

Response to reviewers

Rice et al., 2010

Isotopic fractionation during soil uptake of atmospheric hydrogen

Biogeosciences Discussions, 7, 8001-8018, 2010

Overall

We have carefully considered each comment made by the reviewers and respond to each individually comment in the pages below. Listed are the reviewer comments in “quotes” and our responses in *italics*. We thank reviewers for their helpful suggestion and key points. Overall, the study and manuscript have benefitted from the resulting changes. We thank editors for facilitating this review of our manuscript.

Anonymous Referee #1

“My only comment is that the authors might want to consider going a bit deeper in their discussion about the kinetic isotope effect (KIE). They state that they assume small fractionation due to microbial (I assume enzymatic) consumption. They either have to explain why they make this assumption or cite previous work where an explanation can be found.”

To address this point, we have included a more substantial discussion of variability of the KIE. Specifically to point 1, our assumption that the microbial fractionation is small is based on the preponderance of small observed KIEs in this studies and by others this work but also see Gerst and Quay, 2001; Rahn et al., 2002b). If the net KIE is a function of diffusional and oxidation fractionation, and diffusional effects are known to be large (i.e., -170‰ for molecular diffusion to -180‰ for Knudsen diffusion – see below), then microbial oxidation must be small to account for the -57‰ average KIE and the -24‰ to -109‰ range. Though we made this point in the previous version (p. 8010 line 7), we have clarified in the text in the current version.

“Regarding the dependence of KIE on soil moisture and rate of uptake, I believe it depends to some extent on interplay between effects of binary gas diffusion and Knudsen diffusion which, it turn, depend on the size of air filled passages among soil grains.”

Reviewers are correct in pointing out that H_2 diffusion in the soils will be a combination of molecular and Knudsen diffusion. Though isotopically the effects are very similar for H_2 (resulting from its low mass), we have included this explicitly in the discussion. We have also included the magnitude of both effects for clarity.

“They might want to go further and propose future experiments for testing these effects in sterilized soils where there is no microbial uptake. But as stated above, I

would leave it up to them to decide whether to include my suggested addition in the discussion.”

A helpful point. We have added mention of potential future experiments in the conclusions section of the paper.

Anonymous Referee #2

“The values of kinetic isotope effect (KIE) the author determined are not different from those of previous studies. In particular, the mean value of KIE is exactly the same as what found by Gerst and Quay (2000) in summer season. Perhaps this may indicate insignificant role of soil moisture in KIE, which is also displayed in Figure 2. The paper only confirmed the previous results of KIE.”

Reviewer #2 is correct to reiterate that, on average, we agree quite well with the two previously published values for the KIE of H_2 during soil uptake. We believe this point was clear in the manuscript. As a result, we hope this additional study will bring the community closer to consensus on the average KIE during H_2 uptake by soils. We feel that previous studies ($n=2$) hardly represent a closed-book on the subject. As a corollary, consider the comparatively large number of studies ($n>10$) of the uptake rate of H_2 (see Ehhalt and Rohrer, 2009). Additional studies continue to be published on this subject (e.g., Schmitt et al., 2009) which add to the body of work and explore controlling parameters.

With regards to the insignificance of the dependence on both uptake rate and soil moisture content we respectfully disagree with the reviewer. In studying any system it is important to characterize both its mean state and the natural variability around that mean. This is the first study to do so for the KIE during H_2 uptake by soils. We also explore potential drivers of this variability. Our particular findings are that the KIE is dependent on soil moisture and uptake rate – dependencies which are statistically significant at high levels. Of additional importance, the KIE range observed (from –24‰ to –109‰) is of considerable variation in magnitude and could impact the D/H ratio of atmospheric H_2 in certain regions.

“Another aspect to be concerned is the source of H_2 produced in soil. The authors determined asymptotic value of H_2 (H_2e) and HD (HDe), which contains isotopic signature of the H_2 produced in soil, but did not mention and not discuss them how they are related with experimental conditions. Of course, the paper focuses on destruction of H_2 in soil. However, as the asymptotic values are used in determination of deposition velocity and KIE, it would be useful for the reader to describe the asymptotic values of H_2 and HD obtained during the experiments and how they are related to soil conditions.”

