**Atmospheric
Chemistry
and Physics
Discussions**

Interactive comment on "Interpreting methane variations in the past two decades using measurements of CH$_4$ mixing ratio and isotopic composition" *by* G. Monteil et al.

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Answer to major comments:

0.1   Intercalibration of δ^{13}C-CH$_4$ measurements:

The referee is asking for more details on the measurements that we used. In particular, there is a gap between the end of the isotopic measurements from Quay et al. (1999)

and the start of those from the INSTAAR network.

There is indeed a period of one to two years without measurements, which makes difficult to judge the consistency between the two datasets. Lacking any further information about the relative calibration of these measurements, we made the assumption that there is no offset between the datasets. Obviously, there is an uncertainty involved in this assumption, but we consider it unlikely for this to have an important impact on our conclusions:

Our main interest is to understand the measured trends, in the particular the fact that the isotopic measurements by Quay et al. (1999) clearly show an upward trend of the isotopic ratio, whereas the INSTAAR records show a rather constant level of δ^{13}C-CH$_4$. This change of slope is also visible in the NIWA records (at Baring Head and Arrival Heights), which cover the full period and suggest that the transition took place around the year 1999. The upward trend before 2000 is also confirmed by older records (Francey et al., 1999), and by firn measurements (Ferretti et al., 2005). It is unfortunate that the isotopic trend changed when several sites show data gaps, but because of the additional observational evidence and the fact that a growth rate change cannot easily be explained by a calibration offset between laboratories we consider it unlikely that the observed growth rate changes are affected by the uncertainty of network intercalibration.

Plots shown:

The referee is wondering why we specifically focus on Cape-Grim in figures 3 and 4, rather than Baring-Head or Arrival Heights, which have longer records.

At Cape-Grim, measurements from Francey et al. (1999), are available for the period 1978-1994, as shown in Figure 2 of the discussion paper. The measurements from Quay et al. (1999) at Cape Grim cover the period 1988-1996, followed by the INSTAAR

measurements starting in 1998. The combination of these three datasets makes Cape Grim the station with the longest atmospheric record of δ^{13}C-CH$_4$. The measurements by NIWA at Baring Head and Arrival Heights started only respectively in 1991 and 1992. This guided our initial choice of showing results at Cape Grim. Nevertheless, we didn't limit our analysis to the sites shown in the discussion paper, but extended our comparisons to about 30 sites (for δ^{13}C-CH$_4$). The four sites shown in the paper were selected according to the quality and the quantity of the measurements, and for their geographical representativeness.

Uncertainty of isotopic signatures of sources and sinks:

The referee is asking about the uncertainty of the isotopic fractionation constants used in the model, in particular about the potential impact of changing isotopic signatures.

It is true that the assumption of constant process-specific isotopic signatures is a fundamental assumption in our study. As explained in section 1.1.1, a slightly different isotopic value for one specific process would only offset the simulated atmospheric δ^{13}C-CH$_4$, which would not change our conclusions. On the contrary, changing isotopic ratios would have strong implications for our simulations. The question is how likely it is that such changes have taken place.

- The average isotopic ratio of a source could change due to a change in the isotopic ratio of the organic material from which methane is produced. Since our period of study is quite short in this context, this is not likely to be very important. Alternatively, some isotopic signatures can vary depending on specific conditions (for example the balance between bacterial production and consumption in wetlands). Whereas we cannot exclude such a change, this topic has received little attention in the past and no supporting data are available. Therefore we don't investigate this further.

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- The fractionation factors induced by methane sinks are due to the differences in the reaction rates coefficients of the reactions consuming 12CH4 and 13CH4 methane, which themselves are very unlikely to have changed significantly over time.

Interest of looking at seasonal cycles:

The referee is asking whether looking at seasonal cycles could help us in narrowing our list of possible scenarios.

It would indeed help to look at seasonal cycles, since OH is the main factor driving the methane seasonal variations, but this requires a different modeling setup (high resolution model, not necessarily on a such long time period, but with much higher spatial resolution, and better implementation of the seasonality of fluxes). From our current modeling setup, we cannot draw reliable conclusions from examining the seasonal cycles.

Possible marine boundary layer chlorine sink:

The referee is wandering why we didn't include a scenario to test the hypothesis of a chlorine sink in the marine boundary layer, and is pointing at the potential importance of such a sink for the isotopic budget.

The possibility of a methane sink due to reaction with chlorine radicals in the marine boundary layer was first proposed by Allan et al. (2001a), and has been further investigated in several subsequent papers by Allan and Lassey (Allan et al., 2005, 2007; Lassey et al., 2011). Allan et al. (2005) describe the potential effect of such a sink on methane and d13C-CH4 based on the analysis of measurements of their seasonal cycles in the Southern Hemisphere. Using "ellipse plots" (change in methane mixing

ratio versus change in methane isotopic composition, over one year), they deduced an apparent KIE for the methane sink, which is significantly different from the KIE of the reaction CH4+OH, and they attribute this difference to a chlorine sink in the marine boundary layer. Furthermore, they conducted this study using several years of measurements, and found a strong interannual variability of this apparent KIE, ranging from -18‰in 1997 to -5‰in 1999 at Baring Head, with overall smaller values after the nineties.

This potential sink has not been taken into account in most of the recent studies dealing with the methane budget, including ours. In our case, the reason is that tropospheric chlorine chemistry is still associated with large uncertainties, and therefore it is unclear if an implementation of chlorine in the model would make it more realistic. The question is whether or not this omission is critical for the interpretation of our results.

