

***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.**

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Dear Dr. Josie Geris,

Please find our author comments for the manuscript Combination of soil water extraction methods quantifies isotopic mixing of water held at separate tensions in soil. The comments from both anonymous referees were very insightful and have helped highlight how to improve the manuscript.

Following the guidelines, we have responded to each referee comment and when nec-

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essary we have indicated our planned changes to the manuscript. Given the reviewers comments, we intend to: • Add more information related to the two water worlds (TWW) hypothesis to the introduction, as well as provide additional insights, relevant to our research, in the discussion; • Provide a more complete discussion of the soil physical processes important in our analysis – again adding needed information in the introduction and discussion sections; • Highlight in the discussion additional issues related to fractionation that are still not completely resolved (e.g., missing processes not included in our time-dependent self-diffusion model) We hope the planned changes will help future readers understand how this method relates to helping the community address the TWW hypothesis as well as the limitations and future directions that should be considered by the community.

Sincerely,

William Bowers, Jason Mercer, Mark Pleasants, and David Williams •

Thank you for your positive comments on our manuscript and we hope that we will have a chance to revise the manuscript as we think we can address all the comments raised by both Referee #1 and Referee #2.

Author's responses to anonymous referee #1:

(1) 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.

Response: We appreciate your insight and acknowledge the potential fractionations that may be expressed as water interacts with clay particles. However, based on observations reported in the literature such effects would likely cause fractionations to occur in a different direction than the slight offset we report here (Gaj et al., 2017). The offset between "light" water applied soil and water extracted from soil with "light" water (BSElight) was in the direction that is typical of fractionation due to evaporation (Allison et al., 1983). This evaporation is likely due to the small amount of water applied to exposed soil samples in the dry atmosphere of our laboratory environment in Laramie, WY. Our soil had roughly 9% clay, and water extracted from clay-rich soils are generally observed to be depleted in heavy isotopes (Gaj et al., 2017), not enriched as we observed. Thus, we feel the offset observed at this stage of our experimental water additions was more likely due to slight evaporation, and we therefore feel justified to exclude this effect from the mass balance determinations. Since the water had changed likely due to evaporation after application, we felt it was more realistic to use BSElight water as input in two-part mass balance determinations. More details on observed offset in d18O for samples with longer equilibration periods is addressed in response to referee #1 general comment 3.

Planned changes: A statement will be added in the methods section 2.5 after acknowl-

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edging the slight offset that states “This slight offset could be explained by evaporative fractionation of both hydrogen and oxygen isotopes that likely occurred when applying the “light” water to the recently oven dried soil and is inconsistent with expected isotope effects due to interactions with clay minerals (Gaj et al., 2017), or carbonates (Meißner et al., 2014) within the study soil.” Further explanation of the fractionation effects considered in this study will be included in a new paragraph of the discussion which will go over this slight offset between “light” water and BSElight extracted water as well as the offsets in d18O data that were observed for samples with longer equilibration periods (discussed more in response to referee #1 general comment 3).

(2) 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.

Response: Thanks for raising your concerns and we agree that more details on the procedure will benefit readers and future application of the procedure. In short, the pool extracted in the first step does contain some freely-draining water, or water above field capacity. Centrifuge inserts were not immersed completely; they were placed in an open container and “heavy” water was poured into the container to a level just below the top of the soil level in the centrifuge inserts. Once the top soil layer of each insert was visibly fully wetted, the inserts were removed from the container. This process allowed the inserts to be filled from the bottom up via the drilled holes on bottom of inserts to reduce the amount of air that could be caught in soil pores. Inserts were not allowed to fully drain before centrifuge steps. According to figure 2, field capacity would drain more than 50% of the effective saturation for a sandy loam soil and with this in mind the light water added would be much less than the field capacity of the soil.

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Inserts were weighed carefully on the scale and placed either into the centrifuge quickly or into the airtight container for storage until being put through the centrifuge at a later time point. There was inherently a small amount of drainage from the holes at bottom of inserts that occurred when removing inserts from container with “heavy” water during the weighing process and during storage. The difference in weight of this drained water was not considered in total weight of samples. We also see a need to clarify that water samples were near saturation and not at saturation as it would likely take longer for soils to reach complete saturation and due to minor drainage from inserts after fully wetting soil. Minor drainage happened when removing inserts from container with “heavy” water due to cohesive forces between water molecules and uncovered holes at bottom of inserts. Minor drainage also happened on the scale during weighing before centrifugation or during storage and was very minimal for both. All minor drainages combined are estimated to be roughly 3-5% of total water weight and would not have a significant impact on our results. Also, the weight of water drained onto scale was not considered in the weight of insert recorded before centrifugation for all mass balance calculations.

