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Biogeosciences Discussions

Interactive comment on "The stable isotopic signature of biologically produced molecular hydrogen (H_2)" *by* S. Walter et al.

Anonymous Referee #1

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The authors present the first systematic study on the stable isotopic compositions of biologically produced H_2. While the values have been already predicted by Bottinga (1969) in past studies to be highly D-depleted, this is the first systematic experimental evaluation on the values. They confirm the deuterium depletion of biologically produced H_2 of biogas, and from microorganisms or green algae. Better estimates on the hydrogen isotopic composition are important for calculating the global isotopic mass balance of atmospheric H_2, especially for those with highly depleted in deuterium.

I recommend accepting this paper with minor revisions. However, there are some issues that need to be addressed prior to publication in Biogeosciences.

General comments:

The way of calibration for the samples having highly D-depleted δD values (less than -535‰ has not been clear. To confirm the linearity of the IRMS system in such low δD range, they showed the relationship between reciprocal mixing ratios of H_2 and δD values for those from –535‰ to +35 ‰ in Fig.1. However, they reported more D-depleted values, ranging from –758‰ to –556‰ for H_2 from microorganisms. They should add further description to verify accurate determination on the highly depleted δD values of biologically produced H_2 by presenting the linearity of their IRMS system in all the data range presented in this manuscript (from –758‰ to +35‰.

The slope of 2.2 ‰°C for the relationship between ϵ_{H2-H2O} and temperature is larger than the theoretically predicted slope (1.4 ‰°C) in Figure 2b. Please discuss clearly whether this discrepancy is significant or not, by giving the uncertainty in the slope.

For yielding the value of ϵ_{H2-H2O} (–728‰ at 20°C, they used the biogas data obtained under the temperature ranging from 45 °C to 60 °C by extrapolation the liner relationship between ϵ_{H2-H2O} and temperature. All the obtained ϵ_{H2-H2O}, including (biogas at 38 °C and the cultures of microorganisms), however, almost corresponds to the theoretically predicted one within their errors. As a result, I guess the theoretically predicted ϵ_{H2-H2O} by Bottinga (1969) might be more preferable to obtain more accurate global average δD value for the biologically produced H_2.

Please add a new figure to facilitate comparison of the relationship between the obtained ϵ_{H2-H2O} and the theoretically predicted ϵ_{H2-H2O} for all data.

Specific comments:

p.12524 L.21 Highly D-depleted δD values on biological H_2 production in soils

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have also been pointed out recently (Komatsu et al., RCM 2011). This recent result should be referred.

p.12525 L.9 "highly depleted H_2" should be "highly depleted in deuterium of H_2"

p.12531 L.20 Is this a typo of 60°C ? or is the temperature really 65°C ? The temperature of biogas in second line in Table 2 is also typo? If the temperature is really 65°C, please give the δD_{H2} in 65°C together with its theoretically predicted ϵ_{H2-H2O} in Table 2 and Figure 2.

Table 1. Please add the uncertainties in measured δD and corrected δD.

Table 1. Please also give each temperature for pure microorganisms cultures as was described in text.

Table 2. Please add the uncertainties in δD_{H2}.

Table 2. Please add the theoretically predicted ϵ_{H2-H2O} by Bottinga (1969) in biogas (38°C) and each microorganism culture.

Figure 1. The each corrected δD value for a temperature range of 45°C to 60°C was different source signature ranged from –743‰ to –703 ‰ as was described in p.12532 L.6. To confirm the linearity of the IRMS system in the low δD range, the Keeling plot using different source signatures is not adequate. Please plot symbols for samples at a treatment temperature of 38°C.

Technical corrections:

p.12532 L.5 There is contradiction between the slope in Fig. 2b (2.3 ‰°C) and

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the slope stated here and abstract (2.2 ‰°C). Please check.

Tables 1 and 2. There is contradiction between the corrected δD at 45°C in Table 1 (–734‰ and that in Table 2 (–743‰. Please check.

Interactive comment on Biogeosciences Discuss., 8, 12521, 2011.