

## Interactive comment on “A very limited role of tropospheric chlorine as a sink of the greenhouse gas methane” by Sergey Gromov et al.

Anonymous Referee #2

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We thank the reviewer very much for the detailed review.

The paper presents an interesting new angle on evaluating previous indirect claims of a globally significant role of Cl for the removal of CH<sub>4</sub>, by analyzing the isotopic composition of the reaction product CO. The results indicate that the previous estimates are strongly overestimated. The paper is well focused on bringing over a clear message and I appreciate that the authors try to keep it short. However, in particular in section 2 and Fig 2, where the new evidence is presented, the information is very dense, and the authors should help the reader by adding more explanation and making more explicit statements.

The information is dense indeed and we have made changes to the text to explain better.

The derivation of equations 2 and 3 should be shown explicitly, either in the main paper or in an appendix, and more information / explanation should be added.

We added requested derivation and explanation in Appendix A.

A parameter  $\lambda_a$  is introduced, but what is it?

As stated, it is an assumed value of the yield of CO from CH<sub>4</sub>, for which one may project our calculations obtained with the diagnosed  $\lambda$  value in EMAC.

An additional parameter  $\mu$  is introduced, is this necessary? It replaces the parameter  $\Delta S$  that is mentioned in the sentence above Eq. 2 to express the sensitivity, but it does not appear in the equation. This should be motivated better.

Parameter  $\mu$  is introduced mostly for the sake of notation convenience in Eq. (3). Indeed, we should have used  $\mu$  instead of  $\Delta S/S$  in paragraph [25]. We put this right in the revised version.

Fig 2 shows results obtained with Eq. 2 and 3, but the authors should help the reader by describing this complex figure step by step, linking it to the equations and the data. For example, why is Fig 2 shown as function of  $\alpha$ , what does this signify, and how does  $\Delta S$  enter this figure? What are the units of the numbers in Fig 2a (permil). I cannot fully follow the argumentation of paragraph 25, but it appears important for the paper. The error ranges given in lines 213 ff do not correspond to the error ranges indicated in Fig. 2.

We would like to keep the caption in its concise and enough descriptive style, that is, we believe that the reader can easily refer to manuscript for the formulation of  $\Delta\delta_c$  and  $\Delta\delta_n$ . The latter are shown as a function

of  $\gamma$  or  $\lambda$  (we assume of these were referred to as “alpha” by the Reviewer) because these are the major unknowns in the issue dealt here. This is introduced and thoroughly explained in the manuscript; adding this information to the caption of Fig. 2 will be rather redundant, whereas moving it from the manuscript body to the caption would disrupt the narrative.  $\Delta S$  is one of the basis parameters used in calculations, i.e. it is not varied to obtain sensitivities (read we do not see how it may enter this figure, apart from indirectly defining the slope of the KIE-only sensitivity shown).

We nonetheless acknowledge that the information in Fig. 2 is presented too densely. Therefore, we have split Fig. 2(a) into two panels showing  $\Delta\delta_c$  and  $\Delta\delta_n$  separately and amended the caption accordingly. The ranges given in paragraph [26] (lines 213 ff) are indeed the ranges of  $\Delta\delta_n$  values obtained under different assumptions, hence these are not the error ranges. In the amended version of Fig. 2(a), bottom panel, we show the errors associated with  $\Delta\delta_n$ .

### Minor points:

Line 100: It would be useful to spell out precisely what the issue is. It is mentioned indirectly in the following lines (the CH<sub>4</sub> derived fraction would be too dominant, line 102), but please provide the line of argumentation explicitly: 1) the bottom-up budget of CO isotopic composition is too negative in <sup>13</sup>C compared to observations, 2) the most negative course is CH<sub>4</sub>, 3) to close the isotope budget required lowering the yield in previous studies, and 4) making CH<sub>4</sub>-derived CO even more depleted in <sup>13</sup>C would aggravate the problem.

We improve the narrative here by writing (line 100) “As Manning et al. have pointed out, budget closure is ...” and mention (line 96) “a negative shift..”, which makes it easier to couple the logic between these 2 paragraphs.

