Author's Final Response

acp-2021-950

We thank all the referees who participated in this peer-reviewed process that started with the submission of the first version of the paper in 2019. As mentioned by Referee #5, "the manuscript has been very much improved" compared to the first version and this is thanks to the precious time of these referees.

Regarding the last iteration, we are very grateful to Referee #2 and Referee #5 for their detailed and fruitful comments which have allowed us to modify and clarify various points. We copy-pasted below their suggestions and concerns. Comments from Reviewers #5 and #2 are in blue and green, respectively. For each comment/suggestion, our responses are in bold black and quotes from the revised text are in italic black.

We first address the technical comments from Referee #5. Then, we try to answer to Referee #2's concerns. We are slightly surprised by the fact that Referee #2 is the only one to be both doubtful about our method and very critical about our scientific language.

Technical comments from Referee #5

- Intro, lines 8-10: replace "do not prescribe the same Cl sink" by "prescribe different Cl sink" (I spent some time trying to figure out "same as what").

This has been corrected accordingly.

- Intro, lines 15-16: you mention that the simulations lead to an impact of 53.8 TgCH$_4$ (~10% of the total CH$_4$ budget). Further in the paper you demonstrate that it is much less in reality (that 54 Tg range include on one hand a simulation with no Cl at all, which isn't realistic, and on the other hand some simulations with unlikely large Cl sink). But putting that 54 Tg value in the intro make it kind of a take-home message for many readers, so it would be important to tone it down.

We agree with this comment and we added a sentence to tone it down:

Prescribing these different Cl amounts in atmospheric inversions can lead to differences of up to 53.8 TgCH$_4$.yr^{-1} in global CH$_4$ emissions and of up to 4.7 ‰ in the globally-averaged isotopic signature of the CH$_4$ source(δ^{13}C(CH$_4$)source), although these differences are much smaller if only recent Cl fields are used.

- Sect 3.3, line 408: "introduced in Sect. 2.5 (Fig. 3)" ==> replace by something like "introduced in Sect 2.5 are shown in Figure 3." (the parenthesis make it look like Fig 3 belongs to Sect 2.5).

We modified the sentence to make it clearer.

The global CH$_4$ flux adjustments resulting from a change in Cl sink have been derived using the three methods introduced inSect. 2.5 and are shown in Fig. 3.

- The labels of the inversions are incorrect in some of the figures ("Patra" instead of "INV-Taki", etc.).

We apologize for this mistake and we thank the referee for pointing it out. To our knowledge, the wrong labels are only displayed in the track-change manuscript and not in the main text. We hope we did not miss any other mistakes in the revised manuscript.

- Figures 4 and 5: poor choice of colors (I can't differentiate INV-Taki from INV-NoTROPO)

We agree and we modified the green colors in Figures 4 and 5 to make it clearer.

General comments from Referee #2

190-191 It is not clear what the statement "long enough to capture the large equilibration time associated with $\delta 13C$" means. Which equilibration time is implied, what means "to capture", from what (non-equilibrated?) state?

The goal of this experiment is to reproduce what inverse modelers would do to estimate the CH_4 budget with an inversion system. We let the atmospheric system evolve from the same initial conditions but with different Cl fields so that a bias can increase in the first place, and then be reduced to zero after the inversion process and the flux and signature adjustments.

Maybe the formulation here is a bit misleading indeed, we only want to make a simulation long enough to let the bias between simulations evolve, (roughly) start to stabilize and use these values in the M3 method.

We decided to remove this sentence as we agree that it can make the reader think that we want to reach an equilibrated state, which is not the case.

supplement, Sect. 1.6 Neither 10 nor 20 years may well be not enough to equilibrate atmospheric $\delta 13C(CH_4)$ from a perturbed state, so without a careful analysis of how far from a realistic CH_4 and $\delta 13C(CH_4)$ atmospheric distribution your initial conditions are, the inversion results you obtained can't be verified for consistency. You refer to the work [1] that demonstrates this problem, yet you neither perform a sufficiently long spin-up nor do the analysis of the initial state for consistency. This issue is the very problem of the earlier study (https://acp.copernicus.org/preprints/acp-2019-925/) and devalues any comparison against observations in the stratosphere.