The use of asymptotic fits for H_2 values in uptake studies is not a new one and has been by numerous groups using chamber studies since the 1980s (e.g., Conrad and Selier, 1985; Smith-Downey et al., 2008; Yonemura et al., 2000; Schmitt et a., 2009). We have

simply applied a natural extension of this approach for HD, which is more accurate for this system than the conventional Rayleigh model. To address the request of the reviewer we have included information about the range of H₂e and HDe values calculated from fits to experimental data in the corresponding sections 3.1 and 3.2.

However, the D/H ratio (or δD value) obtained from HDe and H₂e asymptotic values are not source signatures but are for H₂ and HD sources and sinks in balance – i.e., steady state. Though we have examined these results and there is wide variability in them (H₂ varies 0-188ppb and HD varies 0-0.03ppb), there is no clear pattern in H₂e, HDe, or the resulting δD with environmental variables as suggested. For this reason, because H₂e and HDe are not a direct measure of the source isotopic signature, and (as the reviewer noted) because this manuscript is a study of sink effects we do not chose to focus on these somewhat distracting results in the manuscript.

“1. Experimental section needs to be described in detail. Experiments were carried out only 3 days and a series of experiments were done only for 2 days. Each experiment was run for 20 minutes. However, Exp # 5 ran only for 15 minutes, and Exp #3 started right after finishing Exp #2 with different moisture content in soil. Based on the experimental section, it is difficult to follow the experimental procedure. It would be useful if the authors make a table with providing experimental condition and the concentration and isotopic values of H₂ in time series for each experiment.”

We can see how this is confusing to the reviewer given the inconsistent information in Table 1 and in the text. Indeed there is a typo in Table 1 for Experiment #6 which began at ~12:55 (rather than 12:45 in previous version). In fact experimental conditions were identical and we thank the reviewer for catching this error. To further clarify, as the time of occurrence of experiments is not highly crucial to this work, the timing of the beginning of experiments in Table 1 was rounded to the nearest 5 min increment for simplicity. Thus timing of different experiments may appear closer than they were. “Experiment time” (i.e., 0, 10, 20min) for sample collection was kept with an independent timepiece. The correction to Table 1 (Expt. #6) should help to resolve the apparent discrepancy between the experimental methods as written and the results as shown in Table 1 (particularly the timing of events).

“2. Deposition velocity was determined using Eq. (2) with 3 points of measurement. Since initial value is fixed, 2 points were applied to determine the unknown of H₂e (asymptote) and kH₂. Since this approach considers production of H₂ in soil, it is suggested to show H₂e in Table 1 together with deposition velocity for understanding the process taking place in the experiment.
3. KIE was determined by Eq. (5) which is based on Eq. (2) and (4). To help understanding the role of the source of H₂ during the experiments, it is recommended to show HDe (or δD value). This can be further used to determine the isotopic ratio of source signature.”

As discussed above in some detail, results of H_2e and HDe from iterative fits varied dramatically and do not provide a particularly meaningful measure. As a result we find its presence in Table 1 would be distracting at best from the critical results presented. For the same reason, we note that there is no substantive discussion of H_2e values in previous studies of H_2 soil uptake in the literature. For those who are interested, we have provided the range of observed values in the text of the manuscript and believe this to be sufficient for most readers.

“Although the authors argue that KIE is related to moisture content in soil, Figure 2b show scatter of data points only. It would be better to separate data into “summer” and “winter” season and to plot a regression line showing correlation. The same can be applied for Figure 4. Unfortunately it is difficult to follow the discussion on page 8009 which need to rewrite clearly.”

As suggested, we have modified Figure 2 to separate winter and summer season datasets. Hopefully this will clarify examination of these figures to readers when discussing results, not requiring reference to Table 1 in order to distinguish between summer and winter (wet and dry) seasons. We have also added temperature to Figure 2 in response to a suggestion from reviewer #3 and discussed the implications of its relationships between deposition velocity and KIE in the text. We have reworded the discussion on page 8009, which discusses the relationships between KIE and soil moisture and deposition velocity, while still maintaining our concise style used in this manuscript.

