**Atmospheric
Chemistry
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Discussions**

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# *Interactive comment on* "Centennial evolution of the atmospheric methane budget: what do the carbon isotopes tell us?" *by* K. R. Lassey et al.

**K. R. Lassey et al.**

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On behalf of the authorship, I appreciate the considered comments of the two referees, from which the manuscript will benefit. We propose to modify the manuscript to take account of those comments and to otherwise improve the manuscript as described below.

**Response to Anonymous Referee #1**

This referee refers to "Page 4" etc, which is not the pagination from the ACPD article.

1. A tabulation or glossary of mathematical symbols is, in our view, unnecessarily space-consuming as many of them are local to a section of the paper rather than global, and there are relatively few global symbols. (We note that Referee #2 did not seek such a glossary). Therefore, we do not propose to implement this recommendation.

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2. "impacted" will be changed to "affected"

3. The lines on "Page 5", taken to be Lines 23–24 on Page 4999, will be expanded to explicitly refer to "published constructions of the methane source inventory history", cross-referencing Section 3.

4. We are reluctant to digress too much into discussing the plant-methane source (Keppler et al., 2006), given that its poorly-constrained global strength makes it premature to integrate into source inventories (and even more so into inventory histories). Nevertheless, recognising the topicality of this issue (raised also by Referee #2: see Comment #21 below) we propose to expand discussion on this source. We will also adopt the recommendation to mention the role of varying meteorology (and climate).

5. We will expand the discussion on the chlorine sink in both Sections 4.1 and 4.2. See also Comment #28.

6. We will expand on the roles of $C_3$ and $C_4$ vegetation as biomass-burning fuel (Lines 1–2, Page 5009), identifying the major $C_4$ fuels.

7. The referee's suggestion that the "swing in $\delta^{13}$C" in the early 1990s (lines 25ff, Page 5011) may be consequent in part on the "end of the Soviet coal and sharply increased efficiency in Chinese mining" is speculative, and the existence of the swing itself depends upon the global representativeness of the "anomaly" detected in $\delta^{13}$C at Baring Head but not in the Northern Hemisphere. We therefore prefer not to speculate on causes.

8. We will further reduce overlap between this manuscript and the companion paper (Lassey et al., 2006), consistent with making each paper stand alone.

9. We will append a "powerful last paragraph" that emphasises the answer to the question posed by the title.

**Response to Anonymous Referee #2**

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This referee offers an appreciable number of comments and recommendations. While many of the recommended changes might be of interest to some readers, their implementation would markedly digress from the main theme of the paper, yet would significantly lengthen and delay it. Consequently we are proposing to implement only those recommendations that we believe will improve the content or clarity of the paper, as detailed below.

10. In his/her description of our approach for $^{13}CH_4$, the referee comments that the natural sources constructed by Houweling et al. (2000) "were mainly constrained by OH". However, the sink cannot constrain the breakdown into a source inventory as per Table 1 (also from Houweling et al.). Moreover, as the constraining pre-industrial OH sink was itself a <u>simulation</u>, one could argue that both sink and source inventory were compatible simulations. Furthermore, anthropogenic sources were constructed 'from the bottom up', unconstrained by sink considerations, as explicitly stated (Line 5, Page 4996 (abstract); Lines 1–3, Page 5003; lines 12–14, Page 5020). We will clarify this in Section 3.

11. In that same paragraph, the referee asserts that "since the apparent fractionation is higher than the kinetic effect (KIE) for $CH_4$+OH, the authors conclude that the highly fractionating $CH_4$+Cl reaction must play a significant role in the troposphere". In fact we itemised four potential explanations that might collectively account for the apparent discrepancy in fractionation (lines 11–18, Page 5008) and discussed each of them. (This referee also proposes a fifth: see Comment #14 below). We will clarify and expand this discussion (see also Comment #28). Furthermore, we did not submit that our analysis supplies "solid" evidence for the strength of the $CH_4$+Cl sink, as the referee asserts; rather it supplies strong evidence for the significant participation of that sink to a probable level of at least 10 Tg/yr (conservative). We will remove a quantitative scope from the abstract lest it be interpreted as "solid", but introduce it in the text where it can be better qualified.