The present study is much different from the previous one. This time, we used all available $\delta^{13}C(CH_4)$ observations between 1988 and 1998 to get as close as possible to a realistic state of the atmosphere between those years. The atmospheric distribution is verified, with the little information available from the literature and community : the 1988-1998 inversion ensures that we are as consistent with observations as we can be given the very small number of $\delta^{13}C(CH_4)$ observations available. All the observations that we could use to check our initial conditions are already assimilated. A step further would have been to use additional independent observations that are not assimilated, but we do not have that luxury since the very few observations available were already assimilated. We cannot do more than this and it is already much more than previous published studies on CH_4 and its isotopic ratio, especially inversion studies.

During the peer-review process of the previous paper, you mentioned that a good way to get close to a realistic state would have been to use transient emissions and signatures before 1998 during a sufficient amount of years to generate a realistic state. However, the referee is certainly aware that the only way to get these fluxes and signatures is to run an inversion. And unfortunately, the only observations available start in 1988 so we

cannot go back to the year 1900 to perform a proper spin-up. This is why we also optimize the initial conditions.

217-227 There are no reasonable grounds for choosing the same emission fluxes for all FWD-* simulations. Tested various Cl fields (and hence CH_4 sink) will never correspond to emissions derived for one particular Cl field (be it or not taken from the most comprehensive study). Not only mixing but also isotope ratios will not fit here. The sensible way would be to use each INV-* simulation fluxes to gauge the effect of Cl presence. By design, you end up with inconsistent mixing ratios of simulated CH_4, which further devalues results for isotope ratios. See also the comment to 315-322.

We do not understand this comment. We actually want to do exactly what the referee describes. We do not want to gauge the effect of Cl presence since it is already done in the INV-* simulations. In the FWD-* simulations, we want to let the biases evolve so we can analyze the biases that an inversion system would try to reduce by adjusting the fluxes and isotopic signatures.

Let us clarify again the purpose of the study. Usually, an inverse modeler starts from a realistic state of the atmosphere resulting from a spin-up with transient emissions if available or from an inversion performed over a period of time prior to the period under analysis. This inverse modeler prescribes a Cl field, which can be different from one study to another depending on the estimate he/she has chosen. He/she runs the simulation. He/she will not obtain a perfect state of the atmosphere since it is likely that the prior information is wrong. A bias between the observations and the simulated values will therefore emerge and increase. These observations are represented here by INV-Wang: it is an inversion so it is the closest state of the atmosphere to reality that we can obtain. In the next step, the fluxes and the isotopic signatures will be adjusted by the inversion system to reduce the bias between the observations and the simulated values.

Here, we want
  1. to analyze this bias (FWD-*) and
  2. to investigate how the inversion system modified the fluxes and isotopic signatures to reduce this bias (INV-*).

The referee appears to be suggesting something that we are already doing in the study.

315-322 Authors misunderstand (misanalyse) the obtained results – shown biases mainly result from the various CH_4+Cl sink fields that counteract the same emission term. There are no "non-linear effects associated with isotopes" – the formulation used here and presented in Text S4 is valid, however only for single well-mixed isolated reservoirs which have reached steady-state conditions (which non-linearity is implied?). Please, simulate these equations once yourself (e.g. in a spreadsheet software). You will find that at typical values (S=588 Tg/yr, k=1/10 yrs^-1, α=0.995, B(t=0)=5000 Tg, δs=−52.6‰, δa(t=0)=−47‰, Δα=0.001), B and respective δa in each box will reach their steady-state values at about t=60 yrs. However, Δδa will first decrease until about t=90 yrs to a value of about −9‰, after which it will reach the true steady-state at about t=170 yrs. This problem somewhat reminds the one described by [1]. In contrast, the distributions shown in Figure 2 show merely the average difference in δ13C(CH_4) over 2010-2018 resulting from different local balance between CH_4+Cl sink strength and emissions, which yield spatially variable effective sink fractionation. What is the distribution of Δε value actually simulated, why not deriving these directly from the model? Note that troposphere is turbulent so you cannot assume a given model grid cell an isolated reservoir due to mixing and transport processes, which also renders the statement on L321-322 absurd.