“p.8005, L.25, It would be better to cite original paper, Hagemann et al. (1970)”

We appreciate the reviewers suggestion to site original literature regarding the D/H ratio scale for hydrogen isotope measurements, the Vienna Standard Mean Ocean Water (VSMOW) scale. We have included this reference as well as maintaining a reference to the more recent and superseding 1993 IAEA review of isotope standards and reference materials (IAEA-TECDOC 825).

“p.8006, L.21, Describe how to determine the effective chamber height.”

We have added a phrase clarifying what is meant by effective chamber height, which is equal to the ratio of the volume to the surface area of the chamber.

“p.8008, L. 11 & L. 24, I think $\alpha = k_{HD}/k_{H_2}$ as described in p.8003, L.20. I wonder what is the difference in the definition of KIE and α in the text.”

We have removed the (repetition) of α here in the text. There is essentially no difference in the between KIE and α as they are both referring to the ratio of the rate constants of H_2 and HD. However, in this manuscript we have chosen to use α as the strict mathematical expression of the ratio of the rate constants ($\alpha = k_{H_2}/k_{HD}$) as in equations. We also use fractionation factor, ϵ as defined, i.e., $\epsilon = (\alpha - 1)(1000)$. The

term “KIE” is used more loosely in the text referring to either α or ϵ . This ambiguity within the text of the manuscript is consistent with the isotope literature.

“p.8009, L. 7, Eq. (3) should be replaced with (2). Thus, ..., combining Eqs. (2) and (4):”

Correct, we thank the reviewer for catching this typo.

“p.8009, L. 8, Eq. (5) has a typo on the left-hand side. H₂i should be replaced with HD_i. Thus, $\ln((\text{HD} - \text{HDe})/(\mathbf{HD}_i - \text{HDe}))$ ”

Correct, we thank the reviewer for catching this typo.

“Table 1. Please add the uncertainties in deposition velocity and KIE.”

The uncertainty in deposition velocity is provided as a footnote to Table 1. We have added the uncertainty in the KIE to the table. We have also added a brief note in the footnote describing our estimates of analytical uncertainty. We have also added error bars to figure 2 to show the magnitude of the uncertainties.

“Figure 1b. This plot may confuse the reader. It should be plotted dD vs. time since [HD] changed very small and depends much on [H₂] according to the definition of d (and this is why definition of d is used in general). In addition, this figure does not give an impression of enrichment of deuterium in H₂ during soil uptake, but rather depletion.”

In response to this request and that of reviewer #3, we have added an additional figure to Fig. 1 showing the behavior of δD which, as the reviewer points out, becomes more enriched in time.

“Figure 2. Plot with different symbols for each month (or season).”

Changed as suggested (see above).

“Figure 3. Use different symbols. The title in x- and y-axis should be consistent with Eq. (5).”

As Equation (5) has now been corrected, the x and y axes of Figure 3 are now consistent with Equation (5). However, we do not see the value of distinguishing between wet and dry months here as here we are aggregating data in a single regression to determine the average KIE. Furthermore, there is no grouping of data in this plot by wet and dry seasons.

Figure 4. Use different symbols.

Changed as suggested (see above). There is no grouping of results in this figure by summer and winter.

Referee #3: L. Meredith

“p. 8002, L. 9: The wording in this sentence is awkward: "Considerable variability in deposition velocity observed during winter was not found to be closely related to soil moisture.”

We have reworded this sentence to improve clarity here.

“p. 8002, L. 22: H₂ is not really an energy source, but could be used as an energy carrier and fuel.”

Correct, we have changed “energy” to “fuel” in this phrase to remove the ambiguity from the language.

“p. 8003, L. 11: "Furthermore, there is not consensus" should be "no consensus" or "not a consensus”.”

Correct, typo changed as suggested

“p. 8003, L. 23: The final sentence of this paragraph would be better if broken into two.”

We have split the sentence into two as suggested to improve readability.

“p. 8004, L. 14: Why were sites cleared of duff before experimentation? This has been shown to affect the measured strength of H₂ uptake by Smith-Downey (2008).”