Line 165: Can you comment on the difference in CI levels compared to Hossaini et al. (2016)?

We amend this sentence accordingly.

Line 171: On which basis do you “expect” a factor 1/5 lower variation of the CH<sub>4</sub>-derived CO in the ETS<sub>H</sub> (I assume compared to the SH)?

Perhaps it is not clearly formulated. We imply that variation in the CH<sub>4</sub>-derived [CO] is a factor five less compared to that of the total [CO]. This applies not only to ETS<sub>H</sub> but to entire troposphere (in tropics and NH this difference will be larger) and is also driven by synchronous sink/production of CH<sub>4</sub> and CO via OH. We add a respective elucidation.

Line 176: Provide some more details on  $\eta_c$ . This is a complicated quantity, and relevant here, so some background should be provided in the paper itself rather than referring to Gromov (2013). Specify next sentence: Is it the difference between the atmospheric isotopic composition and a global averaged source mix or the sources at this point and space in time?

$\eta_c$  is neither of the two; rather it singles out the effect of sink fractionation on  $\delta^{13}\text{C}(\text{CO})$ , assuming atmospheric mixing and transport alter the latter near linearly. In other words, if a KIE in CO+OH reaction were absent, the airborne  $\delta^{13}\text{C}(\text{CO})$  would be lower by  $\eta_c$ . We add a respective information on how this quantity is obtained.

Line 192: It is not clear what you want to indicate here: “In a statistical sense. . .” Do you refer to the differences derived for different  $\delta_n$  values, or the difference between the stations. And further, what does this mean?

We are referring to the difference in  $\delta_n$  values derived for different stations (as we hypothesise that there are no significant local sources south of 40°S except CH<sub>4</sub> oxidation). Subsequently, it means the hypothesis stating that “derived  $\delta_n$  values at two stations are different” is rejected at  $p$ -value of 0.31, hence these two values highly likely refer to the same isotope signature (we assume the Reviewer implied  $\delta_n$  variable here).

Fig 2, and caption. What is the unit of the numbers shown as labels in Fig 2a? Is it useful to show a yield from a personal communication (M. Krol, correct spelling) in the figure without relating it to a reference?

Thank you, we have changed Fig. 2 (a) accordingly (see the reply above). We also add a respective reference (Hooghiemstra *et al.*, 2011).

Line 205 ff: Explain better the meaning of the sentence “Importantly, . . .”. It is not immediately clear that you are less sensitive when you add a sink than when you replace a sink.

We add a comparison of the included sink from A07 with the total tropospheric CH<sub>4</sub>+Cl sink simulated in EMAC to emphasise the importance here.

Either reword or remove lines 227 – 229. This is a confusing statement.

We reformulate as: “Assuming that  $\lambda < 0.7$  or that  $\lambda \sim 1$  would be in conflict with basic principles, *i.e.* photochemical kinetics and/or dry and wet removal processes affecting the intermediates of the CH<sub>4</sub> → CO chain, or their erroneous implementation in the global atmospheric models.”

Line 230 – 232: Motivate where the number of “at least one-third” comes from.

Thank you, we add “times 0.7” to ( $\delta_m + \epsilon_m$ ).

Line 233: Motivate the value of 2 per mill.

We add a respective footnote.

Line 234 ff: Phrasing the quantification in terms of lambda values is confusing. We know very well that the yield of CO is higher than 0.12. Is it not more instructive to compare the model results with the experimental data in Fig 2? *I.e.* discuss the “vertical” offset, which would simply imply less change in the Cl sink, rather than the “horizontal” offset, which projects the real cause of the discrepancy to an unrealistic change in lambda?

It is a matter of presentation here. We do indeed compare the model estimate to the experimental data, *i.e.* the latter shows that the sink estimated by A07 can only be supported by <sup>13</sup>CO data when  $\lambda$  is 0.12 or less (*cf.* where the point from SCB “meets” the curves for SH “vertically”). In this sense it is also a comparison of the “horizontal” offset; the latter, however, is caused by the  $\lambda$  value for which we do not have any observational data at all.