By non-linearity, it is implied that the product of the source signature AND the fractionation coefficient has an effect on the steady-state value of the bias. So, to the contrary of the CH_4 bias, the δ13C(CH_4) bias does not have the same spatial distribution as the Cl field. We do not know how to refer to this effect other than using the term "non-linear". We slightly modified the text to be clearer.

Regarding the second point, we plotted (Fig. A below) the distribution of Δε as suggested. Note that it is the effective KIE, not the apparent one. We agree with the referee that Figure 2 shows the average difference in δ13C(CH$_4$) over 2010-2018 resulting from a different local balance between CH$_4$+Cl sink strength and emissions. However, the emissions and isotopic signatures are identical. If there are no other effects, this leaves only the Cl sink fractionation to create the spatially variable bias. However, the effective KIE distribution (Fig. A) is not similar to the bias distribution in Fig. 2. Therefore, we think that there is something more to understand.

Although we are aware that we cannot assume a given model grid cell to be an isolated reservoir, our steady-state 1-D formulation provides a good and simple explanation for the source signature dependence of the bias. Fig. B below shows the time-series on δ^{13}C(CH$_4$) biases between FWD-Taki and FWD-Wang for three specific grid cells located in three regions of interest instead of showing an 2010-2018 averaging as in Fig. 2. Although transport and mixing processes certainly have an influence on the biases, we note that all biases for each grid cell tend to a stabilized value. Therefore, our 1-D formulation is not absurd and is only here to prove the source signature dependence, that's all.

