

Interactive comment on “Global geographic variability in freshwater methane hydrogen isotope ratios and its implications for emissions source apportionment and microbial biogeochemistry” by Peter M. J. Douglas et al.

Anonymous Referee #2

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Review of “Global geographic variability in freshwater methane hydrogen isotope ratios and its implications for emissions source apportionment and microbial biogeochemistry” by Douglas et al.

The paper investigates the relation between the hydrogen isotopic composition of methane emitted from freshwaters on the global scale and the isotopic composition of water and/or modeled precipitation, as well the carbon isotopic composition of methane and carbon dioxide. The authors analyze data from a large number of previous studies and apply statistical methods in order to evaluate correlations between the various sig-

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natures. The statistics are applied in a straightforward manner. I am missing a more detailed/critical scientific analysis of differences between the results of this study and previous studies. This has two aspects: 1) The study uses more sites than previous studies for dD, and it uses modeled fields of dD in precipitation. Which of these differences is primarily responsible for the differences to the previous literature (or is it both)? 2) The study uses less sites than previous studies for d13C. Are the results from these sites still adequate to be used in a global extrapolation? The derived global average 13C source signature derived by the authors is almost certainly too light, given what we know about the fractionation in the sinks. Furthermore, I think that the errors assumed for the bottom-up determination of the global average the source signatures are too optimistic, and the discussion on the implications for the atmospheric isotope budget in section 4.6 and too simplistic. See detailed comments below.

Specific comments:

L37: I suggest citing Worden et al., 2017, where this point is shown particularly well.

L64: Maybe you want to include here, or later in the discussion section, that there are also other lines of evidence that the hydrogen isotopic composition of CH₄ (and other trace gases) depends on the isotopic composition of the precipitation, e.g., CH₄ from biomass burning across climatic zones (Umezawa et al.2011), CH₄ produced by UV irradiation of leaves that were grown with isotopically distinct waters (Vigano et al., 2010) or molecular H₂ produced in the combustion of wood from different climatic zones (Röckmann et al., 2010).

L109: Replace the factor 1000 by 1, the delta value is defined the correct way in line 105, and no factor 1000 is necessary.

L136: What are the 5 categories? This is not clear, to me it sounds like 4 categories.

L159: Is the annual average dD value of precipitation really the best estimator for a source that very likely has a strong seasonality?

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L253, Figure 1: Many of the sites are hidden behind others so I cannot see the colors. Would this improve if the figure is enlarged? It may be useful to show by color or shape for which of the sites you have measured dD-H₂O and for which not.

L244, Table 1: The d¹³C signatures for wetland have an opposite “latitudinal order” compared to what is usually assumed, i.e. they are higher at high latitudes and lower at low latitudes. The data in Table 1 for wetlands do not agree with the data presented in Figure 7. Please explain the difference. You mention that the dataset evaluated here is different from what other studies have used for d¹³C, so is your dataset now representative? Should this limited set of values be used in the upscaling later? The errors presented for the different source categories are too optimistic, especially for the fossil sources at the bottom of the table, but probably also for the wetland category.

L276, Fig 2 and related text: This is a key figure for the following analysis. In principle it is an interesting approach to use modeled dD values in case measurements are not available, but it is also a source of error. Although there is a generally good agreement, the slope is lower than 1 and this may contribute to the differences and thus may affect some of the further analysis.

L284: Maybe you could state briefly whether you can reproduce the slope of Waldron et al. when you use the same dataset. Just as a baseline.

L292: Figure 3a: It looks like the lower slope is caused by a lot of points where you have only modeled but no measured dD data near the low dD-H₂O end. And these are mostly inland waters (Figure 3b). Can you evaluate this in more detail? Can this be caused by a bias in the modeled dDp? Probably not, but it is useful to investigate further to strengthen your argument.

L308: Would you find a correlation if you took the slope of Waldron et al. for calculating CH₄,W₀?

L323, Figure 5: Does it make sense that in b) only few points are classified as oxidation

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influenced and in c) many more points? Does it make sense that in c) the very lowest dD value is in the group of the oxidation influenced points? I find the “pathway trend” concept a bit confusing, this indicates a smooth transition of dD-CH₄, W₀ with alpha_C or d¹³C_CO₂. Is this a real trend, or rather a consequence of two different groups of data (acetoclastic and hydrogenotrophic sites)? Wouldn't it be useful in this case to show these two groups with two different colors, separated by the potential break points, rather than the trend areas?

