 0.2‰ and a solid standard (Nist NBS 18, RM 8543). The results from the DI (n=6) were (-37.49-2±0.081) ‰ for CH₃Cl. The respective δ¹³C values from the GC-GC/IRMS, measured against the machine working gas (Air Liquide, Germany,

((-26.8± 0.2) ‰) were (-36.061±0.24) ‰ resulting in an offset (DI – 2D-GC-IRMS) of -1.13‰ for CH₃Cl. All results were corrected for this offset.

The canister samples were analyzed at the University of Heidelberg using a cryogenic pre-concentration system coupled to a GC-C-IRMS system, developed for δ²H measurements of CH₃Cl (Greule et al. 20132). ~~Notwithstanding,~~
5 ~~A~~ combustion reactor filled with copper (II) oxide at 850°C was used to analyze δ¹³C. The precision and reproducibility of these δ¹³C measurements based on a chloromethane working standard were ± 0.47 ‰ (n = 47) on the 1σ level. ~~The sampled CH₃Cl amounts varied between 0.8 and 15 nmol. Both methods were linear over the whole range of sampled CH₃Cl amounts. The~~ δ¹³C values measured in both laboratories generally agreed within ± 1.3 ‰ on the 1σ ~~level-level~~. ~~This range is somewhat larger than expectable from error propagation and may result from small additional errors of scale adding to the uncertainty. For the purpose of this study no attempts were made to adjust differences of scale in between both laboratories. the measured δ¹³C values.~~ Methane carbon isotope ratios were only analyzed at the University of Heidelberg.

2.1.3 Calculation of ε

The carbon isotope ratios are reported in the δ-notation relative to the VPDB scale (Vienna Pee Dee Belemnite) and
15 the isotope ~~fractionation-effect~~ (ε) is reported in [‰]. We applied an orthogonal regression model (Danzer et al. 1995)

to derive the KIE for each experiment from the slope of the Rayleigh plot:

$$\varepsilon(\alpha - 1) * \ln(f_t) = \ln\left(\frac{\delta^{13}C_t + 1000}{\delta^{13}C_0 + 1000}\right) \quad (1)$$

~~And~~

$$\varepsilon = (\alpha - 1) \frac{\ln(f_t)}{\ln\left(\frac{\delta^{13}C_t + 1000}{\delta^{13}C_0 + 1000}\right)} \quad (2)$$

with ε being the enrichment factor, ~~α being the isotopic fractionation factor,~~ f_t being the residual fraction at time t, δ¹³C₀ being the initial carbon isotope ratio of the substrate [‰], δ¹³C_t being the carbon isotope ratio of the substrate [‰] at time t ~~and KIE being the kinetic isotope effect [‰]~~. To account for the dilution from the air flow through the chamber, the residual fraction (f_t) has been calculated from the mixing ratios of CH₃Cl and the inert tracer PFH as
25 follows:

$$f_t = \frac{[CH_3Cl_t] * [PFH_0]}{[CH_3Cl_0] * [PFH_t]} \quad (3)$$

Here [CH₃Cl] and [PFH] denote the respective concentrations and the indices t and 0 refer to time t and zero respectively. The uncertainty for f_t ranged from 1.4 to 1.8% on the 1σ level.

2.2 Results of the CH₃Cl degradation experiments

30 In total we performed six degradation experiments and two control experiments within this study. To perform the degradation experiments within a day, the experimental conditions were modified as indicated in table 1. For the OH experiments in the presence of methane the light intensity was increased from 55_W to 220_W and the steady state ozone mixing ratios were increased from about 620 nmol mol⁻¹ to about 3570 nmol mol⁻¹. Under these experimental conditions typically 70 to 80% of the initial CH₃Cl and methane were degraded within 6 to 10h. ~~For a~~ more detailed
35 discussion of the experimental conditions with respect to the OH yields and degradation rates is provided in the

[supplementary information](#). Further, the reader is referred to Keppler et al. (2018) reporting on the hydrogen isotope effects from these experiments.

Prior each degradation experiment, we monitored the ratio of CH₃Cl and perfluorohexane (PFH) for at least 2h to assess potential side reactions and unwanted losses of CH₃Cl. For the experiment with chlorine, this was done under dark conditions in the presence of 10 $\mu\text{mol mol}^{-1}\text{ppm}$ Cl₂. For the OH experiments, this was either done in the absence of light or ozone. None of these tests revealed indication for a measurable loss (1.4 to 2.1 %) of CH₃Cl and thus for any biasing side effects or reactions. In the methane degradation experiments CO₂ was used as an internal standard to correct for the methane mixing ratios for dilution. A blank experiment over 9h carried out with a dilution flow of 4 $\text{L dm}^{-3}\text{ min}^{-1}$ of zero air revealed a slope (-0.00118 ± 0.00001) min^{-1} for CH₄ loss and a slope of (0.00117 ± 0.000007) min^{-1} for the CO₂ loss respectively. This corresponds to a dilution flow of (4.1 ± 0.1) $\text{dm}^3\text{L}^{-1}\text{ min}^{-1}$ being in good agreement with the pre-set dilution flow (the major uncertainty in this calculation is the exact volume of the chamber). During this blank experiment, the dilution corrected mixing ratio of CH₄ changed by less than 0.2 %.

In our study, photolysis of ozone (620 nmol mol^{-1} steady state mixing ratio) in the absence of water vapor (relative humidity <1%) but with 2000 $\mu\text{mol mol}^{-1}$ H₂ (experiment 3) resulted in a CH₃Cl degradation of less than 3% over 10 hours and no measurable change in the isotopic composition of CH₃Cl. because of the insufficient OH yield (see also [figure S3 in the supplementary information](#)). The reaction rate constants of O(¹D) with H₂ and H₂O at 298 K are $1.1\cdot 10^{-10}$ and $2.2\cdot 10^{-10}$ $\text{cm}^3\text{ molecule}^{-1}\text{ s}^{-1}$ respectively (Burkholder et al., 2015). At a relative humidity of 70% (corresponding to 25000 $\mu\text{mol mol}^{-1}\text{ppm}$), the reaction with H₂O is by far the main pathway to form OH (with the H₂ pathway contributing less than 4% to the OH yield). This is consistent with the previous study, where ozone levels of 300 $\mu\text{mol mol}^{-1}\text{ppm}$ were required for a sufficient OH production from H₂ (Gola et al., 2005; Sellevåg et al., 2006). For this experiment the OH lifetime of CH₃Cl can be estimated to about 330 h. In experiment four, where both CH₃Cl and CH₄ were present, the ratio of the measured rate constants for the reaction of CH₃Cl and CH₄ with OH was 5.8. This ratio agrees well with that of the recommended rate constants of 5.6 at 298 K ($6.3\cdot 10^{-15}$ $\text{cm}^3\text{ s}^{-1}$ for CH₄ and, $3.5\cdot 10^{-14}$ $\text{cm}^3\text{ s}^{-1}$ for CH₃Cl at 298K; Burkholder et al., 2015).

The change in stable carbon isotope values of CH₃Cl ($\delta^{13}\text{C}(\text{CH}_3\text{Cl})$) with extent of reaction and the corresponding Rayleigh plots of the CH₃Cl degradation experiments are shown in figure 1. The respective KIEs, derived from the slope of the Rayleigh plot, are summarized in table 2. For the reaction of CH₃Cl with OH, we determined a KIE of $-(-11.2\pm 0.8)$ ‰ (n=3) and for the reaction with Cl we found a KIE of (-10.2 ± 0.5) ‰ (n=1). The results from both laboratories generally agreed within ± 1.5 ‰ (1 σ) and showed no systematic difference. Variations in the initial mixing ratios (5 to 13 $\mu\text{mol mol}^{-1}\text{ppm}$) and isotopic composition ((-47.0 ± 0.5) ‰ and (-40.3 ± 0.5) ‰) of CH₃Cl in the OH experiments had no significant effect on the determination of the KIEs. Further, the increase in the light intensity and ozone mixing ratios in experiment four had no effect on the KIE.

