

## ***Interactive comment on “Isotopic signatures of production and uptake of H<sub>2</sub> 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 H<sub>2</sub>. Hydrogen is oxidized by soil microorganisms, but can also be produced, for example during microbial N<sub>2</sub> 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 H<sub>2</sub> budget. However, fractionation factors for H<sub>2</sub> uptake by soil have rarely been measured. The measurement under field conditions is complicated by the fact that net H<sub>2</sub> uptake is usually the result of simultaneous gross consumption and gross production of H<sub>2</sub>. 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  
C6492

very well designed, presented and interpreted. It reports several field measurements at two sites in the Netherlands, which exhibit H<sub>2</sub> 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 H<sub>2</sub>. Nevertheless, the resulting fractionation factors for H<sub>2</sub> 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 H<sub>2</sub> 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 H<sub>2</sub> by soil.

Due to the sites with net H<sub>2</sub> emission, it was possible to determine the isotopic signature of the H<sub>2</sub> produced in soil. The present study is the first one reporting field experiments.

Specific comment: The deltaD of the emitted H<sub>2</sub> was negative but somewhat larger than the value expected from isotopic equilibrium between H<sub>2</sub> and water (about -700 permil). The authors argue that this may be a characteristic of the nitrogenase reaction (assuming that H<sub>2</sub> was produced by the clover nodules at these field sites). They also discuss the possibility that deuterium was enriched when the freshly produced H<sub>2</sub> 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<sub>2</sub> 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).

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C6494