

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

Anonymous Referee #2

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The paper of Lassey et al. presents a study of the global CH₄ sources and sinks during the last 120 years. Using a 1-box model, the authors analyze recently measured records of ¹³CH₄ and ¹⁴CH₄ from polar ice and firn. The paper is certainly very interesting as it helps interpreting these very important new measurements and as it demonstrates that the isotopic records are basically consistent with the "global source inventory histories (GSIH)" of van Aardenne et al. [2001], and - to a somewhat lesser extent - of Stern and Kaufmann [1996].

However, there are several shortcomings of the analysis. In particular, as further outlined below, I do not agree with the central conclusion of the paper that "Balancing both ¹²CH₄ and ¹³CH₄ budgets requires participation by a highly-fractionating atmospheric sink such as active chlorine". Furthermore, the analysis of the ¹⁴CH₄ measurements

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need some clarifications, in particular in the context of the companion paper [Lassey et al., 2006], as the conclusions of the two papers appear to be not consistent.

(1) $^{13}\text{CH}_4$

Using the GSIHs EDGAR-HYDE (E-H) [van Aardenne et al., 2001], and Stern and Kaufmann (S&K) [1996] for the anthropogenic sources (augmented by estimates for the natural sources from Houweling et al. [2000]), and furthermore using ice/firn measurements of Etheridge et al. [1998] the authors derive the total global CH_4 sink. This approach is rather unusual, as generally the global CH_4 sinks (mainly OH) are believed to be much better constrained than the sources (and in fact the estimate of natural sources by Houweling et al. [2000] were mainly constrained by OH). Nevertheless such an approach may be chosen to investigate the consistency of inventories and in fact the derived CH_4 sink (and its trend) appears quite consistent with various estimates in the literature. Using $\delta^{13}\text{CH}_4$ estimates for the various sources from Houweling et al. [2000], the authors then calculate the average $\delta^{13}\text{CH}_4$ of the total CH_4 sources. By comparing with the recent ice/firn $\delta^{13}\text{CH}_4$ data of Ferretti et al. [2005] (and direct atmospheric measurements during the last 20 years), they then derive the apparent isotope fractionation (between -6.9 and -8.1 ‰). Since this apparent fractionation is higher than the kinetic isotope effect (KIE) of the reaction $\text{CH}_4 + \text{OH}$, the authors conclude that the highly fractionating $\text{CH}_4 + \text{Cl}$ reaction must play a significant role in the troposphere. While there is some independent evidence that the reaction $\text{CH}_4 + \text{Cl}$ plays a role in the marine boundary layer [e.g. Allan et al., 2005], I do not consider the attempt of the presented paper to estimate the $\text{CH}_4 + \text{Cl}$ contribution from the global $\delta^{13}\text{CH}_4$ budgets as very solid, mainly because of 3 reasons:

(a) atmospheric $\delta^{13}\text{CH}_4$ is very sensitive to the relative contribution of CH_4 from biomass burning (with $\delta^{13}\text{CH}_4$ of -12...-25 ‰ by far the most $\delta^{13}\text{CH}_4$ enriched source), but this source is not very well quantified.

(b) the $\delta^{13}\text{CH}_4$ signatures of many CH_4 sources are still relatively uncertain. For most biogenic sources they depend significantly on the exact partitioning of CH_4 production processes (acetate fermentation vs. CO_2 reduction [Whiticar et al., 1986]), and on bacterial CH_4 oxidation. E.g. the compilation of [Quay et al., 1991] gives a $\delta^{13}\text{CH}_4$ range of -31 to -86 ‰ for different wetlands (this may include some individual spot measurement under extreme conditions, but illustrates the large site-to-site and temporal variability, which makes it difficult to narrow down the global mean $\delta^{13}\text{CH}_4$ signatures for the different source categories).