The KIEs for the reaction of methane with OH and Cl, determined for validation purposes, agreed reasonable well with the previously published KIEs (Saueressig et al., 1995; 2001; Tyler et al., 2000; Feilberg et al., 2005). For the reaction of methane with OH we found a KIE of -4.7 ‰ being at the upper end of previous reported fractionation factors and for the reaction with Cl we found a KIE of -59‰ being more at the lower end of previously reported measured KIEs (table 3). [Prior to the CH₄ degradation experiment with OH we performed a blank experiment \(exp. 5 in table 1\) that revealed no CH₄ loss over 10 h. With this we can exclude any interferences from reactive chlorine during the CH₄-OH experiment. The higher KIE for the reaction with OH found here might result from the reaction](#)

of methane with O(¹D). Cantrell et al. (1990), who also used UV-photolysis in the presence of water as an OH source, reported an even higher KIE of (-5.4 ± 0.9) ‰ and estimated that the reaction of CH₄ with O(¹D) showing a KIE of -13 ‰ (Saueressig et al., 2001) may have contributed about 3% to the overall degradation.

2.3 Discussion of the CH₃Cl degradation experiments

5 Our newly determined KIEs for the reaction of CH₃Cl with OH and Cl are five to six times smaller than the previous reported KIEs of (-59 ± 10) ‰ for the reaction with OH and of (-70 ± 10) ‰ for the reaction with Cl (Gola et al. 2005). In this section we first discuss potential sources of error in our study with particular respect to the differences between our study and the Gola study and then provide a more comprehensive comparison of our data with previous data. Gola et al. (2005) used a 250 ~~dm³~~ electro polished stainless steel chamber for their degradation experiments, ~~whereas We~~
10 used a 3500 ~~dm³~~ smog chamber made from FEP foil, for the CH₃Cl degradation experiments. The large volume of our smog chamber may result in incomplete mixing and thus in an underestimation of the KIE due to transport limitation. The effect of mixing on the observed KIE can be approximated from the time scales of mixing and reaction according to the following equation (Morgan et al., 2004; Kaiser et al., 2006):

$$\epsilon_{obs} \approx \frac{1}{2} \epsilon_i \times \left(1 + \sqrt{\frac{1}{1+Q}} \right)$$

15 Here ϵ_i is the intrinsic fractionation factor, ϵ_{obs} is the observed fractionation factor and Q is the ratio of the mixing time and reaction time scale (1/k). The chemical lifetime of CH₃Cl under the experimental conditions was in the order of 6 to 8 h and the turnover of air inside the chamber occurred on time scales of a few minutes. With a reaction time scale of 300 minutes and a mixing time scale of 10 minutes we obtain $\epsilon_{obs} \approx 0.99 \times \epsilon_i$.~~The lifetime of CH₃Cl under the experimental conditions was in the order of 6 to 8h, whereas the turnover of air inside the chamber occurred on~~
20 ~~time scales of a few minutes~~ making incomplete mixing an unlikely source of error. Incomplete mixing would also have affected the determination of the respective KIEs for methane. With those values ~~agreeing well with being within~~ previously reported KIEs we can exclude incomplete mixing as a potential source of error in our experiments. In the Gola et al. (2005) study the mixing ratios and isotope ratios with long path FTIR. In our study the mixing ratios were determined by GC-MS and the isotope ratios were measured by GC-IRMS in two different laboratories. Both labs
25 used different analytical set ups, different sampling methods and different standards. However, the results from both labs generally agree within ±1.5‰ on the 1σ level and show no systematic difference. As outlined before different initial δ¹³C(CH₃Cl) as well as different initial CH₃Cl mixing ratios had no significant effect on the determination of the KIEs. This makes analytical artefacts in our δ¹³C determination unlikely. The Cl radical generation scheme was quite similar among both studies. Gola et al. (2005) used narrow band photolysis of Cl₂ employing a Philips TLD-08
30 ~~fluorescent~~ fluorescent lamp (λ_{max} ~370) nm whereas we used broadband photolysis (300 to 700 nm) making this an unlikely source for the discrepancy in between the KIEs for the reaction of CH₃Cl with Cl.

In our study OH was generated via UV photolysis of ozone (steady state mixing ratios of 0.62 and 3.6 ~~μmol mol⁻¹~~ ~~ppm~~) in the presence of water vapor (RH of 70%) and 2000 ~~ppm~~ ~~μmol mol⁻¹~~ H₂ and ~~whereas~~ in the Gola study OH was generated in the absence of water vapor from the reaction of O(¹D) with H₂ (2000 ~~μmol mol⁻¹~~ ~~ppm~~) after UV-
35 photolysis of ozone (300 ~~μmol mol⁻¹~~ ~~ppm~~). Due to the much lower ozone mixing ratios employed in our study the OH generation in the absence of water vapor was not sufficient in our study. Both OH generation schemes are well

established. However, Cantrell et al. (1990), who used UV-photolysis in the presence of water as an OH source, estimated that the reaction of CH₄ 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

Gola et al. (2005) study suggest an overall higher transient O(¹D) concentration as compared to our experiments.

5 Anyhow, for CH₃Cl interferences from the reaction with O(¹D) are less likely than for CH₄. The reaction rate for methane with O(¹D) ($1.7 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$; Burkholder et al., 2015) is 2.7×10^4 times larger than the respective reaction rate for OH ($6.3 \times 10^{-15} \text{ cm}^3 \text{ s}^{-1}$). In the case of CH₃Cl the ratio is only 7.4×10^3 ($2.6 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$ and $3.5 \times 10^{-14} \text{ cm}^3 \text{ s}^{-1}$; Burkholder et al., 2015). [Hence the reaction with O¹D should contribute to less than 1 % to the observed CH₃Cl loss.](#)

10 None of our tests prior each degradation experiment revealed indication for a measurable loss of CH₃Cl. In the CH₃Cl control experiment all experimental parameters beside the relative humidity and hence the OH yield were comparable to CH₃Cl degradation experiments with OH. The CH₃Cl loss of less than 3% over 10h and can be attributed to reaction with OH. Hence this experiment further confirms the absence of any biasing side reactions and we can safely exclude any measurable effect from potential side reactions on the determination of the KIEs in our study.

15 A comparison of our data with previously measured and calculated KIEs for the reaction of CH₃Cl methane and other VOCs with OH and Cl is provided in table 3. In a follow up study to Gola et al. (2005), Sellevåg et al. (2006) attributed these exceptionally large fractionation factors to higher internal barriers of rotation of the OH radical compared to the CH₄ + OH reaction. Using variational transition state theory, the authors calculated KIEs of -47 ‰ and -37 ‰ for the reaction of CH₃Cl with OH and Cl, respectively. However, a simultaneous theoretical study provided a KIE of only -

20 3.6 ‰ for the reaction of CH₃Cl with OH (Jalili, & Akhavan, 2006). For C-H bond breakage, Streitwieser's semi-classical limit for isotope effects is -21 ‰ (Elsner et al., 2005) and for reactions involving hydrogen radical transfer, a KIE of -15‰, has been reported (Merrigan et al., 1990). Both values support a lower fractionation factor. For the reaction of ethane with OH that can be approximately regarded as a substituted methane a KIE of (-7.5±0.5) ‰ has been reported (Piansavan et al., 2017). One can estimate an upper limit for the reactive site by multiplying δ¹³C with

25 the number of carbon atoms in the molecule (Anderson et al., 2004). This leads to an upper limit of (-15.0±0.7) ‰ for the KIE at the reactive center. In line with this Anderson et al. (2004) reported a group kinetic isotope effect of -(-18.7±5.2) ‰ for the reaction of primary carbon atoms of alkanes with OH. The same group (Anderson et al., 2007) found a group kinetic isotope effect of (-18.6±0.3) ‰ for the respective reaction with Cl. Our smaller KIEs for the reaction of CH₃Cl with OH and Cl are much closer to these group specific KIEs than the previously reported ones of

30 Gola et al. (2005).

To this end, the large discrepancy between our data and those of Gola et al. (2005) remains unresolved and cannot be explained from experimental details. However, the strongest support for our lower KIE arises from the absence of any significant seasonal variation in the tropospheric δ¹³C(CH₃Cl), as outlined in section 3.2.

