

Interactive comment on “Combination of soil water extraction methods quantifies isotopic mixing of waters held at separate tensions in soil” by William H. Bowers et al.

Anonymous Referee #1

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The manuscript presents the results of an experiment designed to estimate the rate of isotopic mixing in a soil between two waters that differ in their H and O isotope ratios added to soils sequentially following oven-drying. They do show what appears to be a time-dependent process and argue that the time to equilibration is on the order of days (>4 for this soil). I think the manuscript is a contribution to the ongoing and needed effort to better understand the underlying processes that control soil water isotope ratio variation. However, I have what I think are important concerns with the current version.

A key, underlying assumption (that the authors acknowledge) is the absence of fractionation effects associated with water addition after oven-drying or with the extraction

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process. While this may be a valid assumption, there is evidence in their results that it's false, particularly for d18O. The authors assess the potential for enrichment as a function of evaporation by mass balance (comparing mass loss with effluent captures) but this does not account for any fractionation effects associated with clay mineral interactions and is itself subject to errors. It is notable that the quantities used in the mass balance calculations were not the isotope ratios of the added waters, but the value of the isotope ratio of the water extracted by CVD immediately after adding the second water. The authors refer to a "slight" offset, but looking at the data in figure 3, there is apparently as much as a 2‰ difference between the "light" water added and the measured CVD-extracted water. This is not a small difference in my view.

I am also curious about the method used to add water. The sequence was: oven dry 350g of soil, add 20 ml of "light" water and mix, subsample into centrifuge inserts and immerse in "heavy" water (presumably completely?). These soils were then presumably saturated. Were they allowed to drain at all before centrifugation, etc.? What is the field capacity of this soil and how does it compare to the amount of water added in the first step? I think it would be useful to know if freely-draining water was part of the pool extracted in the first step.

I think the authors need to more clearly explain their rationale in using the "time-dependent isotope mixing equations." While I see that an exponential fit to the observed data makes sense (at least for d2H) and that there is a tendency for them to converge, I am not sure the logic holds and I think the fitting approach used might obscure the lack of convergence between the CVD data and the centrifuge data (the CVD data plot well below the fitted line in Fig. 4 for d2H on day 7). The idea is that the low → mid → CVD represent a gradient from more to less of the recently added "light" water and capture the mixing process as it proceeds. I don't think this approach captures processes that might involve water interacting with clay and I am not convinced that the mixing is "complete" after 4 days based on the results presented in Fig. 4. The authors also acknowledge but do not attempt to explain the very different patterns observed for

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d18O. I think there's more to these patterns than it taking longer for H218O and H216O isotopologues to mix than those of H. If this were a simple mixing process, shouldn't both H & O behave similarly in terms of trajectory? I think more careful thought needs to go into interpreting these results. I also think the authors should report the clay mineralogy since multiple authors have suggested potential impacts of clay type on extracted water isotope ratios.

I was surprised to see the "wilting point" value of -1.5 MPa used. I know the authors are aware that this value is quite high (less negative) compared to values many plants adapted to low-water environments can achieve and experience no damage.

I think the authors should clarify what they mean by "precision" and "accuracy" in the isotope analysis section. Presumably the "accuracy" is some measure of how different the measured/corrected values of an internal reference material were relative to a consensus value, but I think this should be explicitly stated. Similarly, the "precision" is presumably some estimate of variance of the reference material (1 standard deviation of how many replicates?), but again this should be stated.

In line 169 the authors refer to "atomic fraction" when I think they mean "isotope ratio" (e.g., 18O/16O).

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