Furthermore, this issue is certainly not the main feature of the study and we develop this formulation only in an attempt to explain the distribution of the bias. We might be wrong but I do not think the referee is providing any input that would help discard our assumption.
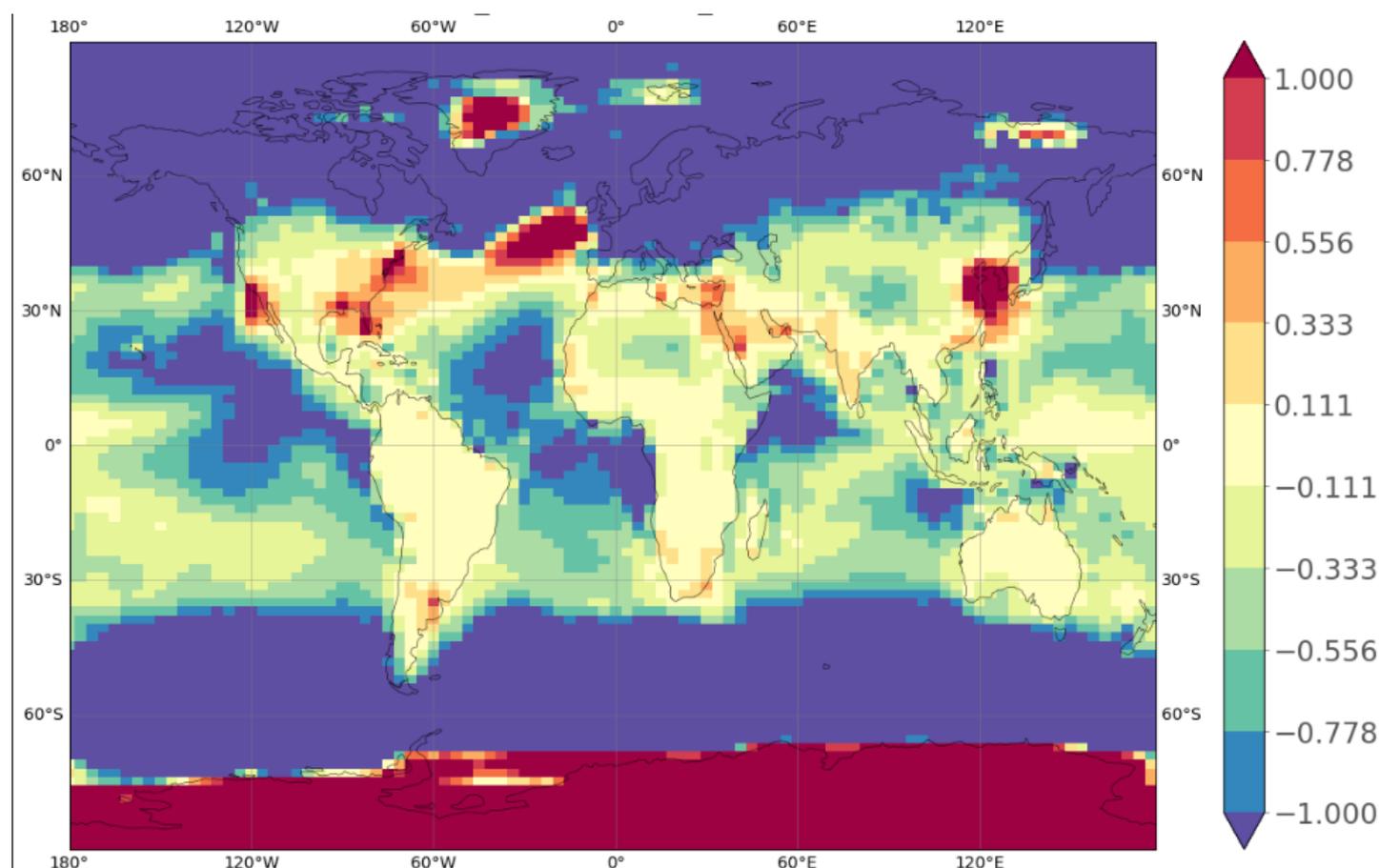
Figure A: Difference of fractionation (Δε) between FWD_Sherwen and FWD_Wang at the surface for 2010-2018.
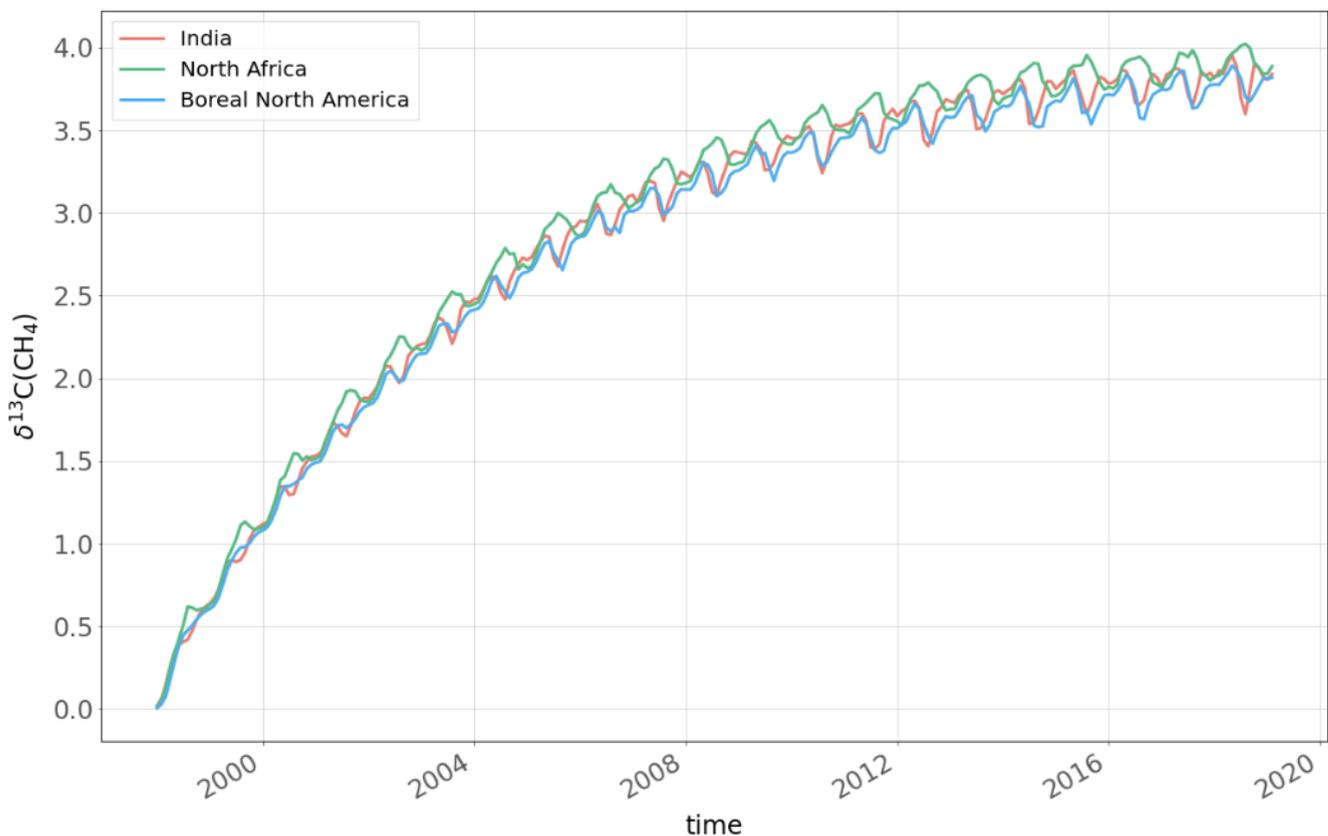
Figure B: Time-series of the δ¹³C(CH₄) bias between FWD-Taki and FWD-Wang at three locations (i.e. grid cells).

