## We thank Referee #1 for the thoughtful comments and respond to individual comments below. Our responses are in **bold**.

#### Anonymous Referee #1

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 d13C. The main conclusion of manuscript, which reads very well and is nicely concise and to the point, is that the d13C 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 the journal. Besides this I have a few methodological issues that require attention to make this work publishable.

We now clarify in the abstract and introduction that our study shows how inter-model diversity in the Cl simulated by state-of-the art global models, not just uncertainty in Cl in general, impacts  $\delta^{13}$ C. We believe this is a novel analysis.

We now state in the abstract: "Global model simulations of halogen chemistry differ strongly from one another in terms of both the magnitude of tropospheric Cl and its geographic distribution. This study explores the impact of the inter-model diversity in Cl fields on the simulated  $d^{13}$ C of CH<sub>4</sub>." And "Consequently, it is possible to achieve a good representation of total CH<sub>4</sub> using widely different Cl concentrations, but the partitioning of CH<sub>4</sub> loss between the OH and Cl reactions leads to strong differences in isotopic composition depending on which model's Cl field is used." We clarify in the introduction: "Here, we investigate the sensitivity of  $\delta^{13}$ C of CH<sub>4</sub> to inter-model diversity in chlorine concentrations to better quantify how much uncertainty in the interpretation of  $\delta^{13}$ C is imposed by the uncertainty in Cl."

We also added an additional section (Section 3.3) quantifying the relationship between the percent of methane loss from Cl and the surface  $\delta^{13}$ C. This addition provides a useful quantitative measure of the impact of Cl on the isotopic budget.

#### 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.

Latitudinal variations in source signatures can indeed influence the isotopic distribution, as we acknowledge in our conclusions when we state "the interhemispheric gradient is also

influenced by spatial variation in the isotopic signatures of the sources, complicating this issue." We also mention in Section 3.4 that "Including spatially-varying isotopic signature for other sources as well could further modify the simulated interhemispheric gradient, potentially correcting some of the flat gradient of e.g. the SimTom simulation". We do incorporate some of the spatial variation in source signatures by separating biomass burning into C3 and C4 fractions with different isotopic signatures, and our SimWet simulation also incorporates the spatial variability of wetland emissions. Incorporation of even more detailed or updated isotopic source data is a useful direction for future work, but beyond the scope of the current 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 it their figure 3 the impact could easily be 0.3 per mil (the impact is a bit larger along the Arctic cost 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.

This is an interesting point. Wetland emissions in our simulation are smaller than those of Ganesan et al (2018), and the strength of other sources differs as well, so we do not expect the impact to be identical. We add the following statement to section 3.4 of our revised manuscript: "The size of the effect of including spatially varying ratios in wetland emissions depends on the strength of the wetland emissions as well as the other sources."

The comparison between simulated and observed CH4 in Figure 2 is very convincing. However, limited information is provided to judge the d13C 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 d13C 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 d13C trend is confirmed by the measurements.

We add an additional figure, included below, showing the simulated and observed  $\delta^{13}$ C for 1998-2004 for 6 GMD sites with records extending back to 1998, the year data becomes available. This figure shows that the differences between sensitivity simulations are large compared to the trend in the observations over this period, so our conclusions are not specific to 2004. Investigating the trend in the isotopic observations is beyond the scope of our study since the portion of our simulation covered by the GMD observations is short for trend analysis. We add the following text to Section 3.2:

"Figure 6 shows the timeseries of observed and simulated  $\delta^{3}$ C for 1998-2004 at the 6 GMD sites with  $\delta^{3}$ C records covering this time period. We begin the figure at 1998 rather than 1990 due to the lack of data availability in the earlier years. The standard and sensitivity

simulations overestimate  $\delta^{3}$ C at the northernmost station, BRW. The observations at the other stations lie within the range of simulations, with most simulations underestimating the observations at the South Pole. The differences between the different sensitivity simulations are large compared to the interannual variability in both observed and simulated  $\delta^{3}$ C. We focus our subsequent analysis focuses on a single year, 2004."



It is unclear why only measurements at the South Pole are used to assess the seasonal cycle of d13C. According to the work of Allen et al., the SimMBL scenario should 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.

We show the seasonal cycle at other stations in Supplemental Figure S5. The seasonal cycle is also apparent in our new figure showing the 1998-2004 time series of  $\delta^{13}$ C. GMD data is not available at Baring Head for the years of our simulation. However, we discuss another southern hemisphere site, CGO, which shows a similar result to the South Pole.

It is unclear why averages of multiple site are used for CH4, but not for d13C.

We used averages for CH<sub>4</sub> to avoid excessive numbers of plots, particularly since total CH<sub>4</sub> is not our main focus. There are less sites with isotopic data, and that is our main focus, so we did not feel it necessary to take averages.

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?

It is difficult to definitively answer this question since the seasonal cycle is also influenced by the seasonal cycle and isotopic signatures of the sources, as we show with the SimWet simulation. However, we do show the potential for a strong MBL Cl source to alter the amplitude of the seasonal cycle in the southern hemisphere with minimal impact on northern hemisphere sites. We add the following discussion to Section 3.2:

"However, since the seasonal cycle amplitude at SPO lies in between SimMBL and the other simulations, it is possible that at an MBL Cl source similar to that of SimMBL but with a smaller average value could reproduce the amplitude well."

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 welldefined observational constraint on what it should be, it would be better not to change the treatment of OH.

The combined Cl and OH fractionation is indeed well outside the observed constraint. However, we recognize that changing the KIE of OH complicates our analysis, so we added an additional sensitivity study, SimTomB, that uses the Cl field of the SimTom simulation but keeps the same KIE of OH as the standard simulation. We use this simulation in the new figure 11, shown below, and add a new Section 3.3 that quantifies the effect of changing Cl when OH fractionation is held constant.



#### 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?

The old bias here relates to the time since the air was in contact with the northern hemisphere midlatitudes, so it is also affected by tropospheric transport. We expect the impact on isotopic composition to depend on the details of the transport bias, which is beyond the scope of this study. However, the bias is small enough that we expect it to be a small uncertainty compared to the uncertainties due to methane's sources and sinks, and their isotopic signatures.

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).

It is true that we, like many others in the literature, used the old value both for partitioning the total methane source into 12C and 13C components, and for converting our simulated 13C and 12C concentrations to  $\delta^{13}$ C. We felt that using the old value for the source partitioning was most consistent with the isotopic source signatures in the literature, such as the compilations by Houweling et al (2000) and Lassey et al (2007), which both cite the Craig (1957) number. We then used the same number for calculating  $\delta^{13}$ C for consistency. However, we tested the impact of this choice by conducting an additional simulation identical to SimStd using the Zhang (1990) value for both the source partitioning and the calculation of  $\delta^{13}$ C. The new simulation gives very similar results to SimStd, demonstrating that our results are robust to the choice of VPDB as long as the same value used to calculate the source partitioning is used to calculate  $\delta^{13}$ C. We elaborate on this important in the Model Description section of our revised manuscript: "We partition each emission source into  ${}^{12}CH_4$  and  ${}^{13}CH_4$  emissions according to a sourcespecific  $\delta^{13}C$  value from the literature, provided in Table 1. We use the Craig (1957) R<sub>std</sub> value to partition the sources since it is cited in the literature used in Table 1 (Houweling et al, 2000; Lassey, 2007), and so for consistency we use the same value in equation 1 to calculate the simulated d<sup>13</sup>C of the CH<sub>4</sub> concentrations. We note, however, that the GMD observations now use a slightly different standard, the VPDB value of 0.011183 (Zhang and Li, 1990). A sensitivity study (not shown) confirms that the choice Rstd has little effect on our results as long as the same value is used for the source partitioning as for the calculation of  $\delta^{13}$ C-CH<sub>4</sub> from simulated [ ${}^{13}$ CH<sub>4</sub>] and [ ${}^{12}$ CH<sub>4</sub>]."

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.

This is a good suggestion. We add a supplemental figure showing the seasonal cycle by latitude of the four surface Cl fields. We add the following description to section 2.2: "SimStd and SimGC have more modest seasonal shifts, while Cl in SimTom remains concentrated in the northern hemisphere throughout the year (Fig. S3)."