3 Carbon isotope modelling

3.1 Model set up

35 The model used in this study is similar to previous two box models (Tans, 1997; Sapart et al., 2012; Saltzman et al., 2004; Trudinger et al., 2004). The atmosphere is divided in two well-mixed semi hemispheric boxes, representing the

northern, and the southern hemisphere and the interhemispheric exchange time is 360 days. The model simulates the major sources and sinks for both, the lighter ($^{12}\text{CH}_3\text{Cl}$) and the heavier isotopologue ($^{13}\text{CH}_3\text{Cl}$), as described by Sapart et al. (2012) for methane. The source and sink terms from the Xiao et al. model study (2010) serve as a starting point for our model. We use a simplified mass balance with four source categories having distinct isotopic source signatures: higher plants / unknown, oceans, biomass burning, and other known sources (table 4). Total net emissions were fixed at 4010 Gg a^{-1} with 2210 Gg a^{-1} in the northern hemisphere and 1800 Gg a^{-1} in the southern hemisphere. Losses are specified by pseudo first order rate coefficients. The sinks implemented in the model are losses due to the reaction with OH, losses to the surface ocean, losses to soils, and losses to the stratosphere (table 4). The seasonal source and sink terms are specified for each hemisphere using monthly means (Fig. 2). For each source category, the carbon isotope source signature was randomly varied within the given uncertainties. Seasonal variations were modeled with a time step of 1 day, using monthly averaged source and sink terms. Variations in the source composition were modeled with a time step of 90 days, using yearly averaged source and sink terms.

3.1.1 Sources

The ocean is treated as a net source for CH_3Cl with annual net emission of 335 Gg a^{-1} (range: 80 to 610 Gg a^{-1} (Hu et al., 2013)). To account for the bidirectional nature of the gas exchange across the air/sea interface, net fluxes are broken down into unidirectional gross uptake and emission fluxes, with the uptake carrying the isotopic composition of the atmosphere and the emission carrying the isotopic information of the concurrent formation and degradation processes in the ocean. The gross uptake is calculated using an average transfer velocity of 17 cm h^{-1} for CO_2 (Wanninkhof 2014) and a mean tropospheric mixing ratio of $540 \text{ pmol mol}^{-1}$. Gross emissions are then calculated as the difference between net emissions and gross uptake fluxes. The reader should note that this approach differs from that of Hu et al. (2013) and results in larger gross fluxes because gross fluxes are calculated for the entire ocean surface. ~~In line with previous studies (Keppler et al. 2005), we estimate the average isotopic composition of dissolved CH_3Cl to $(-36 \pm 6) \text{ ‰}$.~~ Keppler et al. (2005) estimated average isotopic composition of dissolved CH_3Cl to $(-36 \pm 4) \text{ ‰}$. This value refers to Komatsu (2004), who reported a mean $\delta^{13}\text{C}$ of -38 ‰ for CH_3Cl in coastally influenced waters off Japan and more enriched $\delta^{13}\text{C}$ values in the range of -12 ‰ to -30 ‰ from the open North-East Pacific. We obtained average $\delta^{13}\text{C}$ values of $-43 \pm 3 \text{ ‰}$ from a productive lagoon in southern Portugal (Weinberg et al. 2014). Taking the biotic and abiotic degradation of CH_3Cl into account we estimate the mean isotopic source signature of the ocean source to $(-36 \pm 6) \text{ ‰}$.

We applied a source strength of 910 Gg a^{-1} for biomass burning (range from 660 to 1230 Gg a^{-1}) with 68% originating from the northern hemisphere and the emissions peaking during hemispheric spring (Xiao et al., 2010). CH_3Cl from biomass burning shows a $\delta^{13}\text{C}$ of $(-47 \pm 7) \text{ ‰}$ (Czapiewski et al., 2002; Thompson et al., 2002).

The category “other known sources” comprises fungi wetlands and anthropogenic emissions with a total source strength of 365 Gg a^{-1} (range: 79 to 1016 Gg a^{-1}) and an averaged isotopic source signature of $(-45.5 \pm 5.5) \text{ ‰}$ calculated from the source signatures given by Keppler et al. (2005). The emissions from the other known sources were constant over time with 16 Gg month^{-1} in the northern hemisphere and $5.3 \text{ Gg month}^{-1}$ in the southern hemisphere.

The source category “Higher plants / missing” (900 to 3095 Gg a^{-1}) represents mainly emissions from the tropical rain forest (900 to 2650 Gg a^{-1}) with minor contributions from saltmarshes (80 to 160 Gg a^{-1}), rice paddies (5 Gg a^{-1}) and mangroves ($\sim 50 \text{ Gg a}^{-1}$). These emissions are almost equally distributed between both hemispheres and show a slight

seasonal peak during hemispheric summer. In order to evaluate the emissions from higher plants, these emissions were divided into two fractions by introducing a split factor. The first fraction represents “true” emissions from higher plants, having an exceptionally depleted isotopic source signature of $(-83 \pm 15) \text{‰}$ (Saito & Yokouchi, 2008; Saito et al., 2008). The second fraction represents an unknown or missing source. The $\delta^{13}\text{C}$ of this source is scaled to match the $\delta^{13}\text{C}$ of tropospheric CH_3Cl . A more depleted $\delta^{13}\text{C}$ for this source would point towards additional contributions from a lighter source, such as senescent leaf litter, whereas a more enriched $\delta^{13}\text{C}$ for this source points towards additional contributions from a more enriched source.

Saito et al. (2013) recently reported on the bidirectional exchange of CH_3Cl across the leaves of tropical plants with gross uptake rates being roughly $1/6^{\text{th}}$ of gross emission rates. The authors hypothesized that the gross uptake may be related to endosymbiotic bacteria. [This uptake might affect the isotopic composition of \$\text{CH}_3\text{Cl}\$ from tropical rainforests. However,](#) because the incubation methods used in this study were the same as that previously used to determine the isotopic composition of CH_3Cl emitted from tropical plants (Saito & Yokouchi, 2008; Saito et al., 2008) we can reasonably assume that any [potential](#) isotopic effect of this bidirectional exchange is included in the previously reported carbon isotope ratios.

3.1.2 Sinks

The reaction with OH constitutes the single largest sink for CH_3Cl , accounting for approximately 80% of its removal from the troposphere. For this study, we used the OH-concentration fields from Spivakovsky et al. (2000) along with reaction rate constants of Burkholder et al. (2015) to derive monthly resolved lifetimes for both hemispheres. The [lifetimes-monthly loss rates](#) were then forced to reproduce seasonal variations of the mixing ratios at Mace Head in the northern hemisphere and at Cape Grim (Prinn et al., 2000), Tasmania, in the southern hemisphere. This resulted in a total tropospheric sink (OH + Cl) of 3614 Gg a^{-1} , being comparable to previous modeling studies (Xiao et al., 2010). In most global budgets, soils are treated as a small sink for chloromethane of about $\sim 250 \text{ Gg a}^{-1}$, though a larger uptake exceeding 1000 Gg a^{-1} has been suggested (Keppler et al., 2005; Carpenter et al., 2014). Based on Xiao et al. (2010), we a priori assumed a soil sink of 250 Gg a^{-1} with northern and southern hemispheric fractions of 180 and 70 Gg a^{-1} , respectively, reflecting the interhemispheric distribution of the land masses.

