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Comment on acp-2021-950

Anonymous Referee #3

Referee comment on "How do Cl concentrations matter for simulating CH4, δ13C(CH4) and estimating CH4 budget through atmospheric inversions?" by Joël Thanwerdas et al., Atmos. Chem. Phys. Discuss., https://doi.org/10.5194/acp-2021-950-RC4, 2022

General comments

The budget of methane is a timely issue, the past changes in atmospheric methane have not been fully explained, and currently the atmospheric methane burden is rapidly increasing. The effect of the chlorine sink on the atmospheric methane burden is relatively small, but as the authors point out the chlorine sink is especially interesting regarding the C13 methane, and the atmospheric chlorine sink need to be included in top-down atmospheric inversions. Overall, the paper is an interesting study on the effect of the atmospheric chlorine sink on methane and C13 methane, and the results are in-line with earlier findings. The question posed in the title is interesting, but can it strictly speaking be answered based on this study, as the results are based on the forward simulations? There is an additional method of analysis used to derive the expected response to the sources if the changes in atmospheric chlorine sink would be made in an inversion system. However, there are some possible shortcomings in the analysis that should be addressed before the paper can be published.

Specific comments

The research topic/questions, the value of isotopic variations for explaining the methane budget in atmospheric inversions, are well justified in the introduction. The introduction presents a reasonable overview of the atmospheric isotopic signal, and especially the effect of chlorine, also for the stratosphere. However, it would be beneficial for the paper to briefly review the processes included in the models and possible differences between the models. Now the discussion is on a very general level, e.g., lines 61-64 "...have made important developments in tropospheric chemistry modeling...".

For completeness, the photolysis of methane could be added to the reactions (Table 2) as the model extends to ca. 75 km, even though it would likely not impact any of the results in this study.

Lines 135-136. "More details on the modeling of this field are available in the supplement." However, there are not really any further details given on the simulation, practically the same text is given on lines 120-128 as in the supplement lines 49-60, really the only addition is Table S3. Also, table S3 is almost a duplicate of Table 1 in the manuscript, only the sink column and the average KIE is added to table S3 compared to Table 1. Table S3 seems redundant.

Lines 135-140. The main missing reactions/processes could be mentioned.

Lines 169-176, Scaling the Cl-INCA field to match the tropospheric average of Cl in the Cl-Wang field may introduce some differences, at least visually it seems like the Cl fields would differ at high latitudes, even though the tropospheric average would be nearly the same.

Overall, it would be relevant to have an overview of the major differences between the simulations. The global average is interesting, but the latitudinal and vertical distributions are also important for understanding the impact. Here it would be beneficial to have an overview of the model differences, e.g., the Cl-INCA field seems to have a low (or missing) release of Cl from sea-salt aerosols (Figure 1). Elevated halogen concentrations are often observed in the spring at high latitudes, which could affect surface C13 methane concentrations observed at high latitude stations etc. Latitudinal differences in the Cl field would also cause different responses in the source estimates an inversion system.

Section 2.3. The setup, if I understood correctly, is based on an inversion using a Cl burden that is about half of the one used in the forward run, SimREF, that is then used as reference for the other forward runs using different Cl fields. The fluxes are therefore not optimized with the same Cl burden as in the SimREF, but nevertheless SimREF is used as reference for deriving the delta S, i.e., the source change required to adjust for the different loss rates in the different simulations. The total fluxes would not be affected much, but the distribution between the source categories could be affected. This should be elaborated.

Lines 234-236. Should the SimREF be validated more rigorously when it is used as reference for the other simulations? If the SimREF has biases compared to observations, it might affect the conclusions from the box model analysis (delta S).

Line 237. Is it justified to use mean bias in the comparisons? Positive and negative biases (time, latitude or vertical) will cancel out to some extent.

