Atmos. Chem. Phys. Discuss., 5, S2100–S2106, 2005
www.atmos-chem-phys.org/acpd/5/S2100/
European Geosciences Union

Atmospheric Chemistry and Physics Discussions

Interactive comment on "New insight into the atmospheric chloromethane budget gained usingstable carbon isotope ratios" *by* F. Keppler et al.

F. Keppler et al.

Received and published: 15 August 2005

The authors wish to thank both referees for their efforts reviewing and the helpful comments provided on our manuscript. Thanks also to two other members of the scientific community who took the time to contribute comments.

All page numbers referred to below are with respect to the PDF print version

Anonymous Referee #1

Specific comments 1. On pages 3904-3906 and later in paper: I was confused by the sign of the quantity Delta. In the first paragraph of page 3904, depletion relative

to unburnt fuel was quoted as a negative quantity, whereas in the next paragraph, depletion relative to bulk biomass was a positive quantity. Are these consistent?

The sign of the quantity delta should be positive and will be changed throughout the paragraph.

2. Page 3910, 2 lines before equation (5): based on Table 1, delta13C_known sources = -52.5 per mil only if the wetlands and rice sources are taken as having isotopic signatures of 0 per mil. Is this what the authors intended? If these two sources are completely omitted, or if they are assigned a more likely isotopic signature (say -50), the weighted sum is more like -53.3. The authors should clarify this. Would a value of -53.3 make any difference to the conclusions?

The value of -52.5 was calculated including both the wetlands and rice source terms (as having isotope signatures of 0 per mil) in the total source term budget. As no carbon isotope signatures are available for either source both we will follow the reviewers suggestion and assume a more likely isotopic signature of -50 per mil. This will change the value for the delta 13C_known sources from -52.5 to -53.3. Recalculation of the delta 13C value of the missing source for each scenario will be included in the revised manuscript. Replacing the value of -52.5 with -53.3 in equation 5 does not alter the conclusions arrived at for any of the three scenarios considered in the manuscript.

3. Page 3910, equation (5): Deriving this equation requires that delta13C_known sources is weighted versus only the known sources, while Phi_mis is normalized by the sum of all sources, not just the known sources. I think it would be worth mentioning this.

These differences will be mentioned in the revised manuscript.

4. In Figure 1, how is it possible to assign a fairly accurate isotope signature to "Unknown processes" when the known sources "Marine bacteria" and "Soil reactions" only have question marks?

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The "Unknown processes" in the oceanic section of Figure 1 represent the isotope value of the net flux of CH3Cl from the ocean to the atmosphere as measured by Komatsu et al. (2004). The term “unknown processes” was chosen because presently the mechanism by which marine CH3Cl is formed is uncertain. The referee might have been confused by lack of sufficient distinction between the land and ocean segments in the Figure. In the revised manuscript these segments will be more clearly delineated.

Technical corrections 1. Abstract line 22: instead of "...the bulk fraction of atmospheric CH3Cl..." I suggest"...a major fraction of the source of atmospheric CH3Cl...".

We will change the sentence to read as follows "that the largest source of atmospheric CH3Cl (1800 to 2500 Gg yr-1) is the abiotic methylation of chloride in terrestrial ecosytems, primarily located in tropical and subtropical areas where turnover of biomass is highest."

2. Page 3902 lines 2-3: I suggest replacing "...atmospheric chloromethane..." with "...the source of atmospheric chloromethane...".

We will change the sentence to read "could be responsible for a large proportion of the chloromethane entering the atmosphere (up to"

3. Page 3902 lines 14: I suggest deleting the second occurrence of "for atmospheric CH3Cl".

Change accepted.

4. Page 3902 lines 16-22 and elsewhere in paper: Is it necessary to describe sources in terms of both Tg/yr and Gg/yr? For example, 370 Gg/yr is 0.37 Tg/yr, and a few lines later 0.18 Tg/yr is used.

Only the term Gg/yr will be used in the revised manuscript.

5. Page 3903 line 23: Again I suggest "major" rather than "bulk".

In this sentence we will change “bulk fraction” to "largest input"

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6. Page 3904 line 18: Is "experimentally" perhaps a better term than empirically"?

Change accepted.

7. Page 3906, line 10: I suggest replacing "89.9" by "90" as the other values are quoted to the nearest unit.

Change accepted.

8. Page 3910 line 7: "52,5" should be "52.5".

Change accepted.

9. Page 3910, line 18: "an highly" should be "a highly"

Change accepted.

10. Page 3911, line 1: "used in for" should be "used in"

"used for in" will be changed to read “used for”

11. References: The Simmonds et al. (2004) citation in the text is not in the reference list.

Simmonds et al. reference will be included in reference list.

