Point by point reply to J. Rudolph (Referee comment are in italics): 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.

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 before, but the measurements presented here hugely differ from those previously re- ported. 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 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 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 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 exists. Since by definition the seasonal variability of the carbon isotope ratio for an unknown source is not 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 e 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 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 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 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 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 CH_3Cl 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 source signatures have a surprisingly small effect on the tropospheric $\delta^{13}C(CH_3Cl)$, mainly because of the strong dilution effect of the tropospheric background. In our simulations seasonal variations in the combined isotopic source signature of about ±4 ‰ induced seasonal fluctuations in the tropospheric $\delta^{13}C(CH_3Cl)$ of less than 1.1 ‰. Seasonal variations in the range of ±7 to ±11 ‰ in the combined source signature, 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 $\delta^{13}C(CH_3Cl)$ 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 $\delta^{13}C(CH_3Cl)$ 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.

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 lab- oratory studies of isotope effects.

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?

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.

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 CH_3Cl 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 CH_3Cl 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 CH_4/CH_3Cl 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 CH_4 and CH_3Cl, 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 O^1D with H_2. In any case this experiment provides an upper limit of 3% for contributions from other possible reactions to the observed loss of CH_3Cl.

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 ± 1 σ un- certainty 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 ±1 σ uncertainty range with ±1σ 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 form 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±190) Gg a^{-1} to (1100±200) 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 CH_3Cl emissions from tropical rainforests. Apart from the observation that some members of the Dipterocarpacae family are particular strong emitters of CH_3Cl, 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 m^2 in their flux conversion from leaf biomass to m^2. 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 CH_3Cl flux studies in the tropics.

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

Authors reply: Change applied.

1,23 (and other locations): 3500 dm3

Authors reply: We now use dm^3 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.

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.

3, 27: 2 dm3

Authors reply: We now use dm^3 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

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 justified.

Authors reply: Change applied.

4,2: Notwithstanding?

Authors reply: The sentence has been changed to read "A combustion reactor filled with copper (II) oxide at 850°C was used to convert CH_3Cl and CH_4 into CO_2."

4, 5: Based on error propagation the 1 σ error of measurements the difference should be ± 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.

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.

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 “measureable 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.

5,22: ... 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. 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 being switched on. This experiment revealed no methane loss over 10 h. With this we can exclude any interferences from reactive chlorine during the CH_4-OH experiment. The higher KIE 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, found an even higher KIE of (-5.4 ±0.9) ‰ and estimated that the reaction of CH_4 with $O(^1D)$ 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.

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 time scales of mixing and reaction according to the following equation (Morgan et al., 2004; Kaiser et al., 2006) :

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

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

$$\epsilon_{\mathrm{obs}} \approx 0.99 \times \varepsilon_{\mathrm{i}}$$

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 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 δ^{13}C of -38‰ for CH_3Cl in coastally influenced waters off Japan and more enriched δ^{13}C values in the range of -12‰ to -30‰ from the open North-East Pacific. We obtained average δ^{13}C values of -43 ±3 ‰ from a productive lagoon in southern Portugal (Weinberg et al. 2014). Taking the biotic and abiotic degradation of CH3Cl 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 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 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 CH3Cl 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 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.

8,25-30: "The lifetimes where 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".

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 CH_3Cl concentration fields, which cannot be adequately represented in a two box model.
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 $\delta^{13}C(CH_3Cl)$ against seasonal and random variations in the isotopic source signatures.

9,11: spore space
Authors reply: This should be pore space and has been corrected.

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.

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 $\delta^{13}C(CH_3Cl)$ 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 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 ± n σ probability range, a percentile, a firm limit based on a given probability?)*

Authors reply: Please refer to response of comment above.