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Discussions

Interactive comment on “Hemispheric average Cl atom concentration from ^{13}C/^{12}C ratios in atmospheric methane” *by* U. Platt et al.

M. Heimann (Editor)

martin.heimann@bgc-jena.mpg.de

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The following comment and reply have been exchanged between Anonymous Referee #2 and the authors in the course of the review process. Due to a mistake they have not been published immediately during the open discussion but are now disclosed retrospectively:

Comment by Referee #2:

I advice to ask the authors to thoroughly modify the paper, and to consider resubmit it, in a form that really answers the question about the role of tropospheric Cl.

A. The seasonal cycle in the ^{13}C/^{12}C ratio of tropospheric methane in the ETSH cannot

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be explained by the OH sink only.
B. Two previous papers have suggested that a certain Cl sink can form the missing link.
C. The paper tabled here suggests that heterogeneous oxidation of chloride catalysed by bromine supplies the required levels of Cl atoms.
D. The paper brings relatively little new information.

Major questions arise, which however are not yet addressed or properly elucidated. The case presented may seem plausible, but may well be wrong.

1. Can the SH troposphere (for methane) justifiably be considered as an isolated box reactor? Although the effect of the SH stratosphere is mentioned, the possible effect of the NH is not.
2. Changes in large scale circulation, biomass burning and the impact of the Mount Pinatubo eruption may well provide source effects that play a role. Figure 2 suggests the reader that the irregularity of the annual course of ^{13}C points to other causes, not necessarily Cl.
3. Does the proposed mechanism provide a source strength of Cl atoms in the marine boundary layer that is of sufficient magnitude? The presence of Cl atoms in the boundary layer is undeniable. The crux of the matter remains if the mechanism can supply sufficient Cl.
4. Figure 2 shows an annual cycle of about 0.2 per mil for 1999–2002. The text mentions that the amplitude is a factor 4 higher than the amplitude expected from CH_4+OH (from which the reader infers that 0.4 per mil is meant). A curve fitting through the time series 1990–2002 must be provided. The striking change in pattern must be explained to the reader. It seems that the seasonal cycle is related to the measurement uncertainty. This may well be pure coincidence.
5. The same group has shown that the ^{13}C value of CO from Baring Head is higher than can be explained by OH. Thus if Cl would contribute 4% to the sink, this problem would become even worse. This conundrum should be addressed, or at least mentioned (see also point 9).

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6. Explain clearly what was wrong with [Cl]av (=2600 cm^{-3}) used in the model [Allan et al., 2001a, b]. Please explain also how 23 Tg yr^{-1} was derived. This is critical part in this paper that how the authors revise the value.
7. What KIE comes out when the model of [Allan et al., 2001a] runs with revised [Cl] (=24 000 cm^{-3}).
8. The authors show the "KIE line" for 1996 in Figure 3 as being representative. Explain why the KIE in 1996 is representative although [Allan et al., 2001b] used the average seasonal variations for the concentrations and isotopic ratios over the period 1993–1996.
9. Explain why the carbon isotope budget of CO does not need the chlorine chemistry link to CH_4 [Bergamaschi et al., 2001]. If the chlorine reaction with CH_4 is significant (as much as 4%), there should be a discrepancy between measurement and model prediction of the d^{13}C(CO) values in the model shown by [Bergamaschi et al., 2001].

There are inconsistencies and errors in the paper. For instance, it is written that ^{13}C has an abundance of 1.12% (international standard, citation?). It is also mentioned that ^{13}C in CH_4 has an abundance of 1.12%, although CH_4 is depleted in ^{13}C by almost 5%. The paper also states that CH_4 is believed to be removed by OH. Young scientists may well get the idea from this paper that there is some doubt about this (this is a strange statement in the paper, and actually subtly misleading. It suggests a degree of uncertainty about facts, a suggestions that tacidly opens the backdoor for certain speculations. It constitutes an ulterior message to the reader. If we are at the stage of BELIEVING that OH removes CH_4, anything becomes possible. I am sure it is not meant this way by the authors, but I am shocked). A bit later it is mentioned that OH is formed by the photolysis of H_2O, which is not true.