Lines 241-264. The reason for the introduction of the box model analysis is somewhat unclear. It seems that the driver data ended before the models reached steady state, therefore the steady state had to be estimated by the fitting procedure derived using the box model approach. A more straightforward alternative would be to repeat the simulated years until steady state is reached. The seasonal and interannual variability in the bias, seen in Fig 2, is relatively small compared to the bias. Therefore, it would be justified to repeat the same years to reach steady state. The steady state values could then be used in the analysis instead of fitted values. What is the information obtained in the fitting procedure from B in eq(6)? The values of B are not shown, but they should be almost identical for the different fits? Are they realistic?

Lines 245-247. What is meant by negative feedback from both decrease and increase? "CH_4 decrease/increase induces a negative feedback on the magnitude of the sink, leading to a stabilization of the mass of CH_4 after several decades if S and τ_i are constant over time."

Lines 266-268. Is it justified to use the conversion factor of Lassey et al 2000? The distribution of sinks and the resulting methane distribution will affect the conversion factor between mixing ratio and emissions.

Lines 268-269. “For SimNoCl and SimSherwen, these estimations are very close (difference of less than 0.2 $TgCH_4.yr^{-1}$) to the tropospheric Cl sink discrepancies from Table 4.” Maybe the authors meant SimNoTropo? Then the discussion in the following lines is more understandable.

SimSherwen: 9.9-3.2=6.7 from Table 4 vs. 6.6 in Table 5

SimNoCl: 0-3.2=-3.2 from Table 4 vs. -5.7 in Table 5

SimNoTropo: 0-3.2=-3.2 from Table 4 vs. -3.2 in Table 5

Still this comparison to the tropospheric sink in Table 4 is not straight forward, the stratospheric sink also has an influence. You only need to adjust for the fraction of methane that does not return to the troposphere from the stratosphere, therefore the effect is significantly smaller than the sink itself. The Cl in the stratosphere is fairly similar in all simulations except for the SimNoCl and SimTaki. This could be discussed a bit more around line 271.

Table 5. Latitudinal dependency is reported as min/max, but it is unclear which latitude band is associated with which value.

Lines 286-288. How should B be interpreted when fitting eq(6) for delta13C methane?

Lines 290-291. How is it estimated? "We can estimate that each percent increase in how much CH_4 is oxidized by Cl leads to an additional 0.53 ‰ increase in $\delta^{13}C(CH_4)$, ..." Linear fit to Total oxidation in Table 4 and Signature (Source adjustment) in Table 5?

Lines 294-297. The contribution from STE is estimated as 0.3 ‰, a small clarification could be made that the contribution is only from Cl, not the full contribution from stratospheric intrusions. "Intrusions of stratospheric air are therefore responsible of an enrichment at the surface stations of 0.30 ± 0.01 ‰ (depending on the latitude) after 21 years of simulation, larger than the value of Wang et al. (2002) inferred between 1970 and 1992 (0.23 ‰)." Some discussion could be added for the comparison to Wang et al result. Possible reasons for the discrepancy, different years etc. Also, the difference between SimNoCl and SimNoTropo is 0.36 (Table 5), but the value reported here 0.30 ‰, is from Fig. 2, which is not the steady state value, why is that used instead of a steady state value?

Text S2. P could be explained, first seen at line 85 (k*B)

Text S2. Lines 93-96.

Is it reasonable to assume delta_s equal to delta_a? Is it then also assumed that the isotopic fractionation due to the atmospheric sinks are negligible, even though the idea is to estimate the effect of chlorine on the mean atmospheric isotopic signal? Seems like this assumption going from eq(11) to eq(12) needs to be justified more thoroughly.

Lines 298-302. The value for SimREF, -52.6 from table 2, could be given here to aid the reader. Oscillate is not a good choice of word here, the value does not oscillate, it just depends on the simulation.

