Interactive comment on “The stable isotopic signature of biologically produced molecular hydrogen (H₂)” 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 H₂. 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 H₂ 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 H₂, 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 H₂ 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 H₂ from microorganisms. They should add further description to verify accurate determination on the highly depleted δD values of biologically produced H₂ 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 $\epsilon_{H₂-H₂O}$ 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 $\epsilon_{H₂-H₂O}$ (-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 $\epsilon_{H₂-H₂O}$ and temperature. All the obtained $\epsilon_{H₂-H₂O}$, 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 $\epsilon_{H₂-H₂O}$ by Bottinga (1969) might be more preferable to obtain more accurate global average δD value for the biologically produced H₂.

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

Specific comments:

p.12524 L.21 Highly D-depleted δD values on biological H₂ production in soils
have also been pointed out recently (Komatsu et al., RCM 2011). This recent result should be referred.

p.12525 L.9 “highly depleted H₂” should be “highly depleted in deuterium of H₂”

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 $\delta D_{H2}$ in 65°C together with its theoretically predicted $\epsilon_{H2–H2O}$ in Table 2 and Figure 2.

Table 1. Please add the uncertainties in measured $\delta D$ and corrected $\delta D$.

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

Table 2. Please add the uncertainties in $\delta D_{H2}$.

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

Figure 1. The each corrected $\delta D$ 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 $\delta D$ 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
the slope stated here and abstract (2.2 %°C). Please check.

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

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