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Atmospheric Chemistry and Physics
Discussions

Interactive comment on "Isotopic signatures of production and uptake of H_2 by soil" *by* Q. Chen et al.

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We thank the editor and reviewers for their valuable comments. The analytical solution for the flask sampling processes uploaded by the editor as a supplement is very well written and it would be useful for sampling involving large volume sample collection from the chamber. Our evaluations have been double-checked with this analytical solution. Reviewer 1 did not request a change to the manuscript and our response to Reviewer 2 is shown below.

Technical comment: The term "mixing ratio" has been exchanged with the term "mole fraction" in the text. However, the axes of the graphs in Fig. 6 still use "mixing

ratio". This may be confusing (P.23479, L.8).

Response: We will change all the "mixing ratio" into "mole fraction" for the axes of the graphs in Fig. 6.

Specific comment: The deltaD of the emitted H2 was negative but somewhat larger than the value expected from isotopic equilibrium between H2 and water (about -700 permil). The authors argue that this may be a characteristic of the nitrogenase reaction (assuming that H2 was produced by the clover nodules at these field sites). They also discuss the possibility that deuterium was enriched when the freshly produced H2 was partially consumed in the soil. I think that this may be the most parsimonious explanation. The authors argue that a large fraction of H2 needs to be removed in the soil to explain the enrichment of D. I suggest calculating and reporting how large exactly this fraction would need to be.

Response: The estimate of the fraction of H_2 removal within the soil before entering atmosphere (f_{in}) can be very uncertain due to the lack of information about the initial δD of H_2 produced biogenically during N_2 fixation (δD_0) and the fractionation constant during uptake within the soil (α_{in}). f_{in} can be calculated as following.

Assuming initially produced H_2 by N_2 fixers will be consumed within the soil before entering atmosphere and the fractionation constant is α_{in}. Then the Rayleigh equation yields: $(c/c_0)^{\alpha_{in}-1} = (\delta D + 1)/(\delta D_0 + 1)$

where c and c_0 are the remaining and initial H_2 mole fractions, δD and δD_0 are for the remaining and initial H_2. The fraction of H_2 removed within the soil before entering atmosphere would be $f_{in} = 1 - c/c_0$. It should be noted that both δD_0 and α_{in} are unknown. δD (=δD_{soil}) is the isotopic signature of H_2 emitted from the soil, which is measured in our experiments and shown in the manuscript.

By assuming α_{in}=0.945 (overall fractionation factor as determined in our deposition experiments), δD=-530 ‰ (averaged δD_{soil} of Cabauw net-emission experiments) and δD_0=-611‰ (averaged of $\delta D(H_2)$ derived from laboratory experiments in Luo et al. (1991) and Walter et al. (2012), see Section 4.4 in manuscript), we calculate $f_{in} = 1 - c/c_0 = 0.97$. Thus, 97% of H_2 produced by N_2 fixation is removed within soil before entering atmosphere. This is higher than the estimate from Conrad and Seiler (1979), which was from 30% to 90%. By using the lower limit of α_{in} in in our experiment (0.911) and the upper limit of δD_0 in Luo et al. (1991) and Walter et al. (2012) (-569 ‰, we calculate a lower limit of f_{in} to be 0.62. The upper limit of f_{in} is 1.00 when α_{in} approaches 1.

For these calculations we have used a δD of -530 ‰ but it varies from -629 ‰ to -451 ‰ in our experiments. In addition, both δD_0 and α_{in} are unknown. We want to mention that we had such calculations in but removed them because all of the parameters (δD_0 and α_{in}) are uncertain and we do not think that we can constrain the consumed fraction in a meaningful way (other than it has to be a lot). Thus, we suggest not reporting how large exactly the fraction of H_2 removed within soil.

Changes in the manuscript: No changes in the text. We will change all “mixing ratio” into “mole fraction” for the axes of the graphs in Fig. 6.

Interactive comment on Atmos. Chem. Phys. Discuss., 15, 23457, 2015.