The microbial degradation of CH_3Cl in soils is assigned with a large carbon isotope [fractionation effect](#) of -47‰ (Miller et al., 2001; 2004). The only study, we are aware of, (Redeker et al., 2012) that investigates the isotopic composition of soil derived CH_3Cl reports a $\delta^{13}\text{C}$ of $(-34 \pm 14) \text{‰}$. This suggests a substantially smaller apparent KIE for the soil uptake of CH_3Cl . The soil uptake of CH_3Cl can be regarded as a coupled diffusion reaction process, where CH_3Cl is first transported into the soil and then undergoes microbial degradation. The apparent KIE of such coupled processes will depend on the KIEs of both steps and can be estimated from diffusion reaction models (Farquhar et al., 1982):

$$\varepsilon_{app} = \varepsilon_d + \frac{(\varepsilon_m - \varepsilon_d) * (m_d - m_m)}{m_d} \quad (4)$$

with ε_d and ε_m being the kinetic isotope effects assigned to microbial degradation (47‰) and diffusion (4‰) respectively. m_d is the total mass of CH_3Cl that enters the soil via diffusion and m_m represents the net soil sink.

The gross uptake flux (m_d) was estimated using a simple transfer resistance model along with the biomes and respective active seasons as previously used (Shorter et al., 1995). We used an overall atmospheric transfer resistance

governing the transport to the soils surface (aerodynamic transport resistance, quasi-laminar sublayer resistance and in canopy transfer resistance) of 4 s/cm regardless of the biome that was derived from reported typical transfer resistances for different biomes (Zhang et al., 2003). The soil uptake is governed by molecular diffusion through the air filled pore space. The soil side transfer resistance can be estimated from the effective diffusion in the soil column.

5 For a first rough estimate of the soil transfer resistance, we assume an air filled pore space of 0.3 (V/V) and a microbially inactive soil layer of 0.5 cm at the soil surface. Using the Penman model (Penman, 1940) and a diffusion coefficient of $0.144 \text{ cm}^2\text{s}^{-1}$ in air, we obtain a soil transfer resistance of 17 s/cm. With a globally averaged transfer resistance of 21 s cm^{-1} and a CH_3Cl background concentration of $540 \text{ ppt-pmol mol}^{-1}$ and the land use categories from Shorter et al. (1995) we obtain an upper limit of 1300 Gg a^{-1} for m_d .

10 As depicted in figure 3, the apparent KIE of the soil uptake is bracketed by the kinetic isotope effect of both steps and decreases when increasing the net soil uptake. The microbial degradation is rate limiting at low net uptake rates, and the apparent KIE of the soil uptake is close to that for microbial degradation. For instance, a soil sink of 250 Gg a^{-1} reveals an apparent KIE of -38%. When the entire chloromethane diffusing into soils is microbially degraded, diffusion becomes the rate limiting step, and the apparent KIE matches that of diffusion.

15 In turn the imprint on the tropospheric $\delta^{13}\text{C}$ shows a parabolic distribution with a maximum at $m_m = 0.5 m_d$. The isolated effect of the soil sink would result in a maximum enrichment of 3.8‰ in the tropospheric $\delta^{13}\text{C}$ 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 depletion in the tropospheric $\delta^{13}\text{C}$ once the apparent KIE of the soil sink becomes smaller than the KIE of the OH sink.

20 3.2 Modelled seasonal variations in the $\delta^{13}\text{C}$ of tropospheric CH_3Cl

Tropospheric CH_3Cl shows a pronounced seasonal cycle with an amplitude of $85 \text{ parts-per-trillion-by-volume}$ (ppt-pmol mol^{-1}) in northern hemispheric mid-latitudes (Prinn et al., 2000; Yoshida et al., 2006), reflecting the seasonality in the OH sink. This implies an inverse co-variation in the $\delta^{13}\text{C}$ of tropospheric CH_3Cl to an extent that is closely linked to the KIE of the OH sink. Our model ~~nicely~~ resembles mean tropospheric mixing ratios of about ~~539~~

25 $540 \text{ pmol mol}^{-1}$ (ppt-pmol mol^{-1}) (Monzka et al., 2010; Carpenter et al., 2014) and the seasonal cycles of CH_3Cl in both hemispheres within $\pm 4\%$ (Fig. 4 upper panel). In our simulations, a KIE of -59‰ of the OH sink, produces an inverse co-variation of the $\delta^{13}\text{C}(\text{CH}_3\text{Cl})$ with CH_3Cl mixing ratios with a seasonal amplitude of 9.2‰, whereas our new smaller KIE of -11.2‰ results in a seasonal amplitude of only 1.7‰ (Fig 4 lower panel). In both cases, random variations of $\pm 10\%$ on a 30 day base in the isotopic source signatures, seasonal variations of the emission functions and variations in the

30 soil sink resulted in a scatter of $\pm 2\%$ for the $\delta^{13}\text{C}$ of tropospheric CH_3Cl but did not significantly affect the differences in the seasonal amplitude of the $\delta^{13}\text{C}$ signal (See supplement for further details).

Most of the seasonal variation in the combined isotopic source signal ($\pm 4\%$) is attenuated by the large tropospheric background, resulting in seasonal variations of the northern hemispheric $\delta^{13}\text{C}$ of less than $\pm 1.1\%$ attributable to the isotopic source signal. In a year round study carried out in Alert, Canada Thompson et al. (2002) found no clear

35 correlation between the CH_3Cl mixing and isotope ratios. From their data the authors estimated the KIE for the OH sink being less than 5‰. As shown in figure 2 (lower panel) the seasonal variation in the tropospheric $\delta^{13}\text{C}(\text{CH}_3\text{Cl})$ modelled with our KIE of -11.2‰ fit quite well to the measured variation given by Thompson et al. (2002). The lack of a significant co-variation between the mixing ratios and carbon isotope ratios was confirmed in second year round

study (Rhew et al 2007). In sum the lacking covariation between the mixing ratios and carbon isotope ratios strongly supports our new KIE of -11.2‰ and make the previously reported larger KIEs highly unlikely.

3.3 Implications for the tropical rainforest source

A KIE of -59‰ for the OH sink requires a mean mass weighted isotopic source composition of -84.5‰ to balance the tropospheric $\delta^{13}\text{C}(\text{CH}_3\text{Cl})$ of (-36.4 ± 2.1) ‰ (Thompson et al., 2002), as shown in previous studies. Apart from large emissions from higher plants (Keppler et al., 2005; Saito & Yokouchi, 2008) in tropical rainforests, this KIE suggests additional substantial emissions from an even more depleted source, such as senescent leaf litter (Keppler et al., 2005; Saito & Yokouchi, 2008). In contrast, the revised smaller KIE of -11.2‰ requires a mean isotopic source signature of -48.5‰, being close to the mass weighted $\delta^{13}\text{C}$ of all other known sources excluding higher plants. Along with higher plant emissions of 2200 Gg a^{-1} , the new KIE of -11.2‰ yields a mean tropospheric $\delta^{13}\text{C}(\text{CH}_3\text{Cl})$ of -56‰, being depleted by almost 20‰ in comparison to the mean reported tropospheric $\delta^{13}\text{C}(\text{CH}_3\text{Cl})$.

We performed more than 10,000 steady state runs with random variations in the isotopic composition of tropospheric CH_3Cl (-36.4 ± 2.1 ‰), the isotopic source signatures ~~as indicated above (table 4)~~ and the KIE of the soil sink to assess the range of CH_3Cl -emissions from higher plants. The source category “Higher plants” was divided in two fractions, one representing “true” emissions from higher plants and the other representing missing emissions. The $\delta^{13}\text{C}$ of the missing emissions was always scaled to match the tropospheric $\delta^{13}\text{C}(\text{CH}_3\text{Cl})$.

