

[Interactive  
Comment](#)

## ***Interactive comment on “Isotopic signatures of production and uptake of H<sub>2</sub> by soil” by Q. Chen et al.***

**Q. Chen et al.**

chenqjie@uw.edu

Received and published: 28 October 2015

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

[Full Screen / Esc](#)

[Printer-friendly Version](#)

[Interactive Discussion](#)

[Discussion Paper](#)



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  $\delta D$  of the emitted  $H_2$  was negative but somewhat larger than the value expected from isotopic equilibrium between  $H_2$  and water (about -700 permil). The authors argue that this may be a characteristic of the nitrogenase reaction (assuming that  $H_2$  was produced by the clover nodules at these field sites). They also discuss the possibility that deuterium was enriched when the freshly produced  $H_2$  was partially consumed in the soil. I think that this may be the most parsimonious explanation. The authors argue that a large fraction of  $H_2$  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  $\delta D$  of  $H_2$  produced biogenically during  $N_2$  fixation ( $\delta D_0$ ) and the fractionation constant during uptake within the soil ( $\alpha_{in}$ ).  $f_{in}$  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  $\alpha_{in}$ . 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,  $\delta D$  and  $\delta D_0$  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  $\delta D_0$  and  $\alpha_{in}$  are unknown.  $\delta D$  ( $=\delta D_{soil}$ ) is the isotopic signature of  $H_2$  emitted from the soil, which is measured in our experiments and shown in the manuscript.

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper



By assuming  $\alpha_{in}=0.945$  (overall fractionation factor as determined in our deposition experiments),  $\delta D=-530\text{‰}$  (averaged  $\delta D_{soil}$  of Cabauw net-emission experiments) and  $\delta D_0=-611\text{‰}$  (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  $\alpha_{in}$  in our experiment (0.911) and the upper limit of  $\delta D_0$  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  $\alpha_{in}$  approaches 1.

For these calculations we have used a  $\delta D$  of -530 ‰ but it varies from -629 ‰ to -451 ‰ in our experiments. In addition, both  $\delta D_0$  and  $\alpha_{in}$  are unknown. We want to mention that we had such calculations in but removed them because all of the parameters ( $\delta D_0$  and  $\alpha_{in}$ ) 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.

[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)[Discussion Paper](#)