**Atmospheric
Chemistry
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Discussions

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Interactive comment on "Evidence for a major missing source in the global chloromethane budget from stable carbon isotopes" *by* Enno Bahlmann et al.

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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 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 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 s serious gap in the current understanding of the atmospheric budget of chloromethane. 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. 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? 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 that the uncertainty of the measurements and larger than discrepancies reported previously in similar studies, including chloromethane. 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? 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.

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 uncertainty range, a given percentile, or even a firm boundary (which would be difficult to interpret)? Some more explanations are needed. 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.

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.

Technical details:

Page, line 1,21: remove e.g. 1,23 (and other locations): 3500 dm3 1, 28 (and other locations): Avoid inconsistencies in use of isotope fractionation, fractionation factor, kinetic isotope effect (definitions page 4, lines10-14). 1,30: remove tropical, I am not sure how well a two box model can support a specific unknown "tropical" source. 3, 27: 2 dm3 3, 27: baked out at which temperature? 3, 28: packing and dimensions of adsorption tubes should be provided. 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. 4,2: Notwithstanding? 4, 5: Based on error propagation the 1 σ error of measurements the difference should be ± 0.8 ‰ ate the 1 σ level, which is somewhat lower than the observed value. This is not surprising, but still some comment should be added. 4, lines 10-15, eq. 1 and 2: no need to introduce α, it is not used anywhere else in the paper. 4, 24: Table 1 4, 30: Prior to 4, 13 and 5, 6: Provide value for limit of "measureable loss" 5,22: . . .measured KIE. 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. 5,33:.. whereas we used.. 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. 6,24: prior to 7, 33-34: Keppler et al. (2005) give (Table 1) a value of -38 ‰ with an uncertainty range of 4 ‰.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. 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". 9,11: spore space 9,31: "nicely resembles"? 10,11: This conclusion depends strongly on assumption about the seasonal variation of the isotopic signature of emissions.

References should be checked carefully, I noticed that some cited publications are not included in the references. Table 4: The meaning of range should be explained (a $\pm$ n*σ probability range, a percentile, a firm limit based on a given probability?)

2018.