As shown in Figure 5, the strength of the tropical rainforest source is directly linked to the strength and isotopic composition of missing emissions. A tropical rainforest source of $600 \pm 200 \text{ Gg a}^{-1}$ suggests missing emissions of $(16400 \pm 200) \text{ Gg a}^{-1}$, requiring a $\delta^{13}\text{C}$ of (-45 ± 6) ‰ to balance the tropospheric $\delta^{13}\text{C}(\text{CH}_3\text{Cl})$. This $\delta^{13}\text{C}$ is close to the mean isotopic composition of all other known sources. [Increasing the emissions from all other known sources within the given ranges might reduce the missing emissions by about 500 Gg a⁻¹.](#) ~~Increasing~~ A further increase of the tropical rainforest ~~source emissions~~ results in an equivalent reduction in missing emissions but requires a more enriched $\delta^{13}\text{C}$ for the missing emissions. For instance, balancing a tropical rainforest source of $1100 \pm 200 \text{ Gg a}^{-1}$ requires missing emissions of the same magnitude having a $\delta^{13}\text{C}$ of -31 ± 6 ‰. This is at the upper end of reported source signatures and may thus serve as a boundary to constrain the rainforest source from an isotopic perspective.

4 Carbon density based revision of the tropical rainforest source

Interestingly, support for our lower estimate arises from previous studies on the tropical rainforest CH_3Cl source when using above ground carbon density instead of coverage area for upscaling the CH_3Cl emission factors.

Large uncertainties in upscaling of local derived plant emissions to global scales can arise from i) temporal variations in the emissions, ii) spatial variability in environmental drivers, species composition and vegetation cover. Within the widely used FAO land cover classes, forests are defined as land with a tree cover exceeding 10%, a potential tree height of 5 m and an area of at least 0.5 ha (FAO, 2012). Tropical rainforests encompass such sparsely covered areas with a carbon density of only a few Mg ha^{-1} (Asner et al., 2010; Pereira Junior et al., 2016) as well as very dense mature rainforests with a canopy height of more than 40 m and above ground carbon densities sometimes exceeding 300 Mg ha^{-1} (Kato et al, 1978). This suggests a large variability in biomass that cannot be assessed with the previously used area based upscaling approaches. Area based estimates may be improved by leaf area index or above ground

carbon density based approaches. There is some indication that CH₃Cl is mainly emitted by mature trees (Saito & Yokouchi, 2008; Saito et al., 2008; 2013). This is more readily reflected by carbon density than by leaf area. Further the available carbon density data products allow a direct discrimination between tropical forests and other tropical vegetation. We thus propose a carbon density based upscaling approach of experimentally derived emission factors to reduce uncertainties arising from the spatial variability in above ground biomass. We first convert reported area based emission factors to carbon density based emission factors and then multiply them with the carbon stock of the tropical rainforest:

$$F(CH_3Cl) = \frac{E_F * C_{RF}}{C_{st}} \quad (5)$$

Here $F(CH_3Cl)$ is the source strength [Gg a⁻¹], E_F is the experimentally derived emission factor [Gg ha⁻¹ a⁻¹], C_{st} is the above ground carbon density assigned to the sampling site [Gg ha⁻¹] and C_{RF} is the estimated total above ground biomass [Gg] of the respective biome, in this case the tropical rainforest.

The first direct evidence for strong CH₃Cl emissions from tropical plants came from branch incubations of tropical plants in a greenhouse (Yokouchi et al., 2000). This study revealed particularly high emission from dipterocarp species being dominant in tropical lowland rainforests of South and Southeast Asia, and suggested mean CH₃Cl emissions of 74 μg m² h⁻¹. Several follow up studies carried out in tropical rainforests reported ten- to fivefold lower fluxes (Saito et al, 2008; 2013; Gebbhard et al., 2008; Blei et al., 2010). We exclude the high emission factor from the greenhouse study from our reanalysis of the tropical rainforest source and focus on the studies, providing experimentally derived emission factors for CH₃Cl emissions from tropical forests and allowing for a sufficient estimate of carbon densities assignable to them. Details on these studies are provided in table 5. Three studies have been carried out in lowland tropical rainforests of South East Asia, and one has been carried out over Surinam in South America. We are not aware of any CH₃Cl flux measurements from African tropical rainforests. Two studies relied on branch or leaf incubation to measure CH₃Cl fluxes (Saito et al, 2013; Blei et al., 2010). A third study used a micrometeorological approach and in addition performed leaf and branch incubation (Saito et al, 2008). The remaining study (Gebbhardt et al., 2008) derived CH₃Cl emissions factors from concentration gradients above the rainforest. The concentration gradients were obtained from canister samples taken at different heights above the rainforest from an airplane. The results from branch and leaf incubations were first normalized to leaf dry weight and then converted to area based emission factors using reported allometric data for Southeast Asian tropical lowland rainforests along with assumptions on the distribution and abundance of the investigated species. The mean area normalized fluxes (8.0 μg m² h⁻¹ ±45%) from these studies show a notably larger variability than the original leaf biomass normalized fluxes (0.028 μg g⁻¹h⁻¹ ±10%), although all three studies referred to the same allometric data (Yamakura et al., 1986) in their conversion. Noteworthy, the study reporting the lowest emissions factors from branch enclosures reported almost three times higher fluxes using a micrometeorological approach. In sum, the area based factors agree within a factor of 3 and ranged from 5.0 to 14 μg m² h⁻¹ (9.1 μg m² h⁻¹ ±37%).

The three south East Asian studies refer to a dense and mature dipterocarp forest with an above ground carbon density of (265±44) Mg C ha⁻¹ (Yamakura et al., 1986) that we apply here. For the study carried out above the rainforest of Surinam, we derived a carbon density of (160±15) Mg ha⁻¹ from carbon density maps (Saatchi et al., 2011; Baccini et al., 2012). This range agrees with the FAO estimate for French Guyana (FAO, 2015) and is supported by several field surveys carried out in this region (Chave et al., 2001; 2008). With this, we obtain a mean carbon density based emission factor of (4.0±1.2) g Mg⁻¹, referring to a mean carbon density of 202 Mg ha⁻¹. This is well above the average tropical

rainforest carbon density, ranging from 96 to 117 Mg ha⁻¹ (Bachini et al., 2012; Saatchi et al., 2011; Köhl et al., 2015; FAO, 2015).

In consequence, our carbon density based estimates of the tropical CH₃Cl source are 30 to 70% lower than the respective area based estimates (table 6). The difference is in the range of 30% for dense old grown evergreen forests such as the Tierra Firme forests of French Guyana, between 40% and 50% for the moist tropical rainforest, and increases to almost 70% for the entire pantropical forests including dry tropical forests, degraded forests and plantations. This trend reflects the decreasing trend in carbon density in the tropical rainforest biomes as well as the effect of forest degradation. Regardless of the source for the carbon density estimates, our approach suggests a tropical rainforest CH₃Cl source of (670±250) Gg a⁻¹, being 53% to 65% lower than the respective area based estimates in the range 1200 to 2000 Gg a⁻¹ (Saito et al., 2008; 2013; Gebbhard et al., 2008; Blei et al., 2010).

The uncertainty in the area based emission factors is estimated to 24% from the standard deviation of the reported means. Additional uncertainties for our carbon density based upscaling (as compared to the previous area based upscaling) arise from the uncertainties in the total above ground carbon stocks (±8.6%) and the site specific carbon density (±15%). Using error propagation, we estimate the ~~total~~ uncertainty of our approach to ±30.4% with respect to the available data. - However, we note an urgent need for more detailed flux studies. Currently there is no information about how physiological and environmental drivers might affect CH₃Cl emissions from tropical rainforests. Apart from the observation that some members of the Dipterocarpaceae family are particular strong emitters of CH₃Cl, this also holds true with respect to species composition.

5 Conclusions

We reported new KIEs for the reaction of CH₃Cl with OH and Cl of (-11.2±0.8) ‰ (n=3) and (-10.2±0.5) ‰ respectively being five to seven times smaller than the previous reported KIEs for these reactions. The cause for the large discrepancies remains unresolved. However, the strongest support for the reliability of our new fractionation factors arises from the absence of any significant co-variation in the mixing and carbon isotope ratios of tropospheric CH₃Cl.