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

We felt it was more conservative to use the standard deviation rather than the standard error of the measurements within the month. However, when we average multiple years of data (for the seasonal cycle figures), we then use the pooled variance to calculate the standard error across years. We now clarify this in section 2.3 by adding: "When multiple years are observations are averaged together, we use the pooled variance to calculate the standard error, thus reducing the error based on the number of years."

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.

We clarified in the text that it is in "northern Eurasia (around 60°N)". Figure S1 shows that this source is quite large in the model.

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.

We added an additional figure and an additional Section 3.3 dedicated to quantifying the link between CH<sub>4</sub> oxidation by Cl and the surface  $\delta^{13}$ CH<sub>4</sub>. We use this analysis to add the following quantification of the Cl effect to the conclusions:

"Each percent increase in the amount of CH<sub>4</sub> loss occurring by reaction with Cl increases global mean surface  $\delta^{3}$ C of CH<sub>4</sub> by approximately 0.5‰. This relationship can be used to estimate the impact on methane's isotopic values from future model simulations of Cl."

## We thank Referee #2 for the thoughtful comments and respond to individual comments below.

#### Anonymous Referee #2

This study investigates the use of different tropospheric chlorine sinks on the isotopic composition of methane. Through using a series of model runs, the authors test the impact of different Cl fields from the published literature on the isotopic composition of methane in the troposphere. As the authors highlight, because the reaction between CH4 and Cl is highly fractionating, a small change in tropospheric chlorine can have a substantial impact on the isotopic ratio of CH4. As such, the work serves as a reminder not to ignore the impacts of tropospheric chlorine on analyses of the methane carbon isotope ratio. In this regard the work has the potential to be highly relevant to many researchers in the field and sits well within the journal's scope. However, beyond this general point, I'm at a slight loss as to what has been learnt from this study. The conclusions are entirely qualitative and merely serve to reiterate the point that an understanding of the chlorine sink is important when it comes to interpreting isotope ratios. I do not disagree with this point, but surely this work could aim higher by quantifying the impact on isotopic methane ratios (and source composition) of different assumptions regarding the chlorine sink. The paper does not want for brevity, so the inclusion of further analysis would not make it unduly long. I certainly think that there is merit in this work but it could do with a little more refining.

We followed the reviewers' suggestion to make the paper more quantitative by adding an additional analysis, described in Section 3.3. This analysis quantifies the relationship between the fraction of methane oxidized by Cl and the response of surface  $\delta^{13}$ C. We believe that including this single number quantifying the impact of Cl enhances the takehome message of the paper.

#### General comments:

Beyond the general point that the chlorine sink is important, the take-home message of the paper is rather vague. I think this is partially because of the confusing nature of the sensitivity experiments, where multiple variables are changed simultaneously (sink magnitude, sink distribution and fractionation rates) making it all but impossible to draw conclusions on what the key underlying factors are. For instance, although the SimStd and SimGC runs straddle the observations, is that due to the different magnitude of the sink or the different distribution? The SimTom simulation changes all variables at once, leading to an isotope ratio that at first appears conceptually wrong. Despite the larger Cl sink, the isotopic composition becomes more depleted in 13C! There is a throwaway line (P.6 L202) that the larger Cl sink is compensated by lower OH, but really this needs to be shown explicitly. Perhaps the point is that the Cl sink can't be too large, because the OH sink would have to be substantially smaller, making the simulated isotope ratio inconsistent with the observations? But, if so, then more work needs to be done to consider plausible changes to emissions totals so that one wouldn't have to change the OH sink to keep total CH4 consistent with the observations.

A major point of our study was to quantify the effect of the inter-model diversity in Cl fields produced by the current generation of chemistry climate models on methane's isotopic composition. We now clarify this purpose in the introduction and abstract. This inter-model diversity includes differences in the distribution as well as the magnitude of tropospheric Cl. These multiple differences do complicate our analysis as the reviewer points out, but we feel that including all aspects of the model diversity makes the study more applicable to understanding the impact of model differences.

While adjusting the OH fractionation was necessary to maintain consistency with the isotopic observations, we recognize that changing multiple variables at once makes quantifying the impact of Cl difficult. Consequently, we add an additional sensitivity simulation, SimTomB, that uses the same Cl as SimTom but keeps the same OH and OH fractionation as the SimStd and SimGC simulations. We then use these 3 simulations together in our new Section 3.3 and a new figure to quantify the impact of Cl. Since the Cl fields differ in distribution as well as magnitude between the 3 simulations, we use the total fraction of CH<sub>4</sub> lost through reaction with Cl as an integrated measure of these effects. This fraction is reported by other modeling studies, so we expect presenting our results this way will be useful.

The results focus on the model outputs from a single year (2004), and to be more precise from 2 months (January and July) from this single year. However, I was not convinced of the reason why, and it would be helpful if more justification for this were provided. Perhaps I missed the point but why do flat methane concentrations simplify the analysis, when the focus is on the isotopic ratio? What does the isotopic composition trend look like during the same period(1990-2004), and is this well captured by the model (and sensitivity studies)? The authors note (p.6 L205) that since the isotopic composition is not in steady state in 2004, the results diverge with further years of simulation. So, does that mean the conclusion that SimStd and SimGC bracket the observations is only valid in 2004, and if so, what about in other years?

We add an additional figure showing the simulated and observed  $\delta^{13}$ C for 1998-2004 for 6 GMD sites with records extending back to 1998, the year data becomes available. This figure shows that the differences between sensitivity simulations are large compared to the

trend in the observations over this period, so our conclusions are not specific to 2004. We add the following text to Section 3.2:

"Figure 6 shows the timeseries of observed and simulated  $\delta^{3}C$  for 1998-2004 at the 6 GMD sites with  $\delta^{3}C$  records covering this time period. We begin the figure at 1998 rather than 1990 due to the lack of data availability in the earlier years. The standard and sensitivity simulations overestimate  $\delta^{3}C$  at the northernmost station, BRW. The observations at the other stations lie within the range of simulations, with most simulations underestimating the observations at the south pole. The differences between the different sensitivity simulations are large compared to the interannual variability in both observed and simulated  $\delta^{3}C$ . We focus our subsequent analysis on a single year, 2004."

The conclusions seem to be mostly qualitative, raising the question of what the implications are for researchers wanting to use methane isotope data to constrain the evolution of different sources over time? Although it is stated that the choice of Cl field strongly impacts the CH4 source mixture that best fits the observations it would certainly help if this were spelled out more explicitly with some quantitative examples.

As we describe above, we now have a quantitative description of the impact Cl oxidation that can be used to estimate the impact on  $\delta^{13}$ C from future model simulations of Cl. We added this to the conclusions:

"Each percent increase in the amount of CH<sub>4</sub> loss occurring by reaction with Cl increases global mean surface  $\delta^{3}$ C of CH<sub>4</sub> by approximately 5‰. This relationship can be used to estimate the impact on methane's isotopic values from future model simulations of CL."

Specific comments: p.3 L89-90 – Is the OH field seasonally varying but inter-annually constant? Please state.

#### Yes, we add this to Section 2.1: "The OH field varies monthly but repeats every year."

p.3 L89-92 – Given the observational evidence that the NH/SH OH ratio is roughly uniform (e.g. Patra et al 2014) what is the justification for model output ratios with significant asymmetry? Indeed, the Strode et al (2015) paper that is cited seems to suggest that a ratio close to 1 also provides a better match to observations, so the use of a northern hemisphere OH field that is 20% higher is even more confusing.

Since one of our goals is to understand the impacts of model diversity, we thought it best to use an OH distribution similar to what many CCMs, including GEOS when run as a CCM, produce. We now explain this in Section 2.1:

"This modification is designed to make our results more applicable to understanding the impacts inter-model differences in Cl, since it makes our OH distribution more consistent by that produced by many CCMs. The OH field varies monthly but repeats every year."

P3. L106 – There is a reference missing for the fractionation value due to soil absorption. Also, how large is the soil sink as a fraction of total loss? How well is this constrained in the literature? Given the fractionation seems quite large, couldn't small errors in the soil absorption sink also impact on the isotopic ratio of atmospheric methane?

We added the reference to Tyler et al (1994). The soil sink is an additional source of uncertainty, and we now mention this in the conclusions: "However, the interhemispheric gradient is also influenced by spatial variation in the isotopic signatures of the sources and uncertainties in the soil sink, complicating this issue."