Line 235 to 240: Move this paragraph to the description of Figure 2a. Now it is used only in the discussion of the unrealistically low lambda value, but it is helpful for Fig 2a in general.

We add a short elucidation to Fig. 2(a) caption (including a reference to the discussion section), as there is no room in the caption for the details presented in this paragraph.

Line 251/52: Given the timescales for equilibration of the mole fraction and the isotope reservoirs (Tans, P. P.: A note on isotopic ratios and the global atmospheric methane budget, *Gl. Biogeochem. Cycles*, 11, 77-81, 1997), it seems highly unlikely to me that there could be a “stabilization” signal in the isotopic composition before the signal occurs in CH<sub>4</sub>, at least when this is interpreted as a manifestation of steady state between sources and sinks. I suggest replacing “hiatus” by the explicit statement of intermittent stop in the annual growth.

Thank you, we will adopt the kind suggestion of the Reviewer. Indeed, using “hiatus” would not be appropriate here as it may imply “equilibration”, which is not the case. In this sense, the findings of the recognised study by Tans et al. (1997) regarding *equilibration* times of mixing and isotope ratios of CH<sub>4</sub> also may not be applicable here. Slower repartitioning of <sup>12</sup>CH<sub>4</sub> source fluxes (as compared to that of <sup>13</sup>CH<sub>4</sub>, i.e. change in source signatures) may cause a slightly earlier detectable signal in  $\delta^{13}\text{C}(\text{CH}_4)$ ; we do not speak of any equilibration here, it is rather a beginning of an equilibration towards a new state.

Line 259: . . . is useful . . . For what? And on what basis do you make such a statement? The rest of the paragraph is quite vague, I wonder why you did not investigate the seasonal signal if you suggest that it should be a sensitive indicator for CI.

We reformulate as: “Because oxidation of CH<sub>4</sub> is a main source of CO in the ETSH, and the isotopic composition of atmospheric CH<sub>4</sub> is better known than that of its sources, it may well be that variation in the annual average value of  $\delta^{13}\text{C}(\text{CO})$  is more useful variable for estimating [CI]. The relatively long lifetime and small seasonality in sources result in weak seasonal cycles of mixing ratio and  $\delta^{13}\text{C}$  in CH<sub>4</sub>. In contrast, the seasonal cycle of  $\delta^{13}\text{C}(\text{CO})$  is dominated ...”

Our early attempts to use the seasonal  $\delta^{13}\text{C}(\text{CO})$  variations indicated a lack of observational data (large uncertainties due to insufficient statistic) for estimating the CI input signal.

Line 277: As mentioned above, I suggest changing the line of argumentation away from the totally unrealistic values for lambda. You can make the point stronger by staying with the possible lambda range.

Perhaps it is a matter of our writing/presentation style. We write that agreement is only possible if unrealistic yields were to be applied. Because the yield of CO from CH<sub>4</sub> is still an issue, we underscore this problem. When we assume given yields to be “true” we enter this discussion, which we do not wish to do here. In the last sentence of the paper (see reviewer’s comment below), we reiterate this issue. It is a real problem.

Line 288: This range of values in the realistic range for lambda should be presented and discussed in the main text, see comments above. I consider this a (the?) main result, which is not well motivated and presented. Also, you should link it to the maximum possible CI difference between the two periods in the following paragraph, where the message is less clear because the parameter lambda<sub>a</sub> is involved again.

We cannot consider the range of probable  $\lambda$  values as a main result here, as this is not the property we focus on/research in this study, as opposed to the CI based input to  $\delta^{13}\text{C}(\text{CO})$ . We merely review the range of conferred values of  $\lambda$ , and conjecture which range is most realistic. Therefore we present the [CI] estimate using arbitrary  $\lambda_a$  values to specifically draw the Reader’s attention to uncertainty about CO yield from CH<sub>4</sub> (and giving a possibility to derive a better [CI] estimate through improved estimates of  $\lambda$ ). We

note that in the abstract we quote the [Cl] variations which correspond to  $\lambda_a=0.93$ , i.e. that derived with EMAC.