Specific and technical comments from Referee #2

Specific comments

6-7 "kinetic isotope effect … of the sink kinetics"

This has been corrected.

7 "… and thus MAY strongly influence"

This has been corrected.

9 "inversionS do not prescribe"

Thank you for pointing out this mistake. This has been corrected.

20 how is the figure of 0.8% compares to the wetland source uncertainty itself?

We added two sentences to compare this figure to current uncertainties, one in the abstract and one in the main text.

Abstract: **This adjustment is small compared to the current wetland source uncertainty, albeit far from negligible.**

Main text: **This adjustment is small compared to the wetland source uncertainty estimate of 41 TgCH4.yr⁻¹ for 2008-2017 derived by Saunois et al. (2020), albeit far from negligible.**

37-38 precision regarding which characteristic is implied? Do you mean accuracy? Which mitigation policies are implied?

Yes, we mean accuracy. We modified it.

114-115 is nudging applied to the entire atmospheric domain or troposphere only?

The nudging is applied to the entire domain. We did not specify the troposphere.

146-147 the fact that a few studies have evaluated the KIE is the wide range of temperatures does is not the reason that large uncertainties remain; this statement contradicts the following sentence.

Many inversion studies adopted either the value of Cantrell et al. (1990), that of Saueressig et al. (2001) or both, for example using an average of both values and calculating an associated uncertainty. As the two values are very different, additional estimates would likely be closer to one value or the other and therefore would suggest discarding one of them. This would reduce the uncertainty we currently have about which OH KIE value to adopt.

If we understand Referee #2's concern correctly, he/she implies that we are misusing the word "uncertainty" to characterize something that is not an intrinsic uncertainty of a specific value. We simply do not know any other word than "uncertainty" to express the meaning we have just explained.

175-176 context is not clear – is it relevant/important that some inversions did not prescribe this field?

The present study is all about answering this question.

178 what "additional information" would that be? Why using this field at all then?

Same information as the other fields : what kind of developments related to tropospheric and stratospheric chlorine has been conducted in this model in the past years ? What kind of species and reaction have been included in the model to simulate this field ?

Because, as explained in the text, this field is still widely used in inversion studies and it is important to quantify its impact compared to using other Cl fields.

180-186 Tropospheric concentrations differ by an order of magnitude between given Cl fields, yet all of them exhibit similar stratospheric concentrations and vertical gradients. How is that possible?

The scale of Figure 1 is logarithmic. Stratospheric chlorine concentrations, as shown in Figure 1, are particularly high above 40 km and start increasing above 30 km. These high concentrations highly influence the mean stratospheric concentration, whereas the gradient is calculated between the surface and 30 km.

181-183 From the previous statement and Fig. 1 one cannot state that "latitudinal distributions of tropospheric concentrations are similar". Do you mean zonal/altitudinal relative changes? How you define/estimate spatial variability around the mean value? Is it gridcell-based, zonal average-based, how altitudes are considered etc.?