P3. L106 and Fig. 1 - I do not see the value of Figure 1 and any information it may show is largely duplicated in Figure 6. Perhaps it would do better in the supplement. The color gradient is also pretty weak, so if the figure is to be included it might be best to reduce the scale so that differences are easier to determine.

#### We moved the figure to the supplement.

P4. L133-134 - "We find the resulting emissions lead to a good simulation..." Please define "good", be it through RMSE, bias, correlation, etc..

We add that "The simulation has only a 0.1% mean bias compared to the observations for 2004." Other statistics including correlation are provided in Section 3.1.

Also please define NOAA GMD.

Done

P4. L136-149 - What is the temporal variation in the Cl fields. Do they change interannually?

The Cl fields vary monthly but repeat from year to year. We added an additional supplemental figure showing the monthly variations of surface Cl. We added the following clarification to Section 2.2:

"SimStd and SimGC have more modest seasonal shifts, while Cl in SimTom remains concentrated in the northern hemisphere throughout the year (Fig. S3). All simulations repeat the same Cl field from year to year."

P4. L138-139 – For the avoidance of doubt, do all sensitivity studies use the same stratospheric loss fields? Please be explicit.

They are the same above 56 hPa. We now clarify in section 2.2: "We also conduct several sensitivity simulations in which we alter the tropospheric and lower stratospheric Cl fields (Table 2). Cl is not altered above 56 hPa."

P4. L146-147 - Is the 2.5% loss the fraction in the TOMCAT model or in your model

runs? I have assumed the latter but it is unclear.

#### We added "in our simulation" to clarify that it is in our model run.

P5. L154-155 – The Cl field from TOMCAT accounts for 2.5% of CH4 loss. But then the OH concentration is reduced by 2%, so does the Cl sink now account for more than 2.5% of CH4 loss?

#### No, the OH adjustment was already included.

P5. L154-155 – I appreciate the wish to keep total CH4 roughly the same but why do this by altering the OH loss rather than altering the total emissions? Is a 2% change in OH consistent with the oxidation of other species beyond methane such as CO or methyl chloroform? In other words, is this a plausible scenario? The same goes for the 4% reduction used in SimMBL. Wouldn't it be worth increasing the sources to compensate for the increase in sink instead?

These changes in OH are well within the uncertainty of OH derived from either methyl chloroform inversions or global models. We add this to section 2.2: "These changes are small compared to the uncertainty in global OH."

# We could have increased the sources instead, but this would lead to different emissions in different sensitivity runs, which would also complicate the analysis.

P5. L155-156 – The fractionation value is increased in SimTom to avoid too much fractionation. But then the results show that there is too little. So is this change really justified? No evidence is shown for the case where the fractionation is kept the same to support this decision.

#### We now have an additional sensitivity simulation, as noted above, that parallels SimTom but with the fractionation kept the same. This simulation quickly diverges from the observations.

P5. L171-177 – I think it would be pertinent to include some mention of the distribution of observations and how many different locations there are measuring 13C in the observation network.

#### We add the following information to Section 2.3:

"The GMD observations are located at remote sites, shown in Fig. 4 for CH<sub>4</sub> in 2004. Measurements of  $\delta^{13}$ C of CH<sub>4</sub> are available at a subset of the sites, shown in Fig. 5."

P5. L184 – Why choose to focus only on January and June? The answer may be obvious but it still needs to be mentioned.

#### We now clarify in Section 3.1:

"We focus on these two months to represent the seasonal differences."

P6. L194-196 –Perhaps it might help to give the latitude of this isotopically heavy region (\_60 N) to help guide the reader and link to Figure 7.

### We now say:

"the isotopically heavy region in northern Eurasia (around 60°N)"

P6. L205-208 – Should the isotopic composition be in steady state in 2004? Although Fig. 2 shows the model and observed trends in bulk CH4, shouldn't the comparison of the modelled and observed isotopic ratios also be shown to assess the model performance? I.e Is it only in 2004 that the model isotope ratios are broadly in agreement with the observations?

# As discussed above, we added a new figure 6 that shows a comparison for more years and demonstrates that the results are not specific to 2004.

P6. L215-219 – The point is made here that it is the distribution of the Cl sink that is key for the SimTom run, but I really think this needs to be made more prominent. The use of a different OH sink again complicates the issue as well, as the SH effects seem to be mostly a result of OH changes rather than Cl, so are you really analyzing the response to a change in the Cl sink or a change in the magnitude and fractionation of the OH sink?

Given the way the experiments are designed, we cannot completely isolate these effects. We are showing the combined effects of assuming oxidation by Cl versus OH within the observational constraints on the total provided by the observations. To clarify that multiple effects are included, we now state in Section 3.2: "The differences between simulations reflect differences in the locations where CH<sub>4</sub> oxidation occurs and the amount and location of isotopic fractionation due to Cl versus OH".

P7. L221 – Given the reduced hemispheric OH difference improves the simulation again the question has to be asked why this wasn't used as the standard configuration?

As noted above, one of our goals is to understand the impacts of model diversity. We therefore thought it best to use an OH distribution similar to what many CCMs, including GEOS when run as a CCM, produce. We now explain this in Section 2.1: "This modification is designed to make our results more applicable to understanding the impacts inter-model differences in Cl, since it makes our OH distribution more consistent by that produced by many CCMs."

P7. L236-237 – How large would the correction to the geologic source have to be to improve the inter-hemispheric gradient? It seems that the inter-hemispheric gradient is relatively unperturbed by the different Cl fields, and more likely a result of source differences or a change in the interhemispheric OH ratio. The simulation that best approximates the inter-hemispheric gradient is SimWet. Doesn't this point to accurate

source signatures being of primary importance in determining this gradient, rather than the Cl field?

It is beyond the scope of this study to infer the optimum geologic source. Accurate estimates of source magnitudes and signatures are certainly important, and the purpose of this section is indeed to acknowledge that importance. However, we have also shown a significant impact from Cl. Table 3 shows that SimMBL alters the Jan. interhemispheric gradient more than SimWet. Consequently, both sources and sinks are uncertain levers on the interhemispheric gradient.

P7. L239-240 – Would it not be best to include SimWet description in section 2.2? Also it would be useful to give more details of this simulation. By how much does the wetland source signature change versus the single value simulation?

We add a brief description, including the global mean signature, to Section 2.2 as suggested:

"We conduct an additional sensitivity study, SimWet, to illustrate the role of spatial variation in the isotopic source signature. SimWet parallels SimStd, but the isotopic composition of the wetland source uses spatial variation from Ganesan et al (2018). The global mean source signature of the wetland emissions remains -60%."

P8. L265 - "We find that the NH Cl maximum acts to flatten the interhemispheric gradient...". But this isn't the Cl distribution alone that has this effect, as both the OH sink magnitude and fractionation changed. Based on the sensitivity cases shown one cannot conclude that this is down to Cl alone. The same applies for conclusions related to SimMBL.

We now mention the OH change as well:

"We find that the strong NH Cl maximum, along with the resulting reduction in OH fractionation required to maintain consistency with observations, acts to flatten the interhemispheric gradient of  $\delta^{13}$ C"

P8. L271 - "...but combining it with the Cantrell et al (1990) value would lead to an overestimate"

Would it? This isn't shown. Changing the fractionating effect of OH between sensitivity cases without showing the evidence for why this is the most appropriate action seems odd.

We looked at this in the SimTomB simulation, which uses the Cantrell et al (1990) value, and found it quickly becomes too heavy compared to observations. We now mention this is in Section 2.2:

"This simulation becomes too heavy compared to observations, justifying the need to change  $\alpha_{OH}$  in the main SimTom simulation."

P8. L272 – What about the uncertainty in the fractionating effect of other sinks such as soil absorption and Cl. Are they of a similar scale to the uncertainty in OH?

It is true that better constraints on any portion of the methane budget are helpful, but we focus here on the OH fractionation value because it is a very strong hammer on the mean isotopic ratios, and not all of its values are consistent with all the Cl values simulated by global models.

P8. L272-275 - "The choice of Cl field thus strongly impacts..." Yes, but by how much? Under these different assumptions about Cl how different would the source mixtures end up being?

We use our new analysis, described earlier, to make this quantitative. We added the following to the conclusions:

"Each percent increase in the amount of CH<sub>4</sub> loss occurring by reaction with Cl increases global mean surface  $\delta^{13}$ C of CH<sub>4</sub> by approximately 0.5‰. This relationship can be used to estimate the impact on methane's isotopic values from future model simulations of Cl."