The soil surface was removed of duff (primarily leaf litter) prior to experiments for consistency between experiments which varied in space and time. Despite this late publication date, field experiments were actually carried out prior to the release of the Smith-Downey et al. (2008) study which reported the influence of leaf litter on uptake rate. Based on that work, it appears that leaf litter does not consume or release H₂ but may act as a barrier to diffusion. Thus, for actual relevance to atmospheric H₂ uptake future experiments may wish to leave the soil surface unperturbed.

“p. 8006, L. 13: "Though in all experiments consumption outweighed production, evidence for a subsurface H₂ source is demonstrated by the decay of H₂ to non-zero asymptote (Fig. 1a) and previously measured below ground non-zero H₂ concentrations (Conrad and Seiler, 1985; Smith-Downey et al., 2008; Yonemura et al., 2000). " This is interesting. It would be useful to know what was the longest duration the chamber studies were run and what precautions were taken to avoid pressure

effects within the chamber. If overlying air is depleted in H₂ relative to soil pore-space H₂ concentrations, the observed change in H₂ concentrations may just be diffusion-driven out-gassing from the pores instead of active production. Whether concentrations remained stable over a longer duration might be informative here. “

In these experiments, samples were drawn from the chamber at intervals of 0, 10, and 20 minutes as indicated. Additional chamber experiments (mostly in other locations) have been conducted at durations up to 1 hour. In these unpublished data, similar behavior was observed where H₂ concentrations in the chamber approached a non-zero asymptote. As noted, this behavior is well documented in the literature. For experiments at this site, instantaneous pressure changes in the chamber from sample collection were minimal (<2mbar) and are smaller than the typical diurnal behavior in atmospheric pressure.

“p. 8007, L. 17 and p. 8009, L. 16: You write there is no significant correlation between the deposition velocity and soil temperature, but there appears to be some negative correlation between temperature and deposition velocity in the summer. Perhaps you could include a p-value to show the case quantitatively. This comment also applies to KIE vs soil temperature.”

Correct. We thank the reviewer for bringing up this point. To address this point, we have expanded upon our discussion of possible temperature effects on deposition velocity and KIE in the results and discussion section (3.1 and 3.2). We include both a discussion of correlations that exist in the data and an argument as to why it is not temperature – but rather soil moisture – that most likely drives these correlations. We have also included a plot of deposition velocity and KIE versus temperature to facilitate this discussion (Fig 2).

“p. 8010, L. 18: You found a striking variability in the wintertime H₂ uptake and KIE that is not related to soil moisture content as you measured it. In this line, you might add that only “some of this variability may be associated with summertime soil moisture content” then. It would be useful to add why you think your winter time measurements of deposition was so variable and had a larger range than what you measured during the summer.”

As suggested, we have modified this statement to more exactly represent the dependency of KIE on soil moisture in this work – i.e., the smaller KIE at intermediate soil moisture contents (10-30%). Without additional information, it would be difficult to speculate on the mechanisms behind the substantial variability observed here. However, in this revised versions we outline several additional experiments which would be useful to better characterize variability in deposition velocity and KIE.

“p. 8015, Fig 1: It might be more interesting to plot the delta value instead of HD versus time in Figure 1-b, or to include a third plot. The concentration of HD is just changing with the same scaling as the bulk H₂ mixing ratio, so that HD tells us little information.”

We initially plotted H_2 and HD versus time as they accurately reflect the behavior of the two independent tracers in the chamber with time. This relationship is what we use to model the KIE as described, rather than the differential δD representation of the D/H ratio. However, to address this request and that by reviewer #2 we have included a third plot of the δD of H_2 versus time (Fig. 2b). We can see that this adds value to the discussion and it is a clear representation of the clear enrichment in deuterium in the chamber with time.

“p. 8016, Fig 2: It would be better to include more information on these plots by using different symbols for summer vs. winter. I would also consider using a color scale to illustrate temperature of each data point - i.e., red for warmer to blue for cooler temperatures or by using different sized markers for different temperatures. It would be interesting to see whether more patterns emerge. You don't plot vd versus T anywhere.”

As suggested, we have modified Figure 2 to separate winter and summer season datasets. Hopefully this will clarify examination of these figures to readers when discussing results, not requiring reference to Table 1 in order to distinguish between winter and summer seasons. To add to the discussion on temperature effects (see above) we have also included a new sub-figures showing the relationship between T and deposition velocity and KIE (Fig 2).