12. References: The Kalin et al. (2001), Dimmer et al. (2001), and Goldstein et al. (2003) references in the reference list are not cited in the text.

These references will be removed from the reference list.

13. Table 1: Is the range in delta_13C a full range or an uncertainty magnitude, e.g.does the value "12" mean "+/-6" or "+/-12"?

The term "uncertainity magnitude" will replace "range" in Table 1.

14. Table 3: The Scenarios should be labeled "A B C", not "1 2 3"

Change accepted.

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Referee #2 - J. Rudolph

'Nevertheless, I would have liked to see a more rigorous approach to the isotopic budget of atmospheric CH3Cl. In combination with a conventional budget using equation (4) would allow calculation of the combined effect of all unknown sources and sinks. For this purpose the budget equations simply have to be separated into known and unknown sources and sinks. This gives the isotope ratio and magnitude for the sum of all unknown sources and sinks. Based on this and the corresponding uncertainties, which can be derived from the budget equations using simple Gaussian error propagation, it should be possible to identify the range of plausible solutions for the unknown magnitude of the abiotic leaf litter source and bacterial sink of CH3Cl. A similar approach has already been used in the cited paper by Thompson et al., although with limited success due to the at this time very sparse information on isotope ratios for atmospheric sources and sinks of CH3Cl.'

The authors are aware that there are other approaches that could be used for presentation of the isotopic budget of atmospheric CH3Cl. However, we do not consider that in this instance the approach suggested by the referee to be more rigorous or would improve the manuscript and hence we would prefer to retain what we regard as a more intuitive approach.

'There is another point which merits some further discussion. The uptake by soil due to microbial activity and the production from leaf litter are treated as entirely independent processes. However, they may very well to some extent occur simultaneously within the soil. In this case the impact on the atmosphere would be a combined effect from both processes. One example where such combined production and loss processes are very important is methane emissions from wetlands. This has important consequences. Measured emissions (rates and isotope ratios) as well as the response of the atmosphere towards changes in source strength or removal rates will be different. Furthermore, the atmospheric life time of CH3Cl will depend on the actual deposition rates, but not on soil internal turnover. This is important for understanding the variability

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of the atmospheric mixing ratios and isotope ratios of CH3Cl.'

This point raised by the referee regarding uptake by soil due to microbial action is indeed very valid and thus the final sentence in the main body of the manuscript will be modified and an extra sentence added as follows: "Further refinement of this budget will require not only accurate measurement of source strengths in the field and their respective isotopic signatures but also a recognition that source and sink processes, particularly those in the soil and the oceans, are not entirely independent. Thus isotope ratios measured for CH3Cl may be expected to reflect the combined effect of both production and loss processes."

Comment by J. Kaiser

1) It is worth noting that equation (4) assumes steady state, which is probably justified over the relatively short atmospheric lifetime of chloromethane (about 1 year).

The sentence prior to equation 4 will be modified to read as follows: "Assuming the budget is at steady state the isotopic composition of atmospheric CH3Cl reflects the weighted average isotopic signature of all the sources, and the weighted average kinetic isotope effect of all the loss mechanisms:"

2) A small correction is required to equation (4) that is common to a number of publications in the field. I think it therefore justifies this short comment. I derive the amount of the correction in the following, step by step:

The suggested correction will be applied and the appropriate recalculations made for scenarios A, B and C will be recorded in the revised manuscript. The required change does not alter the conclusions arrived at in the original manuscript.

3) There seems to be a minor typographical problem with the superscript "sink": It appears as "sin k", i.e. the sinus of k.

Typographical error will be corrected in revised manuscript.

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Comment by B. Scheeren

I would like to draw the authors attention to an earlier paper by Scheeren et al. (Measurements of reactive chlorocarbons over the Surinam tropical rain forest: indications for strong biogenic emissions, Atmos. Chem. Phys. Discuss., 3, 5469-5512, 2003) presenting clear experimental evidence from the LBA/CLAIRE 1998 campaign for strong biogenic emissions from the Amazon rainforest ('tropical vegetation') of the order of 0.5 Tg per year, complementary to the work of Y. Yokouchi.

The work of Scheeren et al. (2003) will be commented on in the script on pages 3910-11 as follows: "Furthermore the source strengths of CH3Cl used for scenario C are in general agreement with experimental observations by Scheeren et al. (2003) and a three dimensional global model study of atmospheric CH3Cl published recently by Yoshida et al. (2004). On the basis of their measurements Scheeren and co-workers suggest a total global emission of 2000 Gg yr-1 from tropical forests whilst the Yoshida group hypothesise that a missing terrestrial source of 2900 Gg yr-1 is located between 30°N and 30°S."

The Scheeren reference will be added to the reference list.

Interactive comment on Atmos. Chem. Phys. Discuss., 5, 3899, 2005.