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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Strong Sensitivity of the Isotopic Composition of Methane to the Plausible Range of Tropospheric Chlorine" *by* Sarah A. Strode et al.

Anonymous Referee #2

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This study investigates the use of different tropospheric chlorine sinks on the isotopic composition of methane. Through using a series of model runs, the authors test the impact of different Cl fields from the published literature on the isotopic composition of methane in the troposphere. As the authors highlight, because the reaction between CH4 and Cl is highly fractionating, a small change in tropospheric chlorine can have a substantial impact on the isotopic ratio of CH4. As such, the work serves as a reminder not to ignore the impacts of tropospheric chlorine on analyses of the methane carbon isotope ratio. In this regard the work has the potential to be highly relevant to many researchers in the field and sits well within the journal's scope. However, beyond this general point, I'm at a slight loss as to what has been learnt from this

study. The conclusions are entirely qualitative and merely serve to reiterate the point that an understanding of the chlorine sink is important when it comes to interpreting isotope ratios. I do not disagree with this point, but surely this work could aim higher by quantifying the impact on isotopic methane ratios (and source composition) of different assumptions regarding the chlorine sink. The paper does not want for brevity, so the inclusion of further analysis would not make it unduly long. I certainly think that there is merit in this work but it could do with a little more refining.

General comments:

Beyond the general point that the chlorine sink is important, the take-home message of the paper is rather vague. I think this is partially because of the confusing nature of the sensitivity experiments, where multiple variables are changed simultaneously (sink magnitude, sink distribution and fractionation rates) making it all but impossible to draw conclusions on what the key underlying factors are. For instance, although the SimStd and SimGC runs straddle the observations, is that due to the different magnitude of the sink or the different distribution? The SimTom simulation changes all variables at once, leading to an isotope ratio that at first appears conceptually wrong. Despite the larger Cl sink, the isotopic composition becomes more depleted in 13C! There is a throwaway line (P.6 L202) that the larger Cl sink is compensated by lower OH, but really this needs to be shown explicitly. Perhaps the point is that the Cl sink can't be too large, because the OH sink would have to be substantially smaller, making the simulated isotope ratio inconsistent with the observations? But, if so, then more work needs to be done to consider plausible changes to emissions totals so that one wouldn't have to change the OH sink to keep total CH4 consistent with the observations.

The results focus on the model outputs from a single year (2004), and to be more precise from 2 months (January and July) from this single year. However, I was not convinced of the reason why, and it would be helpful if more justification for this were provided. Perhaps I missed the point but why do flat methane concentrations simplify the analysis, when the focus is on the isotopic ratio? What does the isotopic composition trend look like during the same period(1990-2004), and is this well captured by the model (and sensitivity studies)? The authors note (p.6 L205) that since the isotopic composition is not in steady state in 2004, the results diverge with further years of simulation. So, does that mean the conclusion that SimStd and SimGC bracket the observations is only valid in 2004, and if so, what about in other years?

The conclusions seem to be mostly qualitative, raising the question of what the implications are for researchers wanting to use methane isotope data to constrain the evolution of different sources over time? Although it is stated that the choice of Cl field strongly impacts the CH4 source mixture that best fits the observations it would certainly help if this were spelled out more explicitly with some quantitative examples.

Specific comments:

p.3 L89-90 – Is the OH field seasonally varying but inter-annually constant? Please state.

p.3 L89-92 – Given the observational evidence that the NH/SH OH ratio is roughly uniform (e.g. Patra et al 2014) what is the justification for model output ratios with significant asymmetry? Indeed, the Strode et al (2015) paper that is cited seems to suggest that a ratio close to 1 also provides a better match to observations, so the use of a northern hemisphere OH field that is 20% higher is even more confusing.

P3. L106 – There is a reference missing for the fractionation value due to soil absorption. Also, how large is the soil sink as a fraction of total loss? How well is this constrained in the literature? Given the fractionation seems quite large, couldn't small errors in the soil absorption sink also impact on the isotopic ratio of atmospheric methane?

P3. L106 and Fig. 1 – I do not see the value of Figure 1 and any information it may show is largely duplicated in Figure 6. Perhaps it would do better in the supplement. The color gradient is also pretty weak, so if the figure is to be included it might be best

to reduce the scale so that differences are easier to determine.

