

Atmos. Chem. Phys. Discuss., referee comment RC2
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Comment on acp-2021-950

Anonymous Referee #2

Referee comment on "How do Cl concentrations matter for the simulation of CH₄ and δ^{13} C(CH₄) and estimation of the CH₄ budget through atmospheric inversions?" by Joël Thanwerdas et al., Atmos. Chem. Phys. Discuss.,
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The manuscript of Thanwerdas et al. describes an attempt to quantify the effect of applying various assumed/model-generated Cl radical fields on the CH₄ mixing and ¹³C/¹²C isotope ratios simulated within a CTM (i.e. using offline pre-calculated chemical kinetics and transport). Whilst I find the idea of such quantification useful (nothing innovative but another set of simulations will add to statistic and perhaps could thus help quantifying the uncertainties about other AC-GCM/CTM-specific terms, e.g. dynamics), no marked advance in Cl-CH₄ interaction in the atmosphere is obtained, plus the analysis offered ruins the attempt. I foremost imply Section 3.2 (after which I could not continue with required scrutiny) which introduces very questionable "fit methodology" (see the general comment below). Even provided that this is repaired, my other major concern (seconding the Reviewer #1) is in that the study is largely based on results of another – to date not peer-review-completed – study by the same first and another four authors. It is necessary that the latter is finally reviewed in order to be certain that CH₄ fluxes used in the simulations are adequate. After that, my suggestion is to consider resubmission of the current work to the GMD, as this journal appears to be more appropriate for the content presented. Compared to other manuscripts submitted to Copernicus journals by Thanwerdas et al. recently, the current one is somewhat better in terms of composition and information content but not sufficiently clearer in conveying the story and presenting methods and discussion (see the specific/presentation comments below). The authors still have to put a considerable effort in improving this.

line General comments

235, 340 I am not fine with the averaging of absolute biases (in both surface- and column-wise comparisons) – their average may be spuriously reduced through the summation of negative and positive members. Thus obtained low global mean biases do not guarantee that local (per-station or per-altitude) biases are at their optimum. Also, an indication that Cl spatial distribution is wrong will be lost. As a remedy, use squares of

biases (as conventionally used in, e.g., least-square fit); I also suggest not to use latitudinal averaging due to the same reasons.

Sect. 3.2 This section is full of confusing and contradictory statements, appended with an apparently erroneous "fitting" approach, see below:

244-246 What is meant by "temporal evolution of CH₄ budget is not linear"? If you state that sink is proportional to CH₄ abundance, how can both decrease/increase introduce both negative feedback? What feedback is meant here?

246- You perform simulations with varying CH₄ emissions and sinks (biases are derived for varying S and τ_i) yet you assume S and τ_i constant over time in the analysis. How valid is this approach? How large are the errors introduced by this assumption?

Eqs. 4-7 Why inventing a cumbersome apparatus when you can simply diagnose changes in sink terms (hence ΔS) directly from the simulations? If you still like to use the "box-model" apparatus, why not writing solutions for Eq. 3 for each simulation and their differences (read biases) in analytical form? Ultimately, you confuse the Reader (and yourself) so much that in Eq. 7 you fit both A and B parameters. On which grounds? B represents τ_{ref} and should be the same for all simulations (it is from a reference simulation, isn't it?) At $t \rightarrow \infty$ (steady state), Eq. 6 reduces to $b(t) = \Delta S' \tau_{ref}$. Using the biases from Table 5, this yields various τ_{ref} for different simulations (about 8 yrs for three of them and 12 yrs for the rest!), how do you explain that? My explanation is that by fitting A and B simultaneously you receive their whatever combination that minimises error-prone averaged absolute biases in the first two decades of simulations. What is the value of τ_{ref} in the reference simulation?

Sect. 3.3 Same argumentation as for Sect. 3.2 applies, plus you have to show how the fitting is done for isotope ratios, specifically how $\delta^{13}C$ biases are obtained. In any case, regarding the erroneous fitting of total CH₄, I suspect same or greater problems with ¹²CH₄ and ¹³CH₄.

line Specific/presentation comments

Some of CI fields are referred to in the manuscript as "realistic" – I strongly discourage that, as it creates impression that the regarded fields were (in)directly compared to CI observations (they were not, although indirect estimates exist). If they were, would there be the need to test five different distributions?

3,32,41,etc. just use "composition" instead of "signal" (see the definition of the latter in the dictionary)

5 there is a lot of processes which may fractionate whatever elements in whatever phases, so you have to be specific here, e.g. use "sink kinetics is $^{13}\text{C}/^{12}\text{C}$ fractionating"

22-23 how large is "slight imbalance"?

34-35 this definition is wrong, δ notation always uses ATOMIC ratios, not molar ones – e.g. try to use your definition with isoprene (5 carbon atoms, most of isotopologues are singly substituted)

36-37 there exists the (V-)PDB belemnite-based $^{13}\text{C}/^{12}\text{C}$ standard isotope ratio, however there is no standard ratio of PDB known to me

40 overlaps ® overlap

43 "sinks are also fractionating" – in addition to which process? Emissions introduce molecules of with various isotope ratios, but this is not a fractionation process. See also comment to l. 5

71 level of detail

83-84 you can't claim that/reference the study that is not peer-reviewed yet

86 do not use "modelling" in this context (modelling is an overall process of creating and applying models, what you refer "reproducing X and Y in the model" or similar)

88 use "through the prism", that'll bear physical sense

95, 98 do not use "dedicate" (you can dedicate a poem to CH₄ and Cl, however).
Model levels are located in stratosphere and above

108-109 do prescribed species have a diurnal cycle in the model? It is relevant for T-dependent reactions and KIEs, e.g., average OH concentration may be times lower than that at midday, so most of the sink occurs at higher air temperatures in the low troposphere

149 irrelevant statement ("... was not mandatory")

Figure 1 please use the same colour scale for both upper and lower panel

161 exhibits ® exhibit

169-170 vague statement – how may your wish influence the model so that it infers a good model-observation agreement? Most comprehensive studies by no means guarantee delivering most realistic results

208-209 the second sentence repeats the message of the first one, remove

215 to what estimates "our own estimates" refers to?

Table 4 Cl concentrations are implied in columns 3 and 6?

267 why not using a conversion factor derived directly from your model simulations? You are using a factor from a study employing a model actual for early 1990s using a very different OH field (Spivakovsky climatology) and meteorology. You may introduce an error in conversion larger than that of any other assumptions used...