Conjoining our new KIEs of the tropospheric CH₃Cl sinks and the biomass based upscaling of previously reported emission factors suggest a tropical vegetation source of only (670±210) Gg a⁻¹, being about threefold smaller than suggested in current budgets. We assign δ¹³C of -45±6‰ to the missing emissions of (1530±190) Gg a⁻¹. Notably increasing the soil sink by 750 Gg a⁻¹ and decreasing biomass burning emissions by 460 Gg a⁻¹, as suggested in the latest assessment on ozone depleting substances (Carpenter et al., 2014)³ would substantially increase this gap but have a negligible effect on the isotopic composition of the missing emissions. The δ¹³C value of the missing emissions matches with the mean source signature of the other known sources (except rainforests). Increasing these emissions within the given ranges might reduce the gap to (1100±200) Gg a⁻¹. From a purely isotopic perspective, in particular larger emissions from biomass burning could further reduce this gap. However, this is highly speculative as virtually any source combination providing a mean δ¹³C of -45±6‰ could fill the gap.

With CH₃Cl being the single largest natural carrier of chlorine to the stratosphere, predicting future baselines of stratospheric chlorine require a better understanding of the global CH₃Cl cycle and an identification of the missing emissions.

Data availability. The data used in this publication and the model code are available to the community and can be accessed by request to the corresponding author.

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Author contributions E.B., F.K, J.W. and C.Z. designed the experiment, E.B, J.W and C.Z carried out the Smog chamber experiments. M.G carried out the isotope analysis in Heidelberg and E.B carried out the isotope analysis in 15 Hamburg. E.B performed the modelling work. All authors contributed equally to the preparation of the manuscript.

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7 Tables

Table 1: Experimental conditions of the degradation experiments with OH. The O₃ mixing ratios are average steady state mixing ratios throughout the experiment, the Cl₂ mixing ratios refer to the initial mixing ratios at the beginning of each photolysis sequence.

Exp.	reactant	$\frac{\text{ppmv} \cdot \mu\text{mol}}{\text{mol}^{-1}}$	oxidant	$\frac{\mu\text{mol mol}^{-1}}{\text{ppmv}}$	O ₃ Cl ₂	Irridiation	H ₂	$\frac{\mu\text{mol mol}^{-1}}{\text{ppmv}}$	rel. Hum.	T	OH
								%	°C	cm ⁻³	
1 & 2	CH ₃ Cl	5, 10	OH	0.62		1x55W, $\lambda_{\text{max}} = 254 \text{ nm}$	2000	65	20.7	2.9×10^9	
3	CH ₃ Cl	0.13	OH	0.62		1x55W, $\lambda_{\text{max}} = 254 \text{ nm}$	2000	< 1	20.6	8.7×10^7	
4	CH ₃ Cl, CH ₄	13, 5	OH	3.7		4x55W, $\lambda_{\text{max}} = 254 \text{ nm}$	2000	65	20.4	1.6×10^{10}	
5	CH ₄	5		0		4x55W, $\lambda_{\text{max}} = 254 \text{ nm}$		72	20.3		
6	CH ₄	6	OH	3.7		4x55W, $\lambda_{\text{max}} = 254 \text{ nm}$		72 to 75	20.3	1.6×10^{10}	
7	CH ₃ Cl	10	Cl	10		7x1200W 300 - 700 nm		< 1	20.7		
8	CH ₄	5	Cl	10		7x1200W 300 - 700 nm		< 1	20.5		

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Table 2: Summary of the kinetic isotope effects for the reaction of CH₃Cl and CH₄ with OH and Cl from this study. We used orthogonal regression to calculate ϵ and the respective uncertainties on the 1 σ level for each experiment. In experiment 4 the ϵ for methane has not been determined.

		Hamburg		Heidelberg		
		ϵ	R ²	ϵ	R ²	
Exp. 1	CH ₃ Cl + OH	-12.1 ± 0.6	0.95	-11.7 ± 0.4	0.99	
Exp. 2		-12.1 ± 0.3	0.99	-10.5 ± 0.3	0.99	
Exp. 4		-10.4 ± 0.4	0.99	-10.6 ± 0.6	0.99	
Exp. 7	CH ₃ Cl + Cl	-10.3 ± 0.7	0.96	-10.4 ± 0.4	0.98	
Exp. 5	CH ₄ + OH			-4.7 ± 0.2	0.99	
Exp. 8	CH ₄ + Cl			-59.0 ± 1.3	0.99	

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Table 3: Compilation of kinetic isotope effects for the reaction of CH₃Cl, CH₄ and alkanes with OH and Cl

Reaction	ϵ	Method	Reference
CH ₃ Cl + OH	-58 ± 10	Smog chamber; O ₃ +H ₂ +hv (254 nm), FTIR	Gola et al., 2005
	-44	theoretical at 298K	Feilberg et al., 2005
	-3.6	theoretical	Jalili, S. & Akhavan, 2006
	-5 ± 3	derived from field data	Thompson et al., 2002
	-11.2 ± 0.8	Smog Chamber; O₃+H₂O+hv (254 nm), GC-IRMS	This study
CH ₃ Cl + Cl	-70 ± 10	Smog chamber; Cl+hv (370 nm), FTIR	Gola et al., 2005
	-35	theoretical at 298K	Feilberg et al., 2005
	-10.4 ± 0.5	Smog Chamber; Cl₂+hv GC-IRMS	This study
CH ₄ + OH	-3.9 ± 0.4	photo reactor; H ₂ O ₂ +hv, GC-IRMS	Saueressig et al. 2001
	-4.7 ± 0.2	Smog Chamber; O₃+H₂O+hv (254 nm), GC-IRMS	This study
CH ₄ + Cl	-58 ± 2	Smog chamber; Cl ₂ +hv FTIR	Sellevåg et al., 2006
	-66 ± 2	photo reactor; Cl ₂ +hv; TDLAS	Saueressig et al., 1995
	-62 ± 0.1	Smog Chamber; Cl ₂ +hv; DI-IRMS	Tyler et al., 2000
	-59	Smog Chamber; Cl₂+hv GC-IRMS	This study
C ₂ H ₆ + OH	-7.5 ± 0.5	reaction chamber; H ₂ O ₂ + hv; GC-IRMS	Piansawan et al., 2017
R-CH ₃ + OH	-18.7 ± 5.2	reaction chamber; R-NO ₂ , NO + hv; GC-IRMS	Anderson et al., 2004
R-CH ₃ + Cl	-18.6 ± 0.3	reaction chamber; Cl ₂ + hv; GC-IRMS	Anderson et al. 2007

Table 4: Simplified CH₃Cl source and sink scheme used in the model

sources	strength [Gg a ⁻¹]		δ ¹³ C (source) / ε (sink) [‰]		
	best	range	best	Range (1σ)	
Biomass burning	910	655 - 1125	-47	-40 - -52	
Oceans	335	210 - 480	-36	-30 ₊ - -42 ₊	
Higher Plants / unknown	2400	0 - 3095	-83	-70 - -96 -39 ₊ 40	
Other known sources	365	79 - 1016	-45	- -50 ₊ 51	
sinks					
				-11.2 ₊ / -	
OH, Cl	3614	3564 - 3000	59		
soils*	250	200 - 1000	-37	-46 - -2	
stratosphere	146		0		

* The apparent KIE of the soil sink depends on its strength. See text for more details

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Table 5: Calculation of carbon density based CH₃Cl emission factors from previously reported area based emission factors.