(c) in the present analysis the authors ignore the return flux from the stratosphere to the troposphere (see footnote b of Table 2). Measurements of [Brenninkmeijer et al., 1995; Sugawara et al., 1997], however, showed an 'apparent' kinetic isotope effects in the lower stratosphere in the order 10 to 13 ‰ (due to the combined influence of the OH, Cl, and O(1D) sink in the stratosphere [Bergamaschi et al., 1996]). Assuming this range of measured apparent KIEs from the lower stratosphere probably reflects the impact of the stratosphere on tropospheric $\delta^{13}\text{CH}_4$ much more realistic than assuming no return flux. Using an effective KIE for the STE of 10 to 13 ‰ results in a decrease of -0.8 ± 0.1 ‰ for the average fractionation of all sinks (recalculation based on otherwise identical values of Table 2), i.e. very close to the KIE values derived by the authors for the EDGAR-HYDE inventory.

Summarizing point (1) I would recommend that the authors include a much more detailed analysis of uncertainties, both for the emissions (in particular biomass burning) and the $\delta^{13}\text{CH}_4$ signatures of the sources. Furthermore, the KIE of the stratosphere should be taken into account.

I think that answer to the question raised in the title "What do the carbon isotopes tell us?" is for $\delta^{13}\text{CH}_4$ that it is constraining the sources (in particular CH_4 from biomass burning), rather than the sinks (as suggested in the paper) which would require very accurate knowledge of the sources.

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(2) $^{14}\text{CH}_4$

In this paper, the authors demonstrate that a fraction of 16-22 % for the fossil sources (as estimated by the E-H and SK inventories) can be reconciled with atmospheric $^{14}\text{CH}_4$ observations during the period 1980-2000. Furthermore, they conclude that their analysis supports the "broad uncertainty" ... "to tightly constrain the fossil fraction in the methane source after ca 1960 AD". In the companion paper, however, [Lassey et al., 2006] derive a fossil fraction of 28.6 ± 1.9 %, i.e. significantly different from the E-H and SK estimates and with very small uncertainty range.

It should be explained much clearer, how these two different estimates and conclusions can be reconciled and understood.

The companion paper derives the fossil fraction from the correlation between measured atmospheric $^{14}\text{CH}_4$ and generated electric power from nuclear pressurized water reactors (PWRs) for the period 1986-2000. The central assumption of this correlation analysis is (1) that the fossil fraction has not changed during the analysis period, and (2) that the "NPR factor" is constant. However, both assumptions may have only limited validity: (1) The E-H and SK inventories suggest significant changes of the fossil fraction, also after 1985 (Figure 4). (2) As the authors discuss in detail, different types of reactors may have different "NPR factors" (e.g. "western-designed" vs. "Soviet-designed"). Thus it seems likely that with increasing electrical power production from PWRs also the average "NPR factor" is changing with time. Therefore, the very small uncertainty range estimated in the companion paper is probably too optimistic.

Furthermore, there is considerable overlap between the two companion papers (in particular in the introductions, and general discussion of $^{14}\text{CH}_4$). Therefore, I would recommend to combine both papers to one consistent analysis with consistent conclusions. "The mathematical framework" of the companion paper could be presented in an appendix of this combined paper.

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Specific comments:

page 4997, line 4-7, "inverse tracer modelling...over limited time range...or global modelling over longer time scales": It should be mentioned that most of the modelling studies "over limited time range" are based on detailed 3D models while the cited studies over "over longer time scales" are based on 1-box models.

page 4997, line 9-11, "The methane source mix and its evolution can be constrained by isotope data... $\delta^{13}\text{CH}_4$ and/or $\Delta^{14}\text{CH}_4$ ". It should be mentioned that also $\delta\text{CH}_3\text{D}$ may be very valuable [Bergamaschi et al., 2000; Wahlen, 1993].

page 4997, line 14-15, "fossil methane sources are intermediate between these ($\delta^{13}\text{CH}_4 \sim -40 \text{ ‰}$)": This is true mainly for natural gas of thermogenic origin, while biogenic natural gas may be strongly depleted in $\delta^{13}\text{CH}_4$ [Schoell, 1980].

page 4998, lines 10-12: add also references to soil sink and stratospheric destruction.

page 4998, lines 14-16, "that global OH levels have declined over the industrial era": add range of estimated change in OH.

page 4998, line 20, "global-mean OH has been remarkably stable". The study of Manning et al. [2005] is based on ^{14}CO measurements in the SH and therefore gives mainly information on OH in the SH.

page 4999, line 9-10, "expressed on the CMDL83 scale". I would recommend to present CH_4 data in the new NOAA04 scale [Dlugokencky et al., 2005]. Even if the difference is small, but the new scale is believed to represent true mixing ratios much better.

page 4999, line 18, "NOAA/CMDL": should be changed to "NOAA Earth System Research Laboratory (ESRL)".

page 5000, line 8, "Etheridge-extended" dataset. This dataset should be presented in a figure (it is quite central to the analysis of this paper).