Technical comments: P. 3 L 83 – GMI is used before being defined

## Fixed

Fig. 4 – I appreciate the scales probably need to be different, but why do the panels use different color maps?

#### We updated the figure to use the same color maps.

Fig 8 and 9 – Units omitted on panels b and c in both figures.

#### We added the units.

#### Strong Sensitivity of the Isotopic Composition of Methane to the 1 Plausible Range of Tropospheric Chlorine 2 3 Sarah A. Strode<sup>1,2,\*</sup>, James S. Wang<sup>1,2,\*\*</sup>, Michael Manyin<sup>2,3</sup>, Bryan Duncan<sup>2</sup>, Ryan Hossaini<sup>4</sup>, 4 5 Christoph A. Keller<sup>1,2</sup>, Sylvia E. Michel<sup>5</sup>, James W. C. White<sup>5</sup> 6 7 <sup>1</sup>Universities Space Research Association, Columbia, MD, USA 8 <sup>2</sup>NASA Goddard Space Flight Center, Greenbelt, MD, USA 9 <sup>3</sup>SSAI, Lanham, MD, USA 10 <sup>4</sup>Lancaster Environment Centre, Lancaster University, Lancaster, UK 11 <sup>5</sup>Institute of Arctic and Alpine Research, University of Colorado, Boulder, CO, USA 12 \*correspondence to: <u>sarah.a.strode@nasa.gov</u> \*\*Now at the Institute for Advanced Sustainability Studies, Potsdam, Germany 13 14 15 Abstract. The <sup>13</sup>C isotopic ratio of methane, $\delta^{13}$ C of CH<sub>4</sub>, provides additional constraints on the CH<sub>4</sub> budget to 16 17 complement the constraints from CH<sub>4</sub> observations. The interpretation of $\delta^{13}C$ observations is complicated, however, 18 by uncertainties in the methane sink. The reaction of CH4 with Cl is highly fractionating, increasing the relative 19 abundance of <sup>13</sup>CH<sub>4</sub>, but there is currently no consensus on the strength of the tropospheric Cl sink. Global model 20 simulations of halogen chemistry differ strongly from one another in terms of both the magnitude of tropospheric Cl 21 and its geographic distribution. This study explores the impact of the inter-model diversity in Cl fields on the 22 simulated $\delta^{13}$ C of CH4. We use a set of GEOS global model simulations with different predicted Cl fields to test the 23 sensitivity of the $\delta^{3}$ C of CH<sub>4</sub> to the diversity of Cl output from chemical transport models. We find that $\delta^{3}$ C is highly 24 sensitive to both the amount and geographic distribution of Cl. Simulations with Cl providing 0.28% or 0.66% of the 25 total CH<sub>4</sub> loss bracket the $\delta^{3}$ C observations for a fixed set of emissions. Thus, even when Cl provides only a small 26 fraction of the total CH<sub>4</sub> loss and has a small impact on total CH<sub>4</sub>, it provides a strong lever on $\delta^{13}$ C. <u>Consequently</u>, 27 it is possible to achieve a good representation of total CHe using widely different Cl concentrations, but the partitioning 28 of CH<sub>4</sub> loss between the OH and Cl reactions leads to strong differences in isotopic composition depending on which 29 model's Cl field is used. Comparing multiple simulations, we find that altering the tropospheric Cl field leads to 30 approximately a 0.52 increase in $\delta_{1}^{13}CH_{e}$ for each percent increase in how much CH<sub>e</sub> is oxidized by Cl. The 31 geographic distribution and seasonal cycle of Cl also impacts the hemispheric gradient and seasonal cycle of $\delta^{13}$ C. 32 The large effect of Cl on $\delta^{3}$ C compared to total CH<sub>4</sub> broadens the range of CH<sub>4</sub> source mixtures that can be reconciled 33 with $\delta^{13}C$ observations. Stronger constraints on tropospheric Cl are necessary to improve estimates of CH<sub>4</sub> sources 34 from $\delta^{13}$ C observations.

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## 38 1. Introduction39

40 The global budget of methane is of great interest due to methane's role as a greenhouse gas, ozone precursor, 41 and sink of the hydroxyl radical. Despite extensive study, major uncertainties in the methane budget remain, with 42 top-down and bottom-up estimates often yielding different results (Kirschke et al., 2013;Saunois et al., 2016;Saunois 43 et al., 2017, and refs therein) for the strength of specific source types. Furthermore, the resumed increase of methane 44 concentrations beginning in 2007 (Dlugokencky et al., 2009; Rigby et al., 2008) can be explained by multiple 45 hypotheses including an increase in fossil fuel emissions (Turner et al., 2016;Thompson et al., 2015;Hausmann et al., 46 2016), an increase in fossil fuel emissions combined with a decrease in biomass burning (Worden et al., 2017), an 47 increase in biogenic sources (Schaefer et al., 2016;Nisbet et al., 2016), or a decrease in hydroxyl concentrations 48 (Turner et al., 2017;Rigby et al., 2017). Variations in hydroxyl concentrations may also be important for the decrease 49 in methane growth from 1999-2006 (McNorton et al., 2016).

50 Observations and modeling of methane's carbon isotopes provides additional information on methane 51 sources since individual sources differ in their <sup>13</sup>C to <sup>12</sup>C ratio ( $\delta^{13}$ C). Isotopic information can be used to better 52 constrain methane sources (e.g. Thompson et al., 2015; Mikaloff Fletcher et al., 2004b, a) and infer how the source 53 mixture changed over glacial (e.g. Hopcroft et al., 2018; Fischer et al., 2008; Bock et al., 2017), millennial (e.g. Ferretti 54 et al., 2005; Houweling et al., 2008), and decadal timescales (e.g. Nisbet et al., 2016; Schaefer et al., 2016; Kai et al., 55 2011; Schwietzke et al., 2016; Thompson et al., 2018). However, there are considerable uncertainties in the processes 56 that control methane's isotopic composition that may confound source apportionment studies. Many modeling studies 57 use a single value for the isotopic ratio of each source, while in reality sources such as wetlands, biomass burning, and 58 natural gas show large regional or environment-dependent variations in their isotopic signature (Ganesan et al., 2018; 59 Brownlow et al., 2017; Dlugokencky et al., 2011; Schwietzke et al., 2016; Sherwood et al., 2017). 60 The isotopic composition of atmospheric methane is also sensitive to methane's sinks. Reaction with OH, 61 the principal loss for atmospheric methane, has a kinetic isotope effect (KIE) of -5.4% ( $\alpha = k_{13}/k_{12} = 0.9946$ ) to -3.9%

62 ( $\alpha$ =0.9961) (Saueressig et al., 2001; Cantrell et al., 1990) and contributes to the interhemispheric gradient of  $\delta^{3}$ C 63 (Quay et al., 1991). Mass balance (Lassey et al., 2007) and observations of the seasonal cycle of  $\delta^{13}$ C versus methane 64 concentration, however, suggest larger apparent KIE values, which may indicate a role for methane oxidation by 65 chlorine (Cl) in the marine boundary layer (MBL) (Allan et al., 2001;Allan et al., 2007) since Cl has a KIE of -61.9‰ 66 ( $\alpha$ =0.938) at 297K (Saueressig et al., 1995). Inclusion of the MBL Cl sink alters the source mixture inferred from 67 inverse modeling of  $\delta^{13}$ CH<sub>4</sub> (Rice et al., 2016). Nisbet et al. (2019) point out that interannual variability in the CH<sub>4</sub> 68 Cl sink could explain some of the variability of  $\delta^3$ C. Cl is also an important methane sink in the stratosphere, and the impact of this sink on surface  $\delta^{13}$ C is a source of uncertainty in modeling  $\delta^{13}$ C (Ghosh et al., 2015). Reaction with 69 70 stratospheric Cl contributes approximately 0.23% to the  $\delta^{13}$ C of surface methane and makes a small contribution to 71 the observed trend in surface  $\delta^{13}$ C over the last century (Wang et al., 2002).

The global concentration of Cl in the MBL and its role in the methane budget is still uncertain. Clconcentrations are highly variable and not well constrained by direct observations. Modeling work by Hossaini et al.