Site	Method	Carbon density	Emission per			Carbon density	Ref.
			leaf mass	dry	area		
		Mg ha ⁻¹	μg g ⁻¹ h ⁻¹	μg m ⁻² h ⁻¹	g ha ⁻² a ⁻¹	g Mg ⁻¹ a ⁻¹	
Glass house, Japan	branch enclosure	325	0.32	74,0			Yokouchi et al., 2000
Pasoh Forest Reserve, Malaysia	micrometeorological	265		14,0	1226	4.6	Saito et al., 2013
	branch enclosure		0.03	5,0			
Pasoh Forest Reserve, Malaysia	branch enclosure	265	0.026	7,0	615	2.3	Saito et al., 2013
Danum Valley, Borneo	branch enclosure	265	0.03	12,0	1051	4	Blei et al., 2010
Borneo							
Surinam, French Guyana	gradient above canopy	160		9,5	832	5.2	Gebhardt et al., 2008
mean					931	4	
SD					265	1.2	

5 **Table 6: Comparison of calculated area based and carbon density based emissions from tropical forests**

Region	Area	C density	Area based		Carbon density based		
	10 ⁶ ha	10 ⁶ g ha ⁻¹	Gg a ⁻¹		Gg a ⁻¹		% of area based
Brazil	586	112 ¹	496	± 143	247	± 73	50
Indonesia	165	112 ¹	140	± 40	69	± 20	50
Congo	205	92 ¹	173	± 50	71	± 21	41
Trop. Africa	775	62 ¹	655	189	182	± 53	28
Trop America	1209	77 ¹	1022	295	356	± 103	35
Trop Asia	474	98 ¹	401	116	176	± 51	44
Pantropics	2458	78¹	2079	± 601	720	± 212	35
Trop. Africa	393	82 ²	332	± 96	121	± 36	36
Trop America	788	116 ²	666	± 192	343	± 101	52
Trop Asia	289	119 ²	244	± 71	129	± 38	53
Pantropics	1470	105²	1243	± 359	580	± 171	47

¹ Saatchi et al. , 2011; ² Bacchini et al., 2012

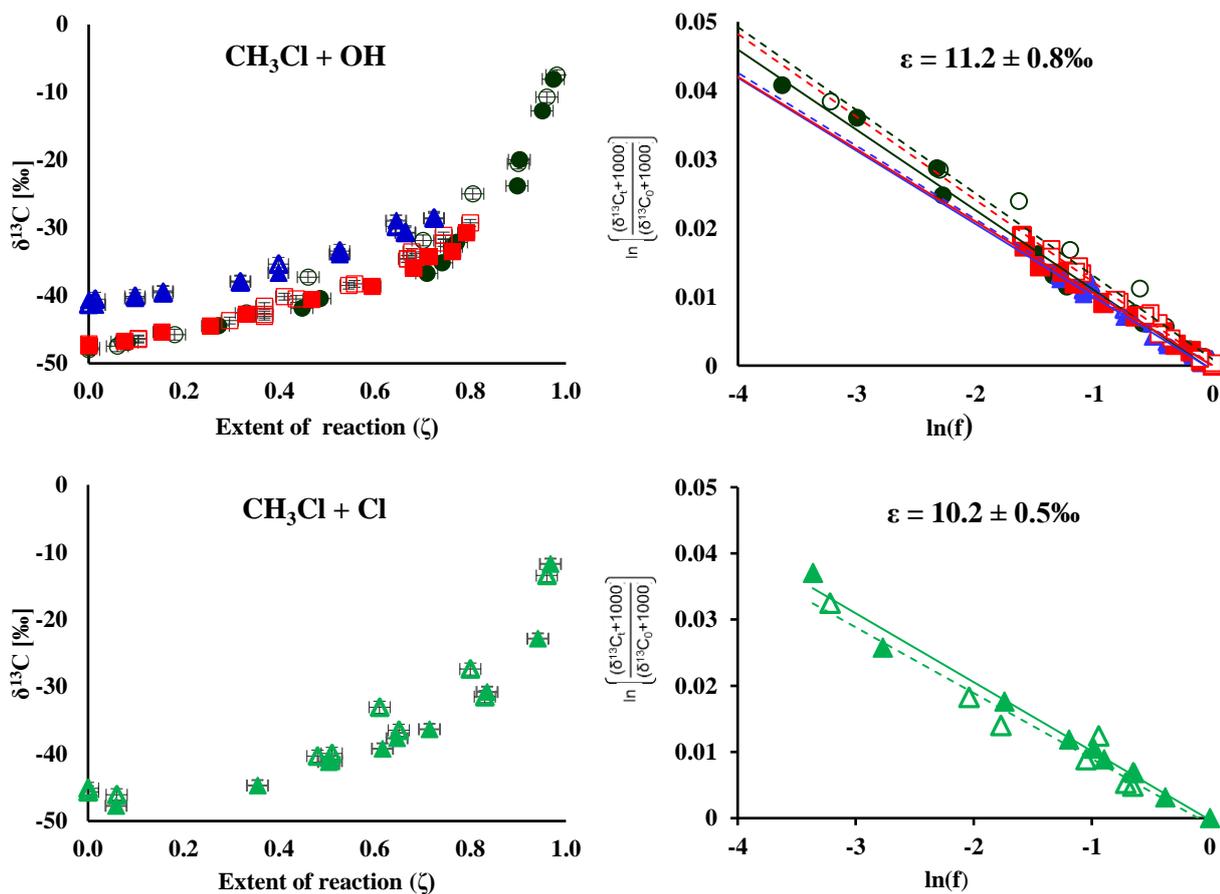
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8 Figures