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page 5003, line 13-16, "...methane source from vegetation (Keppler et al., 2006)... Thus, while we discuss the implications of this sources, we do not include it in our source constructions."

I would recommend to extend the discussion of the CH₄ source from plants. It would be interesting to discuss which constraints on the plant source arise from $\delta^{13}\text{CH}_4$. Furthermore, I would recommend to put this study in context with the recently published ACPD paper of [Ferretti et al., 2006], which - mainly based on the same $\delta^{13}\text{CH}_4$ records - concludes that plant emissions "during the last 2000 years ... are likely to lie in the range 0-46 Tg yr⁻¹"

page 5008, lines 3-9, "The BHD record features an 'anomaly' in ca 1992": It should be mentioned that also in the extra-tropical SH some uncertainty exists about this anomaly: E.g. it is not visible in the Cape Grim Air Archive samples [Francey et al., 1999].

page 5008, lines 19 ff: The discussion of $\delta^{13}\text{CH}_4$ uncertainties should be extended (as outlined above). It would be very helpful to add $\delta^{13}\text{CH}_4$ uncertainty ranges in Table 1.

The authors mention here some of the points which I raised above (e.g. "Uncertainties in individual source assignments can therefore account for uncertainty in inferred ϵ at least of order 1 ‰" and the importance of biomass burning. Therefore it is not clear why the authors nevertheless conclude that "Balancing both ¹²CH₄ and ¹³CH₄ budgets requires participation by a highly-fractionating atmospheric sink such as active chlorine (removing at least 10 Tg yr⁻¹)" (abstract), and "In the present work we have shown that the global E-H source inventory for the 20th century is indeed generally compatible with newly-emergent $\delta^{13}\text{CH}_4$ data from air trapped in Antarctic ice (Ferretti et al., 2005), with one a notable caveat. The isotopic fractionation... is larger in magnitude than commonly accepted for the OH sink either alone or in tandem with a soil sink" (conclusions, page 5020).

page 5010, lines 16-23, "...possibly significant co-generation of other oxidations (e.g.

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O(1D))...." Both studies [Cantrell et al., 1990; Saueressig et al., 2001] tried to exclude the influence of the CH₄+ O(1D), see detailed discussion on this topic by [Saueressig et al., 2001] (page 23131), where it has been concluded that the potential influence of O(1D) in the study of [Cantrell et al., 1990] can probably not explain the difference of the derive KIEs for the CH₄+OH reaction..

page 5010-5011, "Inverse modelled $\delta^{13}\text{CH}_4$ ": Why has the inverse modelled $\delta^{13}\text{CH}_4$ based on the S&K inventory much higher inter-annual variability than that based on the E-H inventory (Figure 2b) ?

page 5011, line 25, "pronounced swing in $\delta^{13}\text{CH}_4$ ": Which change of source mix would be required to explain such a swing ?

page 5018, lines 14-23, how large are the uncertainties in the "assignment of a mean air age" and the $^{14}\text{CH}_4$ measurement uncertainties for the firn samples, and what is the resulting uncertainty for the τ_{lag} (which as the authors state is mainly constrained by one single firn measurement around 1972; Figure 4a).

Figures 2 and 4 should be enlarged.

References

Bergamaschi, P., M. Bräunlich, T. Marik, and C.A.M. Brenninkmeijer, Measurements of the carbon and hydrogen isotopes of atmospheric methane at Izana, Tenerife: Seasonal cycles and synoptic-scale variations, J. Geophys. Res., 105 (D11), 14531-14546, 2000.