74 (2016) and Sherwen et al. (2016) suggests that chlorine provides 2-2.5% of tropospheric methane oxidation. This

agrees well with estimates based on the isotopic fractionation, which also suggest Cl provides several percent of the
total sink (Allan et al., 2007;Platt et al., 2004). However, Gromov et al. (2018) suggest that these are overestimates
as values over 1% are inconsistent with the δ<sup>t3</sup>C of CO, which is a product of CH<sub>4</sub> oxidation. The recent modeling
study of Wang et al. (2019) also suggests a value of 1%. There is thus considerable uncertainty in the role of chlorine
in the budget and isotopic composition of methane.
Here, we investigate the sensitivity of δ<sup>t3</sup>C of CH<sub>4</sub> to inter-model diversity in tropospheric chlorine
concentrations to better quantify how much uncertainty in the interpretation of δ<sup>t3</sup>C is imposed by the uncertainty in

81 concentrations to better quantify how much uncertainty in the interpretation of  $\delta^{13}$ C is imposed by the uncertainty in 82 Cl. Section 2 describes the modeling framework. We present results for total CH<sub>4</sub> and its isotopic composition 83 compared to surface observations in Section 3, and discuss the implications for the global CH<sub>4</sub> budget in Section 4.

compared to surface observations in Section 3, and discuss the implications for the global CH4 budget in Section 4.

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#### 2.1 Model Description

2. Methods

88 We simulate atmospheric methane with the Goddard Earth Observing System (GEOS) global earth system model 89 (Molod et al., 2015; Nielsen et al., 2017). The model has 72 vertical levels extending from the surface to 1 Pa. We 90 conduct simulations at C90 resolution on the cubed sphere, which corresponds to approximately 100 km horizontal 91 resolution. The simulations' meteorology is constrained to the MERRA-2 reanalysis (Gelaro et al., 2017) using a 92 "replay" method (Orbe et al., 2017). The GEOS replay agrees well with the tropospheric mean age of the Global 93 Modeling Initiative (GMI) chemistry and transport model (CTM) (Orbe et al., 2017), which shows reasonable 94 agreement with the age derived from SF6 observations, albeit with an old bias in the southern hemisphere (Waugh et 95 al., 2013). We thus expect the simulated interhemispheric transport time to be reasonable.

96 The GEOS CH4 simulation can be interactively coupled to CO and OH (Elshorbany et al., 2016), or run 97 independently with prescribed OH fields. We take the latter approach in this study, since this approach is able to 98 capture many of the observed variations in atmospheric methane (Elshorbany et al., 2016). We prescribe the OH field 99 following (Spivakovsky et al., 2000), but modify the OH to be approximately 20% higher in the Northern Hemisphere 100 than the Southern Hemisphere, consistent with the OH field produced by many global atmospheric chemistry models 101 (Naik et al., 2013;Strode et al., 2015). This modification is designed to make our results more applicable to 102 understanding the impacts inter-model differences in Cl, since it makes our OH distribution more consistent by that 103 produced by many CCMs. The OH field varies monthly but repeats every year. We also include stratospheric losses 104 for CH4 from reaction with OH, Cl, and O<sup>1</sup>D. These fields are prescribed from output of the GML CTM 105 (https://gmi.gsfc.nasa.gov) (Strahan et al., 2007; Duncan et al., 2007). 106 We implement the CH<sub>4</sub> isotopes in GEOS by separately simulating <sup>13</sup>CH<sub>4</sub> and <sup>12</sup>CH<sub>4</sub> tracers. We then calculate total CH<sub>4</sub> as the sum of the two carbon isotopologues and calculate  $\delta^{13}C$  of CH<sub>4</sub> in per mil using the standard definition: 107 108  $\delta^{13}$ C-CH<sub>4</sub> (‰) = ([<sup>13</sup>CH<sub>4</sub>]/[<sup>12</sup>CH<sub>4</sub>]/R<sub>std</sub> - 1) \* 1000

108  $\delta^{13}$ C-CH<sub>4</sub> (‰) = ([<sup>13</sup>CH<sub>4</sub>]/[<sup>12</sup>CH<sub>4</sub>]/R<sub>std</sub> - 1) \* 1000 (1) 109 where R<sub>std</sub>=0.0112372 is the peedee belemnite isotopic standard (Craig, 1957). We partition eas

- where  $R_{std}=0.0112372$  is the peedee belemnite isotopic standard (Craig, 1957). We partition each emission source
- 110 into  ${}^{12}CH_4$  and  ${}^{13}CH_4$  emissions according to a source-specific  $\delta^{13}C$  value from the literature, provided in Table 1. We
- use the Craig (1957) R<sub>gtd</sub> value to partition the sources since it is cited in the literature used in Table 1 (Houweling et

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11/	al, 2000; Lassey, 2007), and so for consistency we use the same value in equation 1 to calculate the simulated $\beta_{1}$ . Col	FOI
118	the CH4 concentrations. We note, however, that the GMD observations now use a slightly different standard, the	For
119	VPDB value of 0.011183 (Zhang and Li, 1990). A sensitivity study (not shown) confirms that the choice Rstd has	For
120	little effect on our results as long as the same value is used for the source partitioning as for the calculation of $\delta^{13}$ C-	
121	CH4 from simulated [13CH4] and [12CH4].	For
122	The reaction rates for CH4+OH, CH4+Cl, and CH4+O <sup>1</sup> D differ between the <sup>12</sup> CH4 and <sup>13</sup> CH4 simulations to	Fo
123	account for the kinetic isotope effect (KIE). In particular, we assume $\alpha$ values of 0.987 and 0.938 for CH <sub>4</sub> +O <sup>1</sup> D and	For
124	CH <sub>4</sub> +Cl, respectively (Saueressig et al., 1995;Saueressig et al., 2001). Our standard simulation uses α <sub>OH</sub> = 0.9946	For
125	(Cantrell et al., 1990).	For
126	Methane from different sources is tracked individually using a "tagged tracer" approach, which allows us to	
127	simulate the spatial footprint of CH <sub>4</sub> and $\delta^{13}$ C-CH <sub>4</sub> from individual sources. The soil sink is applied to each tracer as	Del
128	a fraction of its source, modified to account for faster loss of ${}^{12}CH_4$ to soil compared to ${}^{13}CH_4$ ( $\alpha_{soil} = 0.978$ ). (Tyler et	<sup>13</sup> C fro
129	al., 1994). Supplemental figure S1 shows the July 2004 CH4 and d <sup>13</sup> C-CH4 footprints of the biomass burning, wetland,	De
130	and coal + other geologic CH4 sources from the tagged tracers to illustrate the tagged tracer approach. We note that	
131	the $\delta^{13}$ C values of the surface methane from each source is heavier (less negative) than the emission value for that	
132	source (Table 1), especially in regions far from the source, because of the fractionating effects of the sinks.	

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#### 2.2 Description of Simulations

Supplemental Fig. S2 shows the corresponding footprints for January.

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136 We simulate the period from 1990 through 2004, and focus our analysis on 2004. We choose 2004 as our endpoint 137 because it lies within the period when methane concentrations remained relatively flat, simplifying our analysis. 138 Ending the simulations in 2004 also avoids much of the uncertainty about the causes of the resumed growth rate in 139 recent years. The isotopic ratios of methane take longer to adjust to a perturbation than total methane (Tans, 1997). 140 Since we wish to begin our simulations with a state that is as close as possible to "spun up", we choose the initial 141 condition for each tagged tracer based on its present-day distribution and proportion of the total CH4 and scale it back 142 to 1990 levels such that the total CH4 is consistent with the global mean CH4 from surface observations for 1990. We 143 then iteratively adjusted the <sup>12</sup>C- to <sup>13</sup>C-CH<sub>4</sub> tracer ratios at the beginning of 1990 to yield a good match to global 144 mean  $\delta^{13}$ C-CH<sub>4</sub> observations for 1998, when more  $\delta^{13}$ C-CH<sub>4</sub> observations are available. The same initial condition is 145 used for the standard and sensitivity simulations.