References:

Allan, W., D.C. Lowe, and J.M. Cainey, Active chlorine in the remote marine boundary layer: Modeling anomalous measurements of delta C-13 in methane, Geophysical Research Letters, 28 (17), 3239-3242, 2001a.

Allan, W., M.R. Manning, K.R. Lassey, D.C. Lowe, and A.J. Gomez, Modeling the variation of delta C-13 in atmospheric methane: Phase ellipses and the kinetic isotope effect, Global Biogeochemical Cycles, 15 (2), 467-481, 2001b.

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Lowe, D.C., W. Allan, M.R. Manning, T. Bromley, G. Brailsford, D. Ferretti, A. Gomez, R. Knobben, R. Martin, Z. Mei, R. Moss, K. Koshy, and M. Maata, Shipboard determinations of the distribution of C-13 in atmospheric methane in the Pacific, Journal of Geophysical Research-Atmospheres, 104 (D21), 26125-26135, 1999.

Vogt, R., P.J. Crutzen, and R. Sander, A mechanism for halogen release from sea-salt aerosol in the remote marine boundary layer, Nature, 383, 327-330, 1996.

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Reply by Authors:

We like to thank the reviewer for providing an extremely thorough review of the paper. Although we do not understand why this discussion could not be carried out in public as foreseen by the review scheme of ACPD, we are convinced that the quality of the manuscript has considerably improved through this revision. And respond to the reviewer's comments and questions as follows:

On the reviewer's statement "the paper brings relatively little new information": This statement is rather surprising to us and obviously in contradiction to the obviously great

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interest the reviewer showed with the extraordinary detailed (for an ACPD manuscript) report.

Response to the reviewer's "major questions":

1.) NOAA/CMDL have published several papers showing their "flying carpet" time – latitude plot of atmospheric methane mixing ratio measurements. These data show non uniform seasonal cycles in the data north of about 20° S. South of this latitude, which we define as the extra tropical southern hemisphere (ETSH), the cycles are much more sinusoidal in nature and the minima and maxima are phase shifted from the expected OH maxima and minima (around the respective solstice) by about 3 months or 90 degrees. This is precisely the behavior one would expect in a chemical reactor used to study the behavior of the CH_4+OH reaction with a seasonally varying OH level. It is clear that transport effects from the northern hemisphere and limited SH sources will still affect CH_4 data from Baring Head (at 41° S and well within the ETSH). However, because the data are collected during southerly wind trajectories (typical 4 day back calculated trajectories show air descending from 55° S), the shape of the seasonal cycle is dominated by the sink process. North of the ETSH boundary Allan et al. [2001a] have shown that the phase ellipse technique is difficult to use because of the impact of sources on the shape of the seasonal cycles. In the ETSH, NH sources (particularly biomass burning) can change the ellipse shape, but appear not to have a significant effect on the ellipse tilt, from which we deduce the enhanced KIE. The reviewer makes a valid point and text following the reasoning outlined above has been added to the manuscript (pages 3 and 7).

2.) As mentioned above, source effects do play a role in determining the seasonal cycles of atmospheric CH_4 at Baring Head. However in the ETSH previous "phase ellipse" studies published by Allan et al. [2001a] indicate that the dominant effect in shaping the CH_4 seasonal cycles is sink driven. Text has been added to the manuscript as described above (pages 3, 4).