We agree. Thank you for the suggestion "zonal relative changes". It is indeed more consistent with Fig.1 as mean values differ.

supplement, 109 what does "last state of the atmosphere" imply?

It means the state of the atmosphere at the end of the assimilation window, namely January 1998. We corrected this:

The state of the atmosphere in January 1998 was used as initial conditions for the 1998-2018 inversions.

216 explain what "simple forward simulation" means

It means forward simulation, as opposed to inversions. We wanted to highlight the fact that forward simulations are quite simple and much less computationally-expensive to run in comparison with inversions.

245-248 why only δ13C (without mixing ratio) profiles are being compared?

In the first version of the paper, in 2019, we first decided to use CH_4 mixing ratio (x) - $δ^{13}C$ (y) plots because it is more robust to compare both atmospheric quantities together as CH_4 mixing ratios influences $δ^{13}C(CH_4)$ values. We decided to change this because uncertainties are easier to plot when $δ^{13}C(CH_4)$ profiles alone are being compared and because we already compared CH_4 mixing ratios in Figure 4. We think clarity would have been impacted by using a CH_4 - $δ^{13}C$ plot, without increasing the validity of our conclusions.

250-260 the message of the whole paragraph is incomprehensible – what the "4 months" period is referring to, simulated period or CPU wall time? If the latter, on which system?

We modified this sentence to give more information about the "4 months" assessment.

At present, approximately four months (wall-clock time on LSCE computational clusters consisting of Intel(R) Xeon(R) Gold 5317 CPUs with a frequency of 3.00 GHz) are necessary to reach a satisfactory convergence criterion with this system for a 20-year assimilation window, which is highly excessive if one must use this method every time the influence of two Cl fields are to be compared. Only a maximum of 8-10 CPUs can be used in parallel to run the CIF-LMDz-SACS code. Additional CPUs do not reduce the wall-clock computational time due to I/O limits.

254,273 it is not clear in what sense the methods are "more robust" and "less robust", please explain
265 same as for 250-260 – what does (~1 minute) refer to?

When you run a 3-D variational inversion at high-resolution, it appears to be more robust than a 1-D inversion or a 1-D simple mathematical framework. We think it is clear enough in the main text.

1 minute also refers to the wall-clock time, we apologize for not making this clearer. We modified the sentence.

285-288 differences of 20% and 10%, respectively, are not "slight" in this case; since you have all model output data at hand, it is straightforward to find the reason for this discrepancy instead of conjecturing

Compared to other differences in Cl sink estimates, we think we can use the "slight" adjective. Unfortunately, we do not have the data at hand. The modeling teams did not provide either the OH/O1D concentrations that were used to calculate the total chemical sink or the tropopause height/pressure.

287 "tropopause" and "tropopause level" have different meanings and definitions

We agree, we modified this sentence.

This discrepancy is likely due to a slight difference in the definition of the tropopause height or/and in the prescribed OH sink that is used to calculate the total chemical sink.

289-294 same as for 285-288: differences of 30% and more can't be considered "slight"

Again, compared to other differences mentioned in the rest of the sentence, we think we can use the "slight" adjective.

Table 4 how are concentrations (here and throughout the manuscript) weighted (volume/mass/CH_4 MR)?

Quantities in molec/cm3 are averaged using a volume-weighted averaging and quantities in VMR are averaged using a mass-weighted average. We included this sentence in the supplement.

301-302 the mentioned spatial distributions do not exhibit similar patterns

We think that the latitudinal dependency is quite clear and similar and therefore the spatial variations are also similar, and we do not use the word "identical".

312-313 comparing $\delta 13C(CH_4)$ biases is meaningless here because they are derived on top of inconsistent mixing ratio biases (see also comment to 217-227 and 315-322)

See our responses to general comments.

S115 ambiguous 3% uncertainty for $\delta 13C$

We do not understand why it is ambiguous. It is a value large enough (compared to measurement uncertainty and source signature uncertainties) to be sure our initial conditions can be easily optimized by our system since our atmosphere in 1988 is highly uncertain.

Presentation/technical

22 remove "albeit this influence is small below this altitude", redundant

This has been done.

23 "CH_4 vertical" −> "CH_4 mixing ratio vertical"

We think it is clear enough for the reader and such formulation might impact the reading.