146 We use interannually-varying emissions of CH4 from anthropogenic, biomass burning, and wetland sources. 147 Emissions from anthropogenic sources such as oil and gas, energy production, industrial activities, and livestock come 148 from the EDGAR version 4.2 inventory (European Commission, 2011). Biomass burning emissions come from the 149 MACCity inventory (Granier et al., 2011). We treat forest fires as C3 burning and savannas as C4 burning for 150 partitioning the biomass burning emissions between isotopologues. Wetland and rice emissions come from the 151 Vegetation Integrative Simulator for Trace gases (VISIT) terrestrial ecosystem model (Ito and Inatomi, 2012), scaled 152 by 0.69 and 0.895, respectively, for consistency with the Transcom-CH4 study (Patra et al., 2011). Ocean (Houweling 153 et al., 1999), termite (Fung et al., 1991), and mud volcano emissions (Etiope and Milkov, 2004) are also from the

160 emissions showed a substantial underestimate of the CH4 growth rate. Consequently, we scale up all the emissions 161 by 10% for 1990-1998, and by 6.8% for 1998-2004. We find the resulting emissions lead to a good simulation of the 162 timeseries of surface CH4 observations from the National Oceanic and Atmospheric Administration (NOAA) Global 163 Monitoring Division (GMD) (Dlugokencky et al., 2018), especially towards the end of the period (Fig. 1). The 164 simulation has only a 0.1% mean bias compared to the observations for 2004. 165 Our standard simulation (SimStd) uses Cl from the GMI CTM for the tropospheric as well as stratospheric loss 166 of CH4 by reaction with Cl. Tropospheric Cl concentrations are small in GMI since it does not include very short-167 lived species, and reaction with Cl represents only 0.28% of the total tropospheric CH4 loss. We also conduct several sensitivity simulations in which we alter the tropospheric and lower stratospheric Cl fields (Table 2). Cl is not altered 168 169 above 56 hPa. Sensitivity simulation SimGC uses Cl from the GEOS-Chem chemistry module within GEOS (Long 170 et al., 2015; Hu et al., 2018). GEOS-Chem v11-02f with fully coupled tropospheric and stratospheric chemistry was 171 used for this simulation, with halogen chemistry as described in Sherwen et al. (2016). SimGC has higher values of 172 tropospheric Cl than SimStd (Figs. 3,4) and leads to 0.66% of the total CH4 loss occurring via Cl. Both SimStd and 173 SimGC are thus below the 1% loss via Cl suggested by (Gromov et al., 2018). We conduct a third sensitivity 174 simulation, SimTom, which uses Cl from the TOMCAT model simulations that include chlorine sources from 175 chlorocarbons (including very short-lived substances), HCl from industry and biomass burning, and very short lived 176 substances (Hossaini et al., 2016). This simulation leads to Cl accounting for 2.5% of tropospheric CH4 loss in our 177 simulation. Finally, we conduct a fourth sensitivity simulation, SimMBL, which modifies the Cl over the oceans at 178 altitudes below 900 hPa (Fig. 2d) to reflect the marine boundary layer distribution suggested by (Allan et al., 2007). 179 This Cl field is described by the following equation: 180 Cl\_MBL =  $18*10^3$  atoms/cm<sup>3</sup> \* (1 + tanh(3 $\lambda$ )\*sin(2 $\pi$ \*(t-90)/365)) (2) 181 where  $\lambda$  is latitude in radians and t is the day of the year. Elsewhere SimMBL uses the Cl field from SimStd. This simulation has the highest percent of CH4 loss occurring via Cl: 3.9%. If we consider the loss of methane throughout 182 183 the atmosphere rather than just the troposphere, then the percent lost via Cl increases to 1.6%, 2.0%, 3.6% and 5.0% 184 for SimStd, SimGC, SimTom, and SimMBL, respectively. 185 We designed the sensitivity experiments to alter the isotopic composition of CH4 without greatly affecting

Transcom study (Patra et al., 2011) and have a seasonal cycle but no interannual variability. Initial tests with these

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186 the total CH4. Consequently, we reduce the OH concentrations in the SimTom and SimMBL simulations by 2% and 187 4%, respectively, relative to the SimStd OH to offset the effect of increasing Cl. These changes are small compared 188 to the uncertainty in global OH. In addition, the SimTom and SimMBL simulations use  $\alpha_{OH}$ =0.9961 (Saueressig et 189 al., 2001) rather than  $\alpha_{OH}$ =0.9946 (Cantrell et al., 1990) to avoid too much fractionation from the combined Cl and 190 OH sinks. While these changes are necessary to maintain consistent total CH4 and reasonable isotopic ratios, changing 191 multiple factors in addition to Cl makes it difficult to quantify the impact of Cl alone. Consequently, we conduct an 192 additional sensitivity study, called SimTomB, which uses the same Cl field as Cl but retains the OH and aoH values 193 of SimStd. SimTomB is used in Section 3.3. This simulation becomes too heavy compared to observations, justifying 194 the need to change ooH in the main SimTom simulation. We also conduct a sensitivity simulation, SimOHp, that uses Deleted: 2

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the same Cl field as SimStd but does not alter the hemispheric ratio of OH. Table 2 summarizes the standard andsensitivity simulations.

201 The four Cl distributions differ in their vertical and horizontal spatial distributions as well as their 202 tropospheric mean (Figs. 2 and 3). The SimStd Cl is largest in the tropics, nearly symmetric between hemispheres, 203 and increases with altitude. Both SimGC and SimTom have Cl that is larger in the Northern Hemisphere than the 204 Southern Hemisphere in the annual mean and reaches a minimum in the mid-troposphere. However, the maximum in 205 lower tropospheric Cl occurs in the tropics in SimGC but in the extratropics in SimTom. This mid-latitude Cl 206 maximum arises because SimTom has high Cl values over east Asia, whereas SimGC Cl is highest over ocean regions 207 (Fig. 3). SimMBL has a strong maximum in the MBL compared to the free troposphere and land regions. Its annual 208 mean Cl concentrations are higher in the Southern Hemisphere (Fig. 2) due to the larger ocean area in the Southern 209 Hemisphere. However, SimMBL includes a strong seasonal shift in peak Cl between the hemispheres. SimStd and 210 SimGC have more modest seasonal shifts, while Cl in SimTom remains concentrated in the northern hemisphere 211 throughout the year (Fig. S3). All simulations repeat the same Cl field from year to year. 212 The sensitivity simulations listed above are designed to test the role of the Cl sink. We conduct an additional 213 sensitivity study, SimWet, to illustrate the role of spatial variation in the isotopic source signature. SimWet parallels 214 SimStd, but the isotopic composition of the wetland source uses spatial variation from Ganesan et al (2018). The 215 global mean source signature of the wetland emissions remains -60%.

#### 2.3 Observations

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219 We use surface observations from the NOAA GMD Carbon Cycle Cooperative Global Air Sampling Network to 220 evaluate our simulations. We use the monthly mean observations of total CH<sub>4</sub> (Dlugokencky et al, 2018) and  $\delta^{3}$ C of 221 CH4 (White et al., 2018) to compare to the monthly mean simulation results. The isotopic measurements were made 222 at the Institute of Arctic and Alpine Research at the University of Colorado and are referenced to the VPDB scale 223 (Zhang and Li, 1990). The analytical uncertainty of the isotopic measurements is 0.06‰. The variability between 224 measurements taken in a given month may, however, be larger, so we use the maximum of analytical uncertainty and 225 the within-month standard deviation as the uncertainty in the monthly mean. When multiple years are observations are averaged together, we use the pooled variance to calculate the standard error, thus reducing the error based on the 226 227 number of years. The GMD observations are located at remote sites, shown in Fig. 4 for CHe in 2004. Measurements 228 of  $\delta^{13}$ C of CH<sub>4</sub> are available at a subset of the sites, shown in Fig. 5.