Lines 310-328. In the text related to Figure 3 in section 3.4 the reader could be reminded why the SimSherwen has an opposite bias compared to the others. It is also interesting that the SimNoTropo and SimINCA are so similar, this could also be discussed, the tropospheric Cl in SimINCA seems to have a small effect on the delta13C. While SimNoCl seems to have a significant effect on the delta13C amplitude in the northern hemisphere. It is easy to understand that the differences in the bias for methane is small, but to also see small differences in the delta13C is a bit more surprising.

The discussion in section 3.5 on vertical profiles.

The number of profiles in the SH is very low, three observations in tropical latitudes, and one on mid latitudes. The validation of the SimREF is therefore not very convincing, at least for SH. In the NH there are more observations but averaging all profiles from tropical to Arctic soundings into one for the whole hemisphere is probably not good. Already the tropopause height is quite different but also the stratospheric polar vortex might have influenced the Arctic soundings. It is, however, difficult to know the reason for the observed discrepancy without seeing the individual profiles. Now the simulations were only sampled when there was a sounding. To make a more thorough analysis of the differences between the simulations the full fields should also be used. Furthermore, some discussion should be added on the delta13C profile.

Line 343 “The mean bias relative to SimREF is given for all simulations and observations in Table 6.” Are there any values given for observations; I find only simulations?

Line 343-344: “A change in the Cl field (and keeping it realistic) induces a maximum mean bias of 51 ppb in the stratosphere (SimNoCl).” I don't understand the meaning of this statement. It is the difference between a realistic Cl distribution and no Cl.

Text S3.

It is unclear what the TCCON analysis adds to the paper, especially as nothing is mentioned in the paper about the results, results are only presented in the supplementary. It is not clear which bias is presented in Fig. S5 colored dots (surface observations compared to SimNoCl or SimREF). Also, for XCH4 it could be better to compare the simulations without filtering the data only for cases with observations. I understand that the point is to get an idea of differences in areas/times with data, in case the data would be assimilated, but without the assimilations it is not especially useful. It is somewhat interesting that the bias between SimNoCl and SimREF is latitude dependent. Probably a combination of Cl distribution and atmospheric transport but based on this analysis it remains unclear. It would perhaps make more sense to make a more rigorous analysis in another paper.

Lines 377-378 "...the change in the Cl field.." This conclusion should be reworded, unclear what is meant by "the change".

Lines 384-385 This conclusion may need to be reworded once the previous comments have been considered, the result is not from an actual inversion. "In an inversion, this additional percent of contribution would reduce the inferred globally-averaged isotopic signature by 0.53 ‰."

Lines 385-386. The authors probably mean only the contribution from Cl in the stratosphere, rather than the full impact of stratospheric intrusions. The given value is not from a steady state situation, how/why is this value chosen. The driver data ended?

Lines 388-390. This conclusion should be re-worded. This is true for the specific changes made in this study, not in general. Some other change in Cl could result in a change in delta13C methane outside the 10-20 range. “CH4 seasonal cycles are only slightly influenced by a modification of the Cl sink (1-2 % change in the seasonal cycle amplitude). Changing the Cl field can nevertheless modify the amplitudes of δ13C(CH4) seasonal cycle by up to 10-20 %, depending on the latitude”

The conclusions regarding the vertical profiles (Line 390-) may need to be revised once the discussion is updated. The comparison using hemispherical averages is likely not representative due to the large span of latitudes that are averaged.

technical corrections

Line 139. half lower than the mean tropospheric >> half of the mean

Table 2. The abbreviation VPDB is not explained

Lines 221-223 unclear which value is meant “The tropospheric value from Hossaini et al. (2016), used in recent studies (Saunois et al., 2020; McNorton et al., 2018), is also slightly above that of ClSherwen (Table 4: 1.4 times higher) but well above that of Cl-Wang and Cl-INCA (4 and 8.5 times higher).”

Table 4 third column Conc. Is not explained in the caption (average Cl conc. ?)

Line 369. Cl configuration >> Cl distribution