

Interactive comment on “Isotopic signatures of production and uptake of H₂ by soil” by Q. Chen et al.

Anonymous Referee #2

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Soils are the most important sink term in the budget of atmospheric H₂. Hydrogen is oxidized by soil microorganisms, but can also be produced, for example during microbial N₂ fixation, in particular by legume root nodules. The microbial consumption process exerts a kinetic isotope effect, which may serve as constraint for modeling the global H₂ budget. However, fractionation factors for H₂ uptake by soil have rarely been measured. The measurement under field conditions is complicated by the fact that net H₂ uptake is usually the result of simultaneous gross consumption and gross production of H₂. However, this complication can be overcome by analyzing H and D simultaneously. There are only two relevant reports in the literature (Rahn et al. 2002; Rice et al. 2011), which both point out that more field measurements are needed.

The present study by Chen et al. adds substantially to this data basis. The study is
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very well designed, presented and interpreted. It reports several field measurements at two sites in the Netherlands, which exhibit H₂ deposition velocities at the upper end of the range reported in the literature. These measurements include not only sites with net deposition but also sites with net emission of H₂. Nevertheless, the resulting fractionation factors for H₂ consumption were relatively similar, and they were also similar to those found in the previous two studies. Hence, the fractionation factors have now a higher level of confidence. In contrast to Rice et al. (2011), the present study found no relationship between fractionation factors and H₂ deposition velocities, probably because they covered a larger range of deposition velocities.

It is worth mentioning that the present study used a different gas sampling scheme than the study by Rice et al. (2011) and applied a range of corrections concerning the linearity of the GC-C-IRMS and the bias introduced by sampling large gas volumes. Nevertheless, isotopic signatures and resulting fractionation factors fit nicely the model of simultaneous production and consumption of H₂ by soil.

Due to the sites with net H₂ emission, it was possible to determine the isotopic signature of the H₂ produced in soil. The present study is the first one reporting field experiments.

Specific comment: The δD 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.

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).

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

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