#### 3. Results and Discussion

#### 231 3.1 Evaluation of Simulated CH<sub>4</sub>

We find good agreement between the SimStd simulation and the GMD observations for CH<sub>4</sub> (Fig. <u>4</u>) for 2004.
We focus on these two months to represent the seasonal differences. The latitudinal distribution is well-reproduced, and the simulation captures the elevated concentrations of CH<sub>4</sub> observed over Europe in January as well as the January versus July differences in concentration. Overall, the spatial correlation between SimStd and the observations is 0.93

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244           245         3.2 Jmpa           246         247           247         Wen           248         observed           249         the figure           250         simulation           251         range of	$\frac{1}{2} \frac{1}{2} \frac{1}$	
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246 247 Wen 248 <u>observed</u> 249 <u>the figure</u> 250 <u>simulation</u> 251 range of	The presence of $\delta^{13}$ C in SimStd compared to observations. Figure 6 shows the timeseries of d and simulated $\delta^{13}$ C for 1998-2004 at the 6 GMD sites with $\delta^{13}$ C records covering this time period. We begin re at 1998 rather than 1990 due to the lack of data availability in the earlier years. The standard and sensitivity ions overestimate $\delta^{13}$ C at the northernmost station, BRW. The observations at the other stations lie within the formation of the state	
247     We n       248     observed       249     the figure       250     simulation       251     range of	e next examine the distribution of $\delta^{43}$ C in SimStd compared to observations. Figure 6 shows the timeseries of d and simulated $\delta^{43}$ C for 1998-2004 at the 6 GMD sites with $\delta^{43}$ C records covering this time period. We begin re at 1998 rather than 1990 due to the lack of data availability in the earlier years. The standard and sensitivity ions overestimate $\delta^{43}$ C at the northernmost station, BRW. The observations at the other stations lie within the	
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249     the figure       250     simulation       251     range of	re at 1998 rather than 1990 due to the lack of data availability in the earlier years. The standard and sensitivity ions overestimate $\delta^{3}C$ at the northernmost station, BRW. The observations at the other stations lie within the	
250 <u>simulation</u>	ions overestimate $\delta^{l3}C$ at the northernmost station, BRW. The observations at the other stations lie within the	
D51 rongo of		
zu <u>range or</u>	i simulations, with most simulations underestimating the observations at the south pole. The differences	
252 <u>between t</u>	n the different sensitivity simulations are large compared to the interannual variability in both observed and	
253 <u>simulated</u>	ed $\delta^{l_3}$ C. We focus our subsequent analysis on a single year, 2004.	
254 Fig. :	. $\underline{s}_{a,b}$ shows both meridional and zonal variability in $\delta^{3}$ C. Background values are less negative (heavier) in <b>Deleted:</b> 6	
the South	thern versus Northern Hemisphere (NH) (Fig. 7), a feature seen more strongly in the observations, but there is	
256 also varia	iability due to the different source signatures. Areas of biomass burning, such as Tropical Africa, show up as	
257 particular	arly heavy, while regions with large wetland and rice emissions, such as SE Asia, are particularly light.	
258 Another p	r prominent feature is the isotopically heavy region in northern Eurasia (around 60°N) in January, which we Deleted: A	
259 attribute t	e to the influence of the geologic (including oil, gas, and coal) source in this region (Supp. Fig. S2). This signal Deleted: 1	
260 is less evi	vident in July, when greater influence from boreal wetlands lightens the isotopic mix. The spatial correlation	
261  (r2) between	ween the SimStd and observed $\delta^{3}$ C is 0.61 in January and 0.75 in July.	
262 The s	e sensitivity simulations with altered oxidant concentrations alter the global values of $\delta^{3}$ C, but the geographic	
263 patterns r	remain similar to that of SimStd. The larger Cl sink in SimGC leads to an overall less negative $\delta^{13}$ C, which	
264 agrees be	better than SimStd with observations at Southern Hemisphere (SH) sites but worse in the NH (Figs. 6c,d and	
265 7). The is	isotopic effect of the larger Cl sink in SimTom is compensated by the lower OH and $\alpha_{OH}$ values used in that	
266 simulation	ion, flattening the interhemispheric gradient (Figs. 6e,f and 7). In contrast, the very large MBL Cl	
267 concentra	rations in SimMBL lead to an overestimate (insufficiently negative) of the observed $\delta^{t3}$ C (Fig. g,h), but	
268 strengther	nens the interhemispheric gradient. We note that since all simulations began with the same initial conditions	
but have	e different sinks, the isotopic composition is not in steady state in 2004 and the results of the sensitivity	
270 simulation	ions diverge further with additional years of simulation, with SimMBL becoming clearly inconsistent with	
271 observatio	tions. We note that while these results highlight the differences in $\delta^{13}$ C imposed by changing Cl, the absolute	
272 values of	of $\delta^{13}$ C, and hence their agreement with observations, would be different for CH4 source mixtures with a	
273 different	t average $\delta^{13}$ C.	
274 Figur	ure 7 reveals an underestimate in the interhemispheric gradient of $\delta^{13}$ C in both SimStd and the sensitivity runs	
275 compared	ed to the GMD observations. Table 3 presents the observed and simulated $\delta^{13}$ C interhemispheric gradients	
276 calculated	ed as the difference between the $\delta^{13}$ C values averaged over all sites south of 30°S and the average over sites	
277 north of 3	f 30°N. SimStd and SimGC show similar underestimates of the observed gradient, and the underestimate is	
278 more sev	evere in SimTom. The gradient is improved in SimMBL in January. The differences between simulations	

285	reflect differences in the locations where CH4 oxidation occurs and the amount and location of isotopic fractionation		
286	due to Cl versus OH. Fig. 8 shows that the higher Cl values over the NH, particularly China, in SimTom versus		
287	SimStd leads to more CH <sub>4</sub> loss occurring in the NH and higher (heavier) $\delta^{13}$ C in the NH. This effect is particularly		
288	pronounced over China and Europe. Less fractionation by the OH sink in SimTom leads to lighter values in the SH.		
289	Conversely, SimMBL has more loss occurring over the SH oceans in January, leading to heavier $\delta^{13}$ C in the SH (Fig.		
290	9). This effect is not present in July, when the SimMBL Cl loss shifts to the NH (Fig. S4). The reduced hemispheric		Deleted: 2
291	difference in OH in SimOHp leads to a small improvement in the hemispheric gradient in $\delta^{t3}$ C.		
292	We further examine the seasonal cycle of $\delta^{13}$ C in Fig. 10. We focus on the seasonal cycle at the South Pole		
293	Observatory (SPO) site because it is far from large CH4 sources and thus the seasonal cycle depends strongly on the		
294	seasonality of the CH4 sinks. While all simulations lie mostly within the error bars of the observations, SimMBL has		
295	the largest seasonal cycle amplitude, overestimating the seasonal cycle at of the SPO observations with a $\delta^{13}$ C value		
296	that is both too heavy in FebJune and too light in AugNov. In contrast, SimStd and the other sensitivity simulations		
297	underestimate the magnitude of the observed seasonal cycle at SPO. Supplemental Fig. S <sub>4</sub> shows a large enhancement		Deleted: 3
298	in the seasonal cycle amplitude between SimMBL and the other simulations for the Cape Grim site in Tasmania		
299	(CGO), but only a small change at other sites. This suggests that while MBL Cl is attractive as an explanation for the		
300	SH seasonality of $\delta^{13}$ C, this explanation may be inconsistent with the inclusion of non-marine Cl sources. <u>However</u> ,		
301	since the seasonal cycle amplitude at SPO lies in between SimMBL and the other simulations, it is possible that at an		
302	MBL Cl source similar to that of SimMBL but with a smaller average value could reproduce the amplitude well.		
303			
303 304	3.3 Quantifying the Sensitivity of $\delta^{13}$ C to CH <sub>d</sub> Loss by Cl		Formatted: Subscript
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**329** varying isotopic ratios on our SimWet simulation. SimWet increases the amplitude of the seasonal cycle in  $\delta^{13}$ C-CH<sub>4</sub> **330** particularly for northern latitudes sites such as ALT, BRW, and MHD (Supplemental Fig. S5). It has little effect on **331** the seasonal cycle at the SH CGO and SPO sites, where SimMBL shows a large effect on the cycle. SimWet results **332** in improved agreement with the observed interhemispheric gradient (Figs. 5.7); Table 3). The size of the effect of **333** including spatially varying ratios in wetland emissions depends on the strength of the wetland emissions as well as **334** the other sources. Including spatially-varying isotopic signature for other sources as well could further modify the

simulated interhemispheric gradient, potentially correcting some of the flat gradient of e.g. the SimTom simulation.

## 337 4. Conclusions338

The role of Cl as a methane sink is a significant uncertainty in the global CH<sub>4</sub> budget, particularly with respect to isotopes. The global distribution of Cl is not well known from observations, and the Cl distributions simulated by global models varies widely from model to model. We investigated the sensitivity of the surface  $\delta^{13}$ C distribution of CH<sub>4</sub> to the inter-model diversity in tropospheric Cl using a series of sensitivity studies with a global 3D model. Given the uncertainties in CH<sub>4</sub> sources and their isotopic ratios, it is not possible to conclude from this study which Cl field is best. However, the differences between the simulations provides insight on the strong lever that tropospheric Cl exerts on the  $\delta^{13}$ C distribution.