41 "13C:12C atmospheric isotope composition of CH_4" −> "12C/13C isotope ratio in atmospheric CH_4", remove "denoted by d13C(CH_4)"

We modified this sentence.

To better separate these sources, assimilating observations of the $^{13}C/^{12}C$ isotope ratio in atmospheric CH_4, or $\delta^{13}C(CH_4)$, can be relevant.

51 poor formulation, "distributions … are very large with overlapping values". How large? What are "overlapping values"?

We think it is clear enough.

54-55 KIE and isotopic fractionation are not the same phenomena/entity. Read some basic literature on isotopes, e.g. [2]

We understand that isotopic fractionation encompasses more than kinetic isotope fractionation and we do not claim to be isotope experts. In our field, and particularly in atmospheric modeling of CH_4 and $\delta^{13}C(CH_4)$, kinetic isotope fractionation is the only process we need to consider. We therefore consider both expressions as equivalent for ease of reading.

We modified the sentence to make it more suitable.

This effect, called the Kinetic Isotope Effect (KIE), hereinafter also referred to as isotopic fractionation…

77 extraneous semicolon

This has been corrected.

92 "total CH_4" −> "CH_4 mixing ratio"

This has been corrected.

96 vague "with the atmospheric isotope composition", remove

We did not remove but we modified the sentence.

Joint assimilation (CH4 and δ13C(CH4)) is proving to be relevant and necessary in order to reconcile the estimated CH4 budgets with the observed atmospheric isotope composition.

127 "Cl + CH4" −> "Cl"

This has been corrected.

151 remove "generously"

We did not remove this adjective as the authors took some precious time to answer us and provide the fields. Some did not.

153 "version 10" mentioned twice

This has been corrected.

199 what "our system" implies?

This has been corrected.

This system runs a last forward simulation with optimized inputs at the end of the inversion process.

231 full stop missing

This has been corrected.

232 poor language ("observations measured")

This has been corrected.

CH$_4$ observations taken at…

238,240 "The analysis", "35 others" −> "35 profiles are provided"

This has been corrected.

242,246 extraneous commas

This has been corrected.

257-259 poor English, rewrite

This has been done.

Here, we employ this method to 1) take advantage of the high spatial resolution of the CIF-LMDz-SACS system and thus perform analysis at smaller spatial scales and 2) demonstrate that the simpler methods presented below provide good results at the global scale.

271-272 "… biaS increaseS over time but stabilizes after…", "would apply"−> "would have to apply"

This has been corrected.

279-280 "Cl sink" −> "estimate(s)"

This has been corrected.

Table 4 headings are misleading, "oxidation" −> "fraction of total", "Conc." −> "Cl concentration"; use of "oxidation" and "sink" implies these are not the same terms

This has been modified.

Figure 2 "average" −> "averaging", use "left/right column"

This has been corrected.

S23 what "its global concentration" refers to? It can't be parity discussed in the previous sentence

We modified the sentence to make it clearer.

OH-INCA globally-averaged concentrations increase by 4~\% between 2002 and 2014.

S52 do you refer to the supplement Sect. 1.6?

Yes, this has been modified.

S68-S78 use "grid cells" or similar instead of "pixels"; latter refer only to raster images

This has been corrected.

References:

Cantrell, C. A., Shetter, R. E., McDaniel, A. H., Calvert, J. G., Davidson, J. A., Lowe, D. C., Tyler, S. C., Cicerone, R. J., and Greenberg,J. P.: Carbon kinetic isotope effect in the oxidation of methane by the hydroxyl radical, Journal of Geophysical Research: Atmospheres,95, 22 455–22 462, https://doi.org/doi.org/10.1029/JD095iD13p22455, 1990.

Saueressig, G., Crowley, J. N., Bergamaschi, P., Brühl, C., Brenninkmeijer, C. A. M., and Fischer, H.: Carbon 13 and D kinetic isotope effects in the reactions of CH4 with O(1D) and OH: New laboratory measurements and their implications for the isotopic composition of stratospheric methane, Journal of Geophysical Research: Atmospheres, 106, 23 127–23 138, https://doi.org/10.1029/2000JD000120,2001