Bergamaschi, P., C. Brühl, C.A.M. Brenninkmeijer, G. Saueressig, J.N. Crowley, J.U. Grooss, H. Fischer, and P.J. Crutzen, Implications of the large carbon kinetic isotope effect in the reaction CH₄ + Cl for the 13C/12C ratio of stratospheric CH₄, Geophys. Res. Lett., 23 (17), 2227-2230, 1996.

Brenninkmeijer, C.A.M., D.C. Lowe, M.R. Manning, R.J. Sparks, and P.F.J.v. Velthoven,

The ^{13}C , ^{14}C , and ^{18}O isotopic composition of CO , CH_4 and CO_2 in the higher southern latitudes lower stratosphere, *Geophys. Res. Lett.*, 100, 26,163-26,172, 1995.

Cantrell, C.A., R.E. Shetter, A.H. McDaniel, J.G. Calvert, J.A. Davidson, and e. al., Carbon kinetic isotope effect in the oxidation of methane by the hydroxyl radical, *J. Geophys. Res.*, 95 D, 22,455/62, 1990.

Dlugokencky, E.J., R.C. Myers, P.M. Lang, K.A. Masarie, A.M. Crotwell, K.W. Thoning, B.D. Hall, J.W. Elkins, and L.P. Steele, Conversion of NOAA atmospheric dry air CH_4 mole fractions to a gravimetrically prepared standard scale, *J. Geophys. Res.*, 110, D18306, doi:10.1029/2005JD006035, 2005.

Ferretti, D.F., J.B. Miller, J.W.C. White, K.R. Lassey, D.C. Lowe, and D.M. Etheridge, Stable isotopes provide revised global limits of aerobic methane emissions from plants, *Atmos. Chem. Phys. Discuss.*, 6, 5867-5875, 2006.

Francey, R.J., M.R. Manning, C.E. Allison, S.A. Coram, D.M. Etheridge, R.L. Langenfelds, D.C. Lowe, and L.P. Steele, A history of d^{13}C in atmospheric CH_4 from the Cape Grim Air Archive and Antarctic firn air, *J. Geophys. Res.*, 104 (D19), 23631-23644, 1999.

Lassey, K.R., D.C. Lowe, and A.M. Smith, The atmospheric cycling of radiomethane and the "fossil fraction" of the methane source, *Atmos. Chem. Phys. Discuss.*, 6, 5039-5056, 2006.

Quay, P.D., S.L. King, J. Stutsman, D.O. Wilbur, L.P. Steele, I. Fung, R.H. Gammon, T.A. Brown, G.W. Farwell, P.M. Grootes, and F.H. Schmidt, Carbon isotopic composition of atmospheric CH_4 : fossil and biomass burning source strength, *Global Biogeochem. Cycles*, 5, 25-47, 1991.

Saueressig, G., J.N. Crowley, P. Bergamaschi, C. Bruehl, C.A.M. Brenninkmeijer, and H. Fischer, Carbon ^{13}C and D kinetic isotope effects in the reactions of CH_4 with $\text{O}(^1\text{D})$ and OH : New laboratory measurements and their implications for the isotopic compo-

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sition of stratospheric methane, *J. Geophys. Res.*, 106, 23,127-23,138, 2001.

Schoell, M., The hydrogen and carbon isotopic composition of methane from natural gases of various origin, *Geochim. Cosmochim. Acta*, 44, 649-661, 1980.

Sugawara, S., T. Nakazawa, Y. Shirakawa, K. Kawamura, S. Aoki, T. Machida, and H. Honda, Vertical profile of the carbon isotopic ratio of stratospheric methane over Japan, *J. Geophys. Res.*, 24 (23), 2989-2992, 1997. Wahlen, M., The global methane cycle, *Annu. Rev. Earth Planet Sci.*, 21, 407-426, 1993.

Whiticar, M.J., E. Faber, and M. Schoell, Biogenic methane formation in marine and freshwater environments: CO₂ reduction vs. acetate fermentation - isotope evidence, *Geochim. Cosmochim. Acta*, 50, 693-709, 1986.

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