3.) We don't know what the strength of the proposed mechanisms is. In this manuscript

we try and determine exactly that quantity, (assuming that Cl is the cause of the increase in the apparent KIE). In fact around 1.8$\times 10^4$ Cl atoms per cm^3 (in the MBL) would require a net source of Cl atoms of about 5$\times 10^4$ atoms per cm^3 and second since the main sinks of Cl atoms are reaction with O_3:
$Cl + O_3 \rightarrow ClO + O_2$
However for ClO the most likely loss process of ClO in the MBL is photolysis regenerating Cl atoms. So reaction of Cl atoms with CH_4 (R1) remains as the main net sink. The question is: Can R4 and R6 be sufficiently fast to supply this amount of Cl-atoms? A simple calculation shows that it can: Models and measurements show BrO levels around 1 ppt in the troposphere (with an effective BrO_x lifetime of 10 000 s this level requires an average net Br atom source of 2.4$\times 10^3$ Br atoms per cm^3 and second). In other words each Br atom needs to under go the reaction sequence R4 + RS6 once every $\approx$300 s. The gas phase reaction R4 is sufficiently fast, since the time between two reactions is given by 1/([HO_2]$\times$k4)$\approx$100 s. For the heterogeneous reactions this is more difficult to judge, but quite likely in view of the fact that Cl-/Br- is about 600 in sea salt, but the required Cl atom source is only 10 times higher than the Br source.
4.) As requested by the reviewer we have included a fitted curve through the data. We no longer include data before 1993 because of the documented, unexplained anomaly in $\delta^{13}C(CH_4)$ – probably a Pinatubo effect – observed at several southern hemisphere sites during 1991 and 1992 (Lowe et al., Geophys. Res. Lett., 24, 857, 1997) We have changed the text to discuss the change from 0.4 to 0.2 per mil seasonal amplitude after 1998. There is no relationship between the measurement uncertainty and the seasonal cycle.
5.), 6), 7), 9) We have extensively rewritten the Discussion and Conclusions section to cover these points. The effect on the CO budget is discussed. We have described in detail how the mixing of methane from the marine boundary layer into the free troposphere requires more Cl in the MBL, and how we derive the slightly reduced estimate of 19 Tg yr^{-1} for the Cl sink for methane.
6.) See 5).

7.) See 5).
8.) We now explain in the text, where Figure 3 is first cited and that we show the 1996 ellipse to demonstrate that it is similar to the 1993–1996 average ellipse.
9.) See 5).

Response to the reviewer's comments on "inconsistencies and errors":

The "^{13}C abundance of 1.12%" is the internationally agreed value of a marine carbonate PDB widely used in the literature as "VPDB" (Vienna PDB). All the ^{13}C measurements cited in this manuscript are with respect to VPDB. We have changed the text to clarify this. We have removed the erroneous statement that ^{13}C in CH_4 has an abundance of 1.12%. The reviewer is quite correct in pointing out that ^{13}C in CH_4 is depleted cf VPDB by about 50 per mil or 5%. About the source of OH: Of course OH is not produced by photolysis of water vapour but by photolysis of ozone, the resulting excited oxygen atoms react with water vapour (see e.g. Platt et al., J. Atmos. Chem., 42, 359–394, 2002), we thank the reviewer for pointing out this rather careless wording on our side.

On the question of OH being the sink of methane: In fact OH is "believed" to be degraded by OH, but apparently there are other mechanisms as well and as scientists we must be allowed to voice doubts about general beliefs. To avoid any misunderstanding: We are convinced that there is scientific evidence that the bulk of CH_4 is degraded by reaction with OH, however we make the point that a non-negligible fraction is also degraded by other radicals (i.e. Cl atoms). To believe has several meanings: Be of an opinion (based on evidence) or religious type of belief. In any case we see no reason "to be shocked" and we are confident that we are not confusing young scientists (in fact we should think higher of the intelligence of young scientists). We have – nevertheless – removed the statement that OH is "believed" to be the major sink of CH_4 replacing it with text that is more definitive. At some stage we would very much appreciate the opportunity of debating hypotheses and "facts" in science with the reviewer. This is a fascinating philosophical topic that keeps us in science but is beyond the scope of this

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