Line 289/90: This may be overly optimistic. What about source variations of CO (e.g. bb)? If it is mentioned in the conclusions it should follow from a more detailed discussion in the previous section, but it has not been mentioned before at all.

The resulting small variability in the CH<sub>4</sub>-derived [CO] and  $\delta^{13}\text{C}$  is exactly the reason why large variations in other CO sources may help to single out the CH<sub>4</sub> input differentially. We add an elucidation here.

Line 294: What is lambda\_a (see comment above) and why does it come back here in the conclusions, whereas most of the discussion was about lambda?

See the answer to the comment on Line 288 above.

Line 297: This last sentence is not really about your results, and already known, so although the statement is strong, it does not summarize your analysis. Also, one could argue that this implies that there is still at least one big error in the present understanding of the global CO isotope budget parameter, correction of which could offset the budget in a way that there may be room for Cl again.

We agree, however we would like to keep this sentence to draw reader's attention to the <sup>13</sup>CO budget closure problem (which is linked to the issue regarded here) in the Conclusions section. We therefore reformulate as a less strong statement: "Regarding ..., it is unlikely that tropospheric Cl is as high as assumed in the literature."

## Technical points:

Make "incomplete" comparisons complete. As it is now, one has to go back to the previous sentence to exactly locate the reference for the comparison.

Examples:

line 26: It is easier . . . compared to what? (direct measurements)

We reformulate this sentence as: "Not only are indirect measurements easier, the use of trace gases that react with OH and Cl also has the advantage that space- and time-averaged values are obtainable."

line 83: . . . are less complicated . . . compared to what? (the NH)

Yes, thank you, we add the NH here.

line 171: . . . much lower. . . compared to what? NH !

See the answer to the minor comment to Line 171 above.

Line 152: Rephrase sentence “significant or not. . .”. If a signal is not significant, don’t use it to support a scientific argument. Also, in this sentence you write about effects in both directions, in the next sentence you relate this to CO that would work in a “similar” direction (but here it is only one of them). This is confusing, please clarify.

We rephrase the first sentence. Regarding the following one, we see no confusion here: one statement indicates that  $^{13}\text{C}$ -depleted CO is added or removed from the atmospheric reservoir (opposite directions are explained in the parentheses, no “similar” direction is mentioned?). “Similar fashion” mentioned in the next sentence reiterates that changes in sink KIE also add or remove  $^{13}\text{CO}$  from atmospheric reservoir.

Caption Fig 1 mentions pluses but they are not visible (probably the small dashes in the boxes where the vertical part of the cross coincides with the vertical line).

Thank you, indeed. We have replaced pluses with circles (also in the Supplement, Fig. S2).

Line 172: Reword sentence: “The average fraction of the latter . . .” You write that two values are proportional, but one has a fixed value, so the other one as well.

We removed “average”.

Line 181: Reword “... can be approximated as due to ...”

Done.

Line 211 and line 226: replace cf. *ibid.* by Fig 2.

Done.

Line 224: remove “happens to be”, this implicates that this is by chance.

Reformulated.

Line 249 and 250: add “period” after HC and LC

Done.

Line 291: Why “Nevertheless”? The sentence does not seem to require this logical connection.

Agreed, this is an overlooked leftover from an earlier edit.

## References

Hooghiemstra, P. B., Krol, M. C., Meirink, J. F., Bergamaschi, P., van der Werf, G. R., Novelli, P. C., Aben, I., and Röckmann, T.: Optimizing global CO emission estimates using a four-dimensional variational data assimilation system and surface network observations, *Atmos. Chem. Phys.*, **11**, 4705–4723, doi: [10.5194/acp-11-4705-2011](https://doi.org/10.5194/acp-11-4705-2011), <https://www.atmos-chem-phys.net/11/4705/2011/>, 2011.