346 Our standard and sensitivity simulations all reproduce well the geographic distribution of and temporal evolution 347 of CH<sub>4</sub> observed at the GMD surface sites. However, imposing Cl distributions from a range of chemical transport 348 models used in the scientific community leads to large differences in the simulated distribution of the  $\delta^{13}$ C of CH<sub>4</sub>. 349 The CH<sub>4</sub> sinks from Cl in our SimStd and SimGC simulations are both below 1% of the total CH<sub>4</sub> sink, as suggested 350 by Gromov et al. (2018). Yet the SimStd and SimGC simulations underestimate and overestimate, respectively, the 351 observed  $\delta^{13}$ C in 2004, despite the fact that both include only a relatively small CH<sub>4</sub> sink from Cl.

Our ability to reproduce the observed latitudinal distribution of  $\delta^{13}C$  depends not only on the assumed value of 352 353 global mean Cl, but also its geographic distribution. The detailed halogen chemistry model (TOMCAT) of Hossaini 354 et al. (2016) places the maximum Cl values in the continental NH, in contrast to the large MBL Cl sink used in Allan 355 et al. (2007) to explain SH observations. We find that the strong NH Cl maximum, along with the resulting reduction 356 in OH fractionation required to maintain consistency with observations, acts to flatten the interhemispheric gradient 357 of  $\delta^{13}$ C, while the MBL Cl sink increases the hemispheric differences in NH winter and also strengthens the seasonal 358 cycle. However, the interhemispheric gradient is also influenced by spatial variation in the isotopic signatures of the 359 sources and uncertainties in the soil sink, complicating this issue.

Two values for the fractionating effect of OH ( $\alpha_{OH}$ ) on  $\delta^{3}$ C (Cantrell et al., 1990; Saueressig et al., 2001) are widely cited in the literature. Combining the TOMCAT Cl fields with the  $\alpha_{OH}$  of Saueressig et al. (2001) leads to an underestimate of observed  $\delta^{13}$ C, but combining it with the Cantrell et al. (1990)  $\alpha_{OH}$  would lead to an overestimate. Reducing uncertainty in the fractionating effect of OH would thus improve our ability to constrain the role of Cl.

Keducing uncertainty in the fractionaling effect of OH would thus improve our ability to constrain the role of Cl.

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#### 375 Data Availability

The methane and d<sup>13</sup>CH<sub>4</sub> observations are available from the NOAA GMD website:
https://www.esrl.noaa.gov/gmd/dv/data/. Output from the GEOS model is on the NASA Center for Climate
Simulation (NCCS) system.

#### 380 Author Contributions

SS designed and conducted simulation, performed analysis, and prepared the manuscript. JSW contributed to model development and experiment design. MM contributed to model development. BD contributed to model development and conceptualization. RH and CK contributed inputs to the simulations. SM and JWCW contributed data and aided in its interpretation. All authors contributed to the editing and revising of the manuscript.

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**386** The authors declare no competing interests.

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#### <u>**Table 1**</u>: Emission source references and $\delta^{13}$ C values 639

Source	Reference	IAV	δ <sup>13</sup> C (‰) <sup>a</sup>	CH4 Source (Tg yr <sup>-1</sup> ) <sup>b</sup>
Animals (enteric fermentation)	EDGAR	Y	-62	102
C3 Biomass Burning (Forests)	MACCity	Y	-26	16
C4 Biomass Burning (Savannas)	MACCity	Y	-15	10
Coal, energy, and industry	EDGAR	Y	-35	6
Geologic (oil/gas/non-coal fuels, volcanos)	EDGAR, Transcom	Y, except volcanos	-40	124
Waste (solid and animal waste, wastewater)	EDGAR	Y	-55	74
Ocean	Transcom	Ν	-59	8
Rice	Visit model	Y	-63	44
Termites	Transcom	Ν	-57	22
Wetlands	Visit model	Y	-60	149

<sup>a</sup>δ<sup>13</sup>C values from Dlugokencky et al., 2011;Lassey et al., 2007;Monteil et al., 2011;Houweling et al., 2000 and refs

640 641 642 therein

<sup>b</sup>Values for 2004

643

#### 644 Table 2: Oxidants for the Standard and sensitivity simulations

Simulation	[Cl] <sub>Trop</sub> <sup>a</sup> (molec cm <sup>-3</sup> )	Cl Model <sup>b</sup>	Cl Reference	ОН
				modification <sup>c</sup>
SimStd	210	GMI	(Strahan et al., 2007; Rotman et al., 2001; Strahan et al., 2013;Duncan et al., 2007)	$\alpha = 0.9946$
SimGC	384	GEOSChem	(Sherwen et al., 2016)	$\alpha = 0.9946$
SimTom	1710	TOMCAT	(Hossaini et al., 2016)	-2% [OH] $\alpha = 0.9961$
<b>SimTomB</b>	<u>1710</u>	TOMCAT	(Hossaini et al., 2016)	$\alpha = 0.9946$
SimOHp	210	GMI	See SimStd	Not modified for 20% highe in NH
SimMBL	2810	Tanh function below 900hPa over ocean; GMI elsewhere	(Allan et al., 2007)	-4% [OH] $\alpha = 0.9961$
<sup>a</sup> Concentration	of Cl averaged over the t	roposphere		
<sup>b</sup> Name of the r	nodel that generated the o	ffline Cl field		
°Changes to [C	DH] or $\alpha_{OH}$ compared to Si	imStd		
Table 3: Obse	erved and Simulated Interl	nemispheric Gradie	nt in ∂ <sup>13</sup> C-CH4	
	Jan. Gi	adient (‰) <sup>a</sup>	July Gradient (‰)	a
GMD Obs	0.36		0.28	
SimStd	0.17		0.11	
SimGC	0.17		0.098	
SimTom	0.051		0.010	

	Shintibe	0.50	0.15
	SimOHp	0.22	0.15
	SimWet	0.28	0.25
650	<sup>a</sup> Average $\delta^{13}$ C-CH <sub>4</sub> at GMD	site locations south of 3	0°S minus average $\delta^{13}$ C-CH <sub>4</sub> at locations north of 30°N

0.13

0.30

651

SimMBL









#### 



**Fig. 4**: Comparison of 2004 simulated and observed surface CH<sub>4</sub> concentrations for January (left) and July (right). a,b) Surface concentrations of CH<sub>4</sub> from SimStd are overplotted with the concentrations from the GMD observations in circles. c,d) GMD observations (black circles), SimStd (red x), SimGC (dark blue +), SimTom (light blue +), and SimMBL (orange +) CH<sub>4</sub> as a function of latitude. E,f) SimStd CH<sub>4</sub> (ppb) at the observation locations versus the GMD observations (+ signs) as well as the regression line (solid) and 1 to 1 line (dashed). Deleted: 5





b. NWR

c. MLO

a. BRW

687 688 689 690

691

692 693 694 -60

-30 0

latitude

695 696 697

698

(purple). Errorbars represent the maximum of the analytical uncertainty (0.06‰) and the standard deviation of individual measurements in the month for each site. The colored lines represent the simulated zonal mean, while the colored symbols represent the simulation sampled at the location of the GMD observations.

Fig. 7:  $\delta^{3}$ C of CH<sub>4</sub> as a function of latitude in a) January and b) July 2004 for the GMD observations (Black

circles), SimStd (red), SimGC (dark blue), SimTom (cyan), SimMBL (orange), SimWet (green), and SimOHp

-60

0

latitude

-30

30 60 90

30

60 90

38



CH4 loss and d)  $\delta^{13}$ C-CH4 between the SimTom and SimStd simulations.





704 705 706 707

Fig 9: January a) CH4 loss and b) CH4 loss by Cl only in the SimMBL simulation, as well as the difference in c) CH4 loss and d)  $\delta^{13}$ C-CH4 between the SimMBL and SimStd simulations.



Fig. 10: The seasonal cycle of  $\delta^{13}$ C of CH<sub>4</sub> at the SPO site with the annual mean removed averaged over 2002-2004

708 709 710 711 712 713 714 for the GMD observations (black), SimStd (red), SimGC (blue), SimTom (cyan), SimMBL (orange), SimWet (green), and SimOHp (purple). Errorbars represent the standard error, calculated as the maximum of the pooled standard deviation or the analytical uncertainty (0.06‰), divided by the square root of the number of years of

observations.