P4. L133-134 - "We find the resulting emissions lead to a good simulation..." Please define "good", be it through RMSE, bias, correlation, etc.. Also please define NOAA GMD.

P4. L136-149 - What is the temporal variation in the Cl fields. Do they change inter-annually?

P4. L138-139 – For the avoidance of doubt, do all sensitivity studies use the same stratospheric loss fields? Please be explicit.

P4. L146-147 – Is the 2.5% loss the fraction in the TOMCAT model or in your model runs? I have assumed the latter but it is unclear.

P5. L154-155 – The Cl field from TOMCAT accounts for 2.5% of CH4 loss. But then the OH concentration is reduced by 2%, so does the Cl sink now account for more than 2.5% of CH4 loss?

P5. L154-155 – I appreciate the wish to keep total CH4 roughly the same but why do this by altering the OH loss rather than altering the total emissions? Is a 2% change in OH consistent with the oxidation of other species beyond methane such as CO or methyl chloroform? In other words, is this a plausible scenario? The same goes for the 4% reduction used in SimMBL. Wouldn't it be worth increasing the sources to compensate for the increase in sink instead?

P5. L155-156 – The fractionation value is increased in SimTom to avoid too much fractionation. But then the results show that there is too little. So is this change really justified? No evidence is shown for the case where the fractionation is kept the same to support this decision.

P5. L171-177 – I think it would be pertinent to include some mention of the distribution of observations and how many different locations there are measuring 13C in the observation network.

P5. L184 – Why choose to focus only on January and June? The answer may be obvious but it still needs to be mentioned.

P6. L194-196 –Perhaps it might help to give the latitude of this isotopically heavy region (∼60 N) to help guide the reader and link to Figure 7.

P6. L205-208 – Should the isotopic composition be in steady state in 2004? Although Fig. 2 shows the model and observed trends in bulk CH4, shouldn't the comparison of the modelled and observed isotopic ratios also be shown to assess the model performance? I.e Is it only in 2004 that the model isotope ratios are broadly in agreement with the observations?

P6. L215-219 – The point is made here that it is the distribution of the Cl sink that is key for the SimTom run, but I really think this needs to be made more prominent. The use of a different OH sink again complicates the issue as well, as the SH effects seem to be mostly a result of OH changes rather than Cl, so are you really analyzing the response to a change in the Cl sink or a change in the magnitude and fractionation of the OH sink?

P7. L221 – Given the reduced hemispheric OH difference improves the simulation again the question has to be asked why this wasn't used as the standard configuration?

P7. L236-237 – How large would the correction to the geologic source have to be to improve the inter-hemispheric gradient? It seems that the inter-hemispheric gradient is relatively unperturbed by the different Cl fields, and more likely a result of source differences or a change in the interhemispheric OH ratio. The simulation that best approximates the inter-hemispheric gradient is SimWet. Doesn't this point to accurate source signatures being of primary importance in determining this gradient, rather than the Cl field?

P7. L239-240 – Would it not be best to include SimWet description in section 2.2? Also it would be useful to give more details of this simulation. By how much does the

wetland source signature change versus the single value simulation?

P8. L265 - "We find that the NH Cl maximum acts to flatten the interhemispheric gradient...". But this isn't the Cl distribution alone that has this effect, as both the OH sink magnitude and fractionation changed. Based on the sensitivity cases shown one cannot conclude that this is down to Cl alone. The same applies for conclusions related to SimMBL.

P8. L271 - "...but combining it with the Cantrell et al (1990) value would lead to an overestimate" Would it? This isn't shown. Changing the fractionating effect of OH between sensitivity cases without showing the evidence for why this is the most appropriate action seems odd.

P8. L272 – What about the uncertainty in the fractionating effect of other sinks such as soil absorption and Cl. Are they of a similar scale to the uncertainty in OH?

P8. L272-275 - "The choice of Cl field thus strongly impacts..." Yes, but by how much? Under these different assumptions about Cl how different would the source mixtures end up being?

Technical comments:

P. 3 L 83 – GMI is used before being defined

Fig. 4 – I appreciate the scales probably need to be different, but why do the panels use different color maps?

Fig 8 and 9 – Units omitted on panels b and c in both figures.

References: Patra, P., Krol, M., Montzka, S. et al. Observational evidence for interhemispheric hydroxyl-radical parity. Nature 513, 219–223 (2014). https://doi.org/10.1038/nature13721

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