L350 and Figure 7b, wetlands: These numbers do not agree with the data in Table 1.

L374-379: I get a bit confused by the diverging statements on significance with different tests, please try to reformulate, or add a sentence to synthesize.

L395-397: See points above: Are the uncertainties for the different categories adequate? Is there an issue with the difference between values in the text and table 1? Is the rather heavy d¹³C value for high latitude wetlands appropriate?

L406: Figure 10: This figure may require a bit more explanation. What does the x axis “emission flux change” mean for the points from Rice et al.? I think I can guess it, but it could be presented more clearly.

L431 ff: The differences to the previously published values from Waldron et al. should be discussed in some more detail. E.g., is there an influence from the modeled dD values, or a certain sampling region? L439 ff: Same for the discussion of the environment type

L465, section 4.2.1: See comments above on the representativeness of the dataset analyzed here and possible consequences. You write that the dataset is not comprehensive or d¹³C, so should it be considered as representative? In this case, what have other studies potentially missed?

L483 ff: You may want to refer here to the studies I mentioned in the beginning that looked at other (non-microbial) sources.

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L503 ff: See comments on Fig. 5 regarding the samples affected by oxidation.

L519 ff: The authors state that they do not observe a correlation between dD and $d^{13}C$ of CH_4 . Nevertheless, the vast majority of the points in Fig 5a seem to fall in the range of the “pathway trend” (I find the term misleading, see comments above). Does this not mean that the two groups (acetate fermentation and CO_2 reduction) still form distinct distributions?

L549: the remark on the intercepts does not add much and is rather trivial when the slope is different.

L555 - 561: I am also not aware of dD measurements in natural acetate, but the method from Greule et al. (2008) has been used in Viganò et al. (2010) to measure dD in methoxyl groups which were compared to produced CH_4 and modeled dD in water.

L574 – 578: Why do you explain the variability for bogs by the pathway difference, and the high values in rivers by oxidation. Can oxidation not also cause large differences for bogs?

L599: Why should the oxidation signal only be apparent for dD and not for $d^{13}C$ (L603-604)?

L606: I do not understand how you can conclude that “...that the relative balance of diffusive vs. ebullition gas fluxes should not have a large effect on the isotopic composition of freshwater CH_4 emissions.”. The chance for oxidative effects is much larger for a slow process like diffusion compared to the fast process of ebullition.

L611: The analysis in this section has much less scientific rigor than the previous sections and presents some sensitivity calculations involving highly improbable assumptions, see following points.

L619 ff: See comments above on the depleted $d^{13}C$ source signature. Here you argue that three factors may explain this difference. I am quite convinced that the first one (errors in the sink fractionation factors) cannot explain the large difference. The two

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published studies for the fractionation in the CH₄ + OH reaction (Cantrell et al, 1990, Saueressig et al, 2001) are 5.4 and 3.9 per mill, respectively. A contribution from CI may increase this a bit, but not enough to support a global average source signature of -56.4 per mill. So I think that the reason should come from the other two processes mentioned. Given the discrepancy to previous studies I wonder whether it is not mainly the choice of signatures in this study. In line 625 you already show that changing one parameter leads to a change of the global average source signature of 1.3 per mill, which is almost the entire uncertainty range reported.

L628: Rather arbitrarily changing big sources by a factor of 2 is a huge adjustment of the atmospheric CH₄ budget. This investigation on the effect on the atmospheric isotopic composition is too simplistic.

L634 ff: Same comment for the bb source, this should be discussed in a more detailed way. Worden et al. (2017) illustrate the strong influence of the bb source.

L660f: The statement “This flatter slope may be the result of the inclusion of a greater proportion of inland water sites in our dataset.” requires more underlying analysis. I think that the “may be” can be replaced by “is likely”, but this should be investigated. See also other points above.

L662: If possible make more concrete after reevaluation of the impact of modeled data.

L686: Here the second argument of the three presented before (see comment on L619) has disappeared, but as argued above it may be the most important one and particularly the sink argument does likely not explain (at least exclusively) the difference.

L687: Cite Worden et al. (2017), who precisely did that.

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