12. Of the referee's "3 reasons" (p. S2170), we agree with (a) and indeed made

the same points about the uncertainty in the strength and isotopic signature of the pyrogenic methane source (paragraph commencing line 27, Page 5008).

13. We are also in broad agreement with the sentiment of reason (b), but suggest that quoting the extreme range of –31 to –86 per mil for wetland methane as an indication of uncertainty in the global mean is unhelpful. Most commentators would ascribe a mean value within about 5 per mil (usually within 2 per mil) of –60 per mil to the global mean wetland source (e.g. Hein et al., 1997, Table 8; Quay et al., 1999, Table 1), and while we discussed this uncertainty and its implications explicitly (Lines 2–8, Page 5007; Lines 19–26, Page 5008), we may have under-stated its magnitude. We will recast discussion around an uncertainty of $\sim$5 per mil (see Comment #28).

14. Reason (c) was overlooked by us as a possible explanation for the high apparent fractionation, and we agree with the referee that it should be considered. Consequently we will add a further "potential explanation" (Lines 11ff, Page 5008), by addressing the stratosphere-to-troposphere flux of $^{13}$C-enriched $CH_4$ in a separate paragraph. However, the referee does not detail his/her derivation of –0.8$\pm$0.1 per mil as the effect of including this flux on the "effective KIE". Our assessment of this effect is somewhat smaller, based on modelling by Wang et al. (2002).

15. The referee "would recommend . . . a much more detailed analysis of uncertainties" (p. S2171, S2174). We propose a "more detailed" analysis by including uncertainties into Table 1 as recommended in a manner similar to that for sinks in Table 2 (see Comment #23). This approach helps emphasize that our strategy is the isotopic analogue of the "top-down" and "bottom-up" comparison used to good effect to constrain the global methane budget, e.g. in IPCC assessments.

16. The referee's final paragraph on $^{13}CH_4$ (p. S2171) misrepresents our answer to the question raised by the title. Possibly this is because we did not clarify our answer to the question, and will do so more explicitly. Rather, we would see a more balanced answer. The particular bottom-up sources are compatible with our current understanding of the

atmospheric history and sinks provided we can reconcile the "apparent fractionation" with either the weighted-mean sink or the source-mix, or both. This may not be an approach prevalent in the literature, but it is a valid one and novel for it.

17. The referee's opening paragraph about $^{14}CH_4$ (p. S2172) presents an apparent contradiction that results from his/her misreading (or our poor wording) of the text. We will reword the appropriate sentence to provide clarification.

18. The next paragraph refers mainly to the companion paper (Lassey et al., 2006), which should be outside the topic of this review. Therefore, as we do not propose to merge the two papers, we will not respond to those comments here.

19. The referee's digression into a critique of the companion paper (Lassey et al., 2006) appears to be because he/she recommends their merger into a single paper. Indeed early drafts started out that way! They were segregated on the basis that:

- The main findings of the companion paper were potentially far-reaching in their implications and should have a greater accessibility (and 'searchability') than being submerged in a paper whose topic and title were much broader.

- Being confined to an appendix, or later section, would result in not reaching the attention of many researchers who may wish to be alerted to a significant new finding.

- The present paper is a model analysis of the evolving $CH_4$ budget and its $\delta^{13}C$ and $\Delta^{14}C$ counterparts. The companion paper is an almost model-independent analysis of the correlation between time series of atmospheric $\Delta^{14}C$ and of PWR-produced electrical power (as a proxy for the $^{14}CH_4$ generated by the nuclear industry). Relegation of the companion paper to an appendix, or later section, could leave an impression that the inferred fossil fraction and NPR factor are dependent on the model presented in the main part of the paper.

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We strongly resist the recommendation to (re)merge the two papers, but will seek to reduce unnecessary overlap, consistent with their standing independently.

20. We will implement all the "specific comments" on Page S2173–5, except as noted below. While a change to the new NOAA04 scale for methane mixing ratio is inconsequential (atmospheric burdens change by $\sim$1%), we nevertheless propose to incorporate it (Comment #26).

