

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 #1

Received and published: 20 January 2020

This study addresses the interesting and important topic of methane oxidation by chlorine and the uncertainty it introduces in studies of global methane, in particular those that make use of $d^{13}C$. The main conclusion of manuscript, which reads very well and is nicely concise and to the point, is that the $d^{13}C$ signature of atmospheric methane is sensitive to the treatment of Cl. To be honest, I was a bit disappointed by this – because in my perception that was quite clear already, and therefore doesn't bring much new. There are inherent limitations in doing forward simulations, but nevertheless. Having gone through the effort of fine-tuning model runs to be able to make realistic and meaningful comparisons with measurements, in my opinion some more in-depth analysis of the uncertainties concerning Cl should have been made to reach the level of impact of

C1

the journal. Besides this I have a few methodological issues that require attention to make this work publishable.

GENERAL COMMENTS

I was surprised to read that despite the effort made by Schwietzke et al (2016), which is referenced in this paper, to revisit and update isotope signatures by systematically exploring what has been published in recent years, the outcome is practically unused here. It would be useful to know if it has any implications for the latitudinal and seasonal measurement constraints that are central to this study.

The authors rightly mention the limitation of using constant isotopic fractionation factors. The SimWet scenario is introduced to account to variations in isotopic signature for natural wetlands based on the work of Ganesan et al (2018). I was surprised to see an impact of just below 0.2 per mil on the north-south gradient, whereas looking at their figure 3 the impact could easily be 0.3 per mil (the impact is a bit larger along the Arctic coast where the measurement sites are located). 0.1 per mil is about the gap that remains with the measurements in Figure 7. The difference could be due to the size of the global wetland emission that is used, or how it is distributed latitudinally, which introduces an uncertainty that is worth considering.

The comparison between simulated and observed CH_4 in Figure 2 is very convincing. However, limited information is provided to judge the $d^{13}C$ simulation and whether its trend is modelled realistically. The seasonal cycles in the supplement only show deviations from the mean, which are useful, but not sufficient to judge the overall performance. In my opinion the trend in $d^{13}C$ could provide important evidence about the role of Cl chemistry, as a sizeable source component should have been increasing over time – for which it remains the question whether its contribution to the $d^{13}C$ trend is confirmed by the measurements.

It is unclear why only measurements at the South Pole are used to assess the seasonal cycle of $d^{13}C$. According to the work of Allen et al., the SimMBL scenario should

C2

reproduce the seasonal observed at Baring Head. If so, the question is if the GEOS simulations confirm that this is the case, and what it means for the representativeness of either South Pole or Baring Head for the remote Southern Hemisphere. It is unclear why averages of multiple sites are used for CH₄, but not for d13C. The underestimated seasonal cycle at SPO for all the other simulations, with quite different representations of Cl, raises the question how sensitive the seasonal cycle amplitude really is to Cl. This depends not only on the size of the Cl sink, but also on its seasonal cycle, and whether or not it is in the right phase with what is observed. To properly judge this, a 'blank' scenario is missing without accounting for tropospheric chlorine. Do we actually need to account for the tropospheric CH₄ sink due to Cl to be able to reproduce the CH₄ and d13C measurements?

If the aim is to assess the sensitivity of global variations in d13C CH₄ to the treatment of Cl, then an increased Cl sink should not be compensated by a decreasing KIE for OH. The argument that this is needed to keep the overall fractionation in agreement with observations is not so strong, given that earlier estimates of it are based mostly on measurements from Baring Head. The comparison at South Pole presented in this manuscript suggests that the fractionation may be different (depending on the corresponding seasonal cycle amplitude of CH₄ itself, which is not shown in Figure 10). Unless the combined Cl and OH fractionation is really outside the range of a well-defined observational constraint on what it should be, it would be better not to change the treatment of OH.

SPECIFIC COMMENTS

Line 83: 'old bias' What could be the implication of this bias? If the age would be younger, would that increase the signature from stratospheric CH₄ oxidation in the SH troposphere, enlarging the north-south gradient in d13C?

Line 98: As pointed out in the comment of Tonatiuh Nunez Ramirez, there is confusion in the literature on the value of Rstd. PDB is not used anymore. Instead, VPDB is the

C3

standard with a Rstd = 0.01118. A good reference would be Zhang and Lee (1990).

Line 168: This suggests that the other Cl fields do not show significant shifts in the seasonal phasing of Cl between the hemispheres. If so, this would be an important point to provide further information on.

Line 177: But the uncertainty of the monthly mean is not the std of the individual measurements that are averaged.

Line 237: Looking at Fig. 6 I do not quite see the impact of the geologic source in northern Asia mentioned here. Given the modest emission from single geological formations, I wonder how the interhemispheric gradient can be so sensitive to it.

Line 250: Although the d13C simulations do show important differences when varying the treatment of Cl, I did not see a quantification of its significance for the global CH₄ budget. This statement assumes some significant shift in sources in order to explain the measurements, depending on the treatment of Cl. Since this is not what is done in this study, I do not think it can formally be concluded from the results. Since the aim of the study is to assess the importance of the treatment of Cl for global CH₄, I do think some kind of quantification of that importance is needed. However, the conclusion section doesn't provide a single number in support of a conclusion regarding the importance of Cl.

Interactive comment on Atmos. Chem. Phys. Discuss., <https://doi.org/10.5194/acp-2019-1047>, 2019.

C4