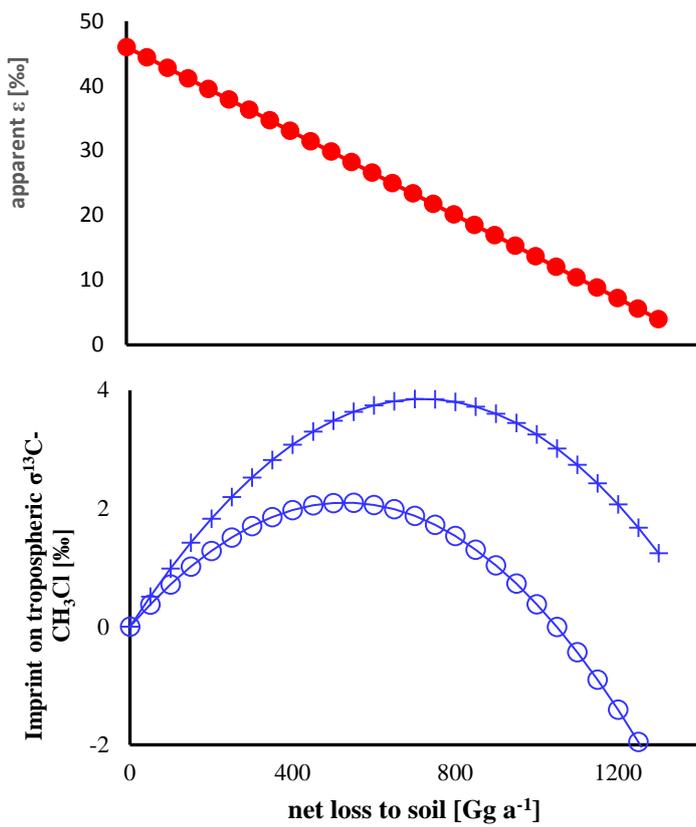
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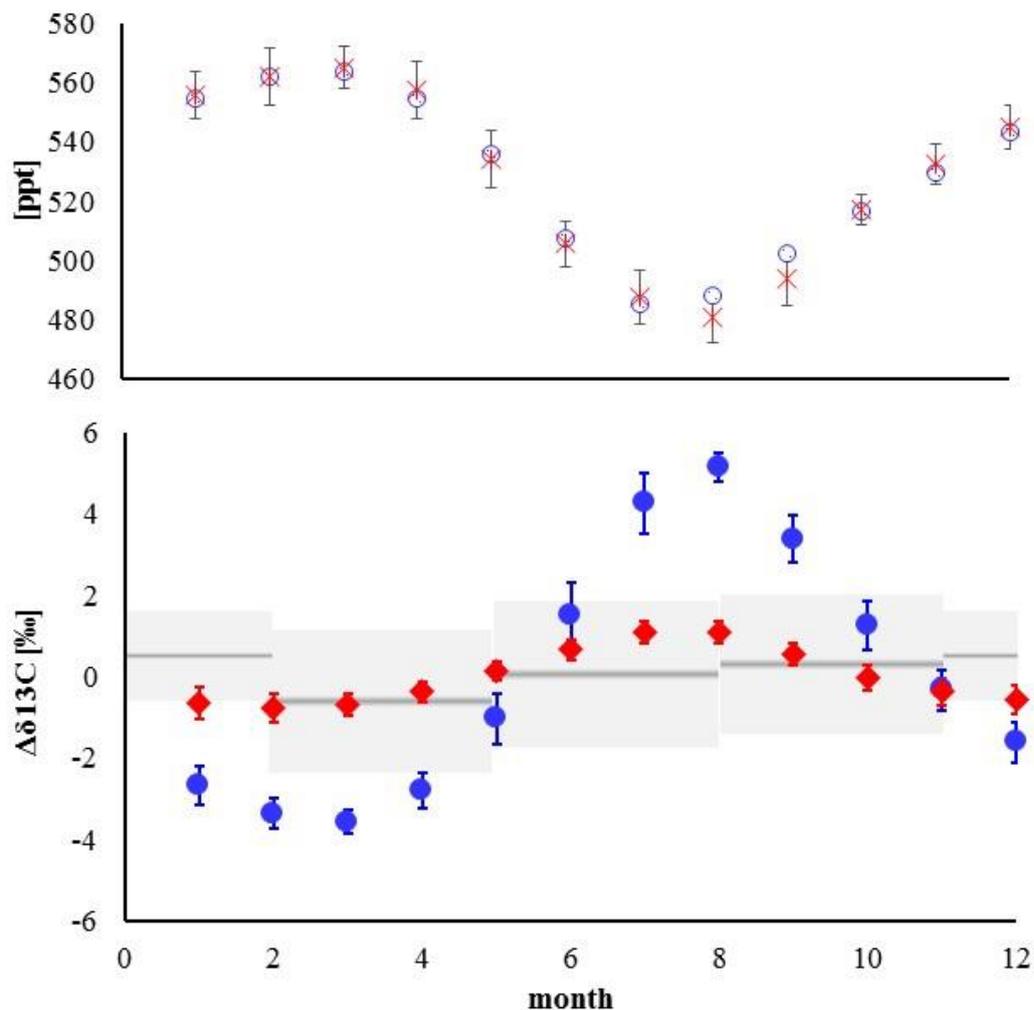
10 Figure 1: Change in $\delta^{13}\text{C}$ over extent of reaction (left hand side) and corresponding Rayleigh plots (right hand) from the CH_3Cl degradation experiments. Filled symbols and regression lines refer to the data from Heidelberg, open symbols and dashed regression lines show data from Hamburg. The colors refer to different degradation experiments (black: experiment 1; red: experiment 2, blue: experiment 4 and green experiment 7). Errors in ζ were $\pm 2\%$ on the 1σ level. Errors in $\delta^{13}\text{C}$, as derived from the regression analysis, ranged from ± 0.4 to $\pm 1.4\%$ on the 1σ level.



Figure 2: Chloromethane emissions in Gg month⁻¹ for the northern (left side) and southern hemisphere (left side) Upper row panel: Combined emissions from higher plants and the unknown source; second row panel: biomass burning, third row panel: ocean net emission fluxes, fourth row panel total emissions. The emissions from the other known sources are constant over time with 16.6 Gg month⁻¹ in the northern hemisphere and 5.8 Gg month⁻¹ in the southern hemisphere.



5 **Figure 3: The upper panel shows the apparent ϵ of the soil sink versus the sink strength. The lower panel shows the resulting effect on tropospheric $\delta^{13}\text{C}$. Crosses show the pure effect e.g. in the absence of any other fractionating sink. Open circles show the resulting effect with an ϵ of -11.2‰ assigned to the OH sink.**



5 **Figure 4:** Upper panel: Comparison of modeled Northern hemispheric mixing ratios (blue open diamonds) with measured
 10 mixing ratios at Mace Head, Ireland (red crosses) for the period from 2004 to 2014 (Prinn et al., 2000). Error bars indicate
 the variations in the monthly means on the 1σ level. Lower panel: Modeled seasonal fluctuations in the $\delta^{13}C$ of northern
 hemispheric CH_3Cl using an ϵ of -11.2‰ (red filled diamonds) and an ϵ of -59‰ (blue filled dots) as reported by Gola et
 al. (2005). The panel shows monthly averages from a 10-year simulation. The error bars indicate uncertainties ($\pm 1\sigma$) from
 monthly random variations in the $\delta^{13}C$ of each source category as indicated in the text. The grey shaded area shows reported
 seasonal variations (seasonal mean $\pm 1\sigma$) from Thompson et al. (2002).

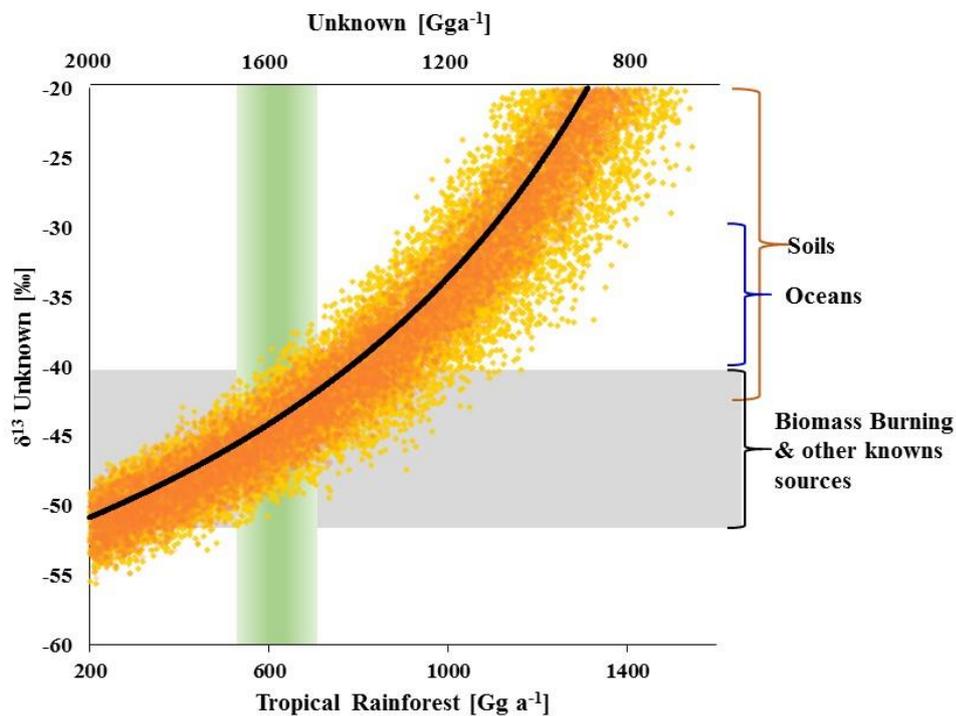


Figure 5: Modeled isotopic composition of the missing source versus tropical rainforest emissions on the lower x-axis and missing emissions on the upper x-axis (rainforest = 2200 – unknown). The black line shows the best estimate derived from the mean isotopic source signatures. Orange dots indicate the range uncertainty (1σ) from uncertainties (1σ) in the $\delta^{13}\text{C}$ of biomass burning ($\pm 7\text{‰}$), ocean net emissions ($\pm 6\text{‰}$) and other known sources ($\pm 6\text{‰}$). Yellow dots mark the additional uncertainty from the $\delta^{13}\text{C}$ of the tropical rainforest source ($\pm 10\text{‰}$). The green column indicates the carbon density based estimate of the rainforest source and the grey bar indicates the range in $\delta^{13}\text{C}$ of biomass burning and the mean from all sources excluding the tropical rainforest.

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