21. As noted in Comment #4, it seems to us premature to integrate the plant source of methane into source inventories. We will cite references to papers that seek to better constrain its global source (4 extra references), which include that of Ferretti et al. (2006). The last-mentioned paper has authors in common with the present paper, but was incomplete at the time that the present paper was submitted. While the source inventories that Ferretti et al. examine provide bounds that could in principle be incorporated into the present model, there remain no guidance for preparing a time series. A digression into constructing possible evolutions of the plant source is outside the scope of this paper, and we believe would not significantly enhance our understanding of that source. Nevertheless, recognising the topicality of the plant source, we will expand discussion.

22. The specific comment about the BHD anomaly is well taken. We covered that point implicitly by referring to limited knowledge about its longitudinal extent, but recognise that a more explicit mention is appropriate.

23. We will add uncertainties into Table 1, appealing to the "lower limits" and "upper limits" to the pre-industrial source components estimated by Houweling et al. (2000). Uncertainties on the $\delta^{13}$C values are themselves uncertain and subjective: Quay et al. (1999, Table 1) cite $\pm$5 per mil (or close to it) as 1 s.d. uncertainty for sources that play an appreciable pre-industrial role, while Hein et al. (1997) cite similar magnitudes as 2 s.d. uncertainties for those sources. We propose to apply an illustrative across-the-board estimate of $\pm$5 per mil (2 s.d.) in order to assess uncertainty in $\delta^{13}$C of the global

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source in a manner analogous to the approach in Table 2. We believe that the effort associated with further analysis would markedly delay publication of the paper without significantly enhancing quantitative understanding of uncertainties.

24. We agree that Figs 2 and 4 are too small. Their sizes appear to have been dictated by page (screen) sizes for ACPD or inadvertently by the supplied *.eps files, and we will seek their enlargement for ACP publication.

**Other proposed changes**

25. We have discovered that the PWR dataset of Table 3 is in error. Unbeknown to us, it did not include electrical generation by Soviet-designed PWRs, which were designated WWERs (Water-cooled Water-moderated Energy Reactors). The two designations have recently been merged by IAEA into one (also termed "PWR") which may have caused the confusion in data collection. We have now incorporated the amended dataset into our model and propose to adjust the paper accordingly. Apart from the early years of the nuclear industry, electrical generation reported in Table 3 is raised by 12–15%. The only appreciable net effect is that fitted "NPR factors" are correspondingly smaller.

26. Recently, a new paper reported a high-resolution methane time series (MacFarling Meure et al., 2006). This dataset offers an advantage over the "Etheridge-extended" dataset that we employed: the latter merges the (smoothed) Etheridge et al. (1998) and (direct) NOAA/CMDL datasets, whereas the new dataset of MacFarling Meure et al. has consistent smoothing throughout the time series to 2000 and beyond. We propose to adopt this newer dataset (converted to the new NOAA04 scale as recommended by Referee #2) to replace the Etheridge-extended dataset. This will entail new figures that differ only very slightly or imperceptibly from the old, and require some minor textual changes including an additional reference. We propose to present this atmospheric dataset in a new figure, as recommended by Referee #2 (Page S2173).

27. On page 5010 we referred to "more recent research" on the strength of the chlorine

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sink that was attributed to "W. Allan (personal communication, 2006)". That research is now incorporated in a paper that has been accepted for publication (Allan et al., in press), so it is appropriate to re-orient the discussion in that light, using the Allan et al. appraisal of that strength in Table 2 to supersede the value sourced from Platt et al. (2004) in the ACPD paper. This necessitates that the appropriate paragraph in Section 4.2 be recast as well as expanded. See also the following comment.

28. We propose to rewrite much of Section 4.2. This is necessary to expand discussion on uncertainty and to better clarify the possible ways that the 'apparent' and 'bottom-up' sink fractionations can be reconciled, taking account of recommendations of Referee #2 as well as including the new Allan et al. (in press) appraisal of the chlorine strength (Comment #27).

29. We propose to replace acronym 'BSR' ("biosphere-sourced radiomethane") with 'BR' ("biospheric radiomethane") to avoid possible confusion with the use of 'BSR' in geophysics as "bottom simulating reflector" (Referee #1, Lassey et al., 2006).

30. We propose many additional minor textual improvements identified by the authorship, mainly to trim text length, clarify presentation, and incorporate feedback from others (M. R. Manning, E. G. Nisbet) who will be acknowledged.

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