The existence of a chlorine sink in the marine boundary layer would not change our conclusions, as long as it does not vary significantly on the time-scale of several years. We deliberately use a fractionation factor for the reaction OH+CH4 of ϵ = 1.0054, which is on the high end of the reported range of ϵ = 1.0039 to ϵ = 1.0054 (Cantrell et al., 1990; Saueressig et al., 2001), in order to minimize the difference with the KIE's inferred from in situ measurements.

However, Allan et al. (2005) report a strong decrease of the apparent KIE of the methane sink in the extra-tropical southern hemisphere in the nineties. Earlier (unpublished) model results in our group indicate that such a strong decrease in the KIE with time is incompatible with the atmospheric trend of δ^{13}C-CH$_4$. Therefore, we did not consider this a realistic scenario for the paper, but in reply to the referee comment we show results from some synthetic scenarios.

Assuming that the effect of a chlorine sink on CH4 concentration would be negligible, we only analyse the effect on δ^{13}C-CH$_4$, by varying the KIE of the reaction CH4+OH. We studied the effect of a drop of apparent KIE by multiplying the KIE of the CH4+OH

reaction in the southern hemisphere by a combination of two sinusoidal functions (as in Figure 1 of Allan et al. (2007)), leading to a maximum decrease of 5‰at the poles, in summer. We tested this with different base KIEs, and applied this approach to different sources/sinks scenarios:

Name	Description
RS0	Similar to base scenario (S0), but the KIE of the OH+CH4 reaction is reduced after 1998, in the southern hemisphere, and depending on season and the latitude, with a maximum decrease of -5‰.
RP1	Similar to RS0, but applied to the scenario P1
RP2	Similar to RS0, but applied to the scenario P2

The results of our simulations are shown in Figure 1 of this document. They clearly show that if the KIE had indeed changed by 5‰as inferred from the phase ellipses by Allan et al. (2005), then this should have been accompanied by huge corresponding changes in δ^{13}C-CH$_4$, which are incompatible with the observations. It can be concluded that the interpretation of the apparent KIE as inferred from phase diagrams needs further investigation. In this context, we would like to refer to Lassey et al. (2011), who investigate alternative explanations of the temporal variations in apparent KIE. We acknowledge that a trend in methane oxidation by chlorine introduces significant uncertainty, and has the potential to provide a different explanation to our results. However, at the moment, we are unable to take this into account, because it is unclear what a realistic chlorine oxidation scenario would look like. For this reason, we made the choice to not consider this sink, but we added a paragraph in the discussion section to motivate this choice and discuss the uncertainties associated with it.

Answers to minor comments:

- Introduction: As suggested by the referee, I modified the introduction to add a general paragraph about isotopic signatures of methane sources and sinks.

- Page 6773, second paragraph: The paragraph was modified for more clarity.

- page 6773, first paragraph: I added the information about Cl and O(1D) sinks.

- page 6773, third paragraph: Reference to Bousquet et al. (2006) was modified to take into account the referee comment.

- page 6774, second paragraph: Reference to Bousquet et al. (2006) and **?** were added.

- page 6776, first paragraph: A quick description of the Velders model will be added in the revised manuscript.

- page 6777, last paragraph: Reference to the Walter model was added.

- page 6781, first paragraph: Our model results were compared to a wide range of measurements from several networks. The pictures showed in the paper are only examples, chosen for their representativeness and for the amount of data available at these four sites. The paragraph was slightly modified to explain why we show these four sites in particular.

- page 6783, first paragraph: We know from experience with this model that there is a resolution dependency in this inter-hemispheric gradient overestimation, but it tends to get worse with lower resolution. We can reasonably assume that the interhemispheric gradient overestimate described by Dlugokencky et al. apply also to our modeling setup.

- Table 1: We didn't consider the spatial variability of C3 and C4 plants. The reason we didn't include uncertainty range is that it is very difficult to distinguish between the uncertainty related to the true variability of one process, the uncertainty related to the (lack of) representativeness of the measurements, and the uncertainty of the measurements themselves. Therefore, the uncertainty range that we could provide may have a different significance, depending of the process. For this reason, we prefer to give in Table 1 the flux and isotopic signatures as they are used in our model, and refer to literature in the text for uncertainty ranges.

- All figures: Remarks were taken into account in the revised manuscript.

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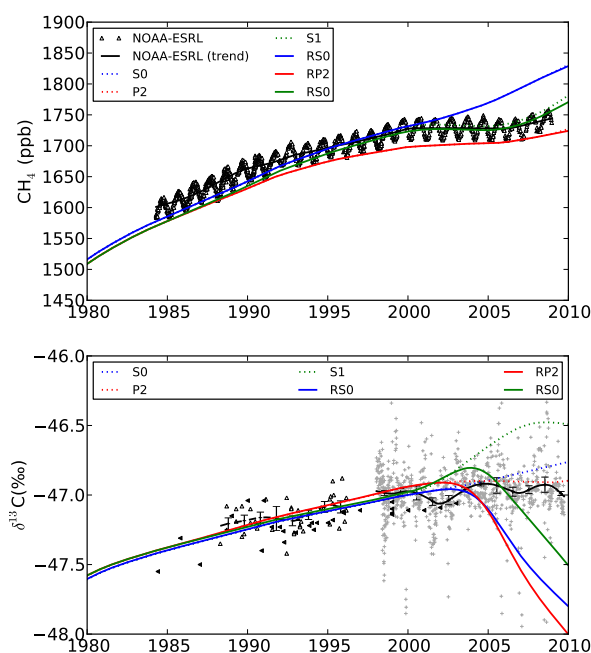Interactive comment on Atmos. Chem. Phys. Discuss., 11, 6771, 2011.

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Fig. 1. Sensitivity of scenarios S0, P1 and P2 to changes in the KIE of the CH4+OH reaction over time.