Planned changes: More details on the wetting process with “heavy” water will be included in the methods section 2.2 as well as how the minor drainage during removal from container used to fully wet samples with “heavy” water, minor drainage during weighing before centrifugation, and minor drainage during storage were not considered in total weight. We will include how the weight of water drained onto scale was not considered in the weight of insert recorded before centrifugation for all mass balance calculations. Due to these minor drainages we will change the verbiage used throughout the manuscript to say that samples were fully wetted and near saturation rather than at saturation before extraction via centrifugation or sample storage for equilibration time. To maintain consistency within manuscript, caption of Fig. 2 will include that for our study the samples were near 100% effective saturation but not at 100%. We will explicitly state that the low tension fraction includes freely draining water and tie this together with definitions used for mobile and matrix water. These details will

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also be addressed in the discussion since the gravitational downward movement of some water may have influenced mixing as well and will help improve the method moving forward. In addition, we will encourage future studies to place saturated inserts into sleeves immediately after fully wetting to capture more of the freely draining water, but highlight that this was not possible for our study design because we would have needed 8 sleeves and only had 4 sleeves. To capture all freely draining water or truly get saturated conditions before extraction, holes at bottom of inserts would need to be covered before removing from container with “heavy” water or a different method for wetting samples would need to be developed.

(3) 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 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.

Response: We appreciate these concerns. To be clear, the idea is that the low → mid → CVD represents a gradient from less to more of the first added "light" water

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and captures the mixing process as it proceeds. Time dependent isotope mixing equations were used because there was a clear change in isotope signature of low-, mid- and high-tension effluents over time and we wanted to see if the process could be explained simply for this proof of concept study. The fitting approach takes into account that the initial conditions were inherently different for each time the experiment was done and because of this there are uncertainty bands around each modeled line (refer back to equation 4 with the heteroskedastic error term). We agree the simple model suggests that other processes need to be accounted for in the equilibration/mixing process and we need to incorporate more nuances in the discussion of our manuscript. As mentioned in the discussion (line 264), we cannot explain the offset in d18O data with previous observations of isotope effects due to interactions with clay minerals (Gaj et al., 2017) or carbonates (Meißner et al., 2014) as those have been observed to deplete extracted waters in d18O. However, after further exploration of isotope fractionation effects from interactions with ions, the shift in our d18O could be due to interactions with K<sup>+</sup> or similar cations with lower ionic potential. But, the shift is greater than previous observations by Oerter et al., 2014, which did not exceed 1 per mil enrichment like that of our data.

Planned changes: We will modify the current statements in the discussion (currently around line 264) to not include that isotope effects are not explained by interactions with ions. This will be done by expanding the discussion to have a separate paragraph that covers the nuances of the isotope effects observed and possible explanations. We will explain that they do shift in similar direction to previous observations related of interactions with K<sup>+</sup> (Oerter et al., 2014), but are of greater magnitude than the enrichment previously observed. This greater magnitude could be due to longer equilibration time before extraction and possibly due to ions being dissolved into solution over time within the soil. We will urge the community to consider the time of equilibration used when assessing isotope effects due to interactions with minerals and chemical constituents in soil. We will also provide a suggestion for future studies to consider using more inert soil or soil with a high concentration of K<sup>+</sup> for future applications of the method that aim

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to evaluate this in more detail. The offset is present in all tension ranges of extractions (low, mid, and high), but is more evident in the high-tension fraction, so it is not solely due to CVD extractions. In addition, this extra paragraph will discuss how the simple time-dependent mixing model suggests that other processes need to be accounted for within future models. One suggestion would be to incorporate the mass ratio with  $\partial(t)$  and  $\partial\theta$  as the amount of isotopologues in each tension range effluent (low, mid, and high) may drive the rate of diffusion. Another suggestion would be to incorporate terms from the equation for diffusion of solutes in soil (covered in more detail in response to referee #2 specific comment L277). To help frame this discussion, we hope to also include a new figure of a conceptual box model for each of the tension ranges and how we interpret the extracted fractions (each as a box) interacting over time and the amount of mixing that occurs between each fraction (box) in relation to equation for rate of diffusion of solutes in soil and soil physical properties, like pore size. However, we will also go over the nuances of how this is commonly depicted in a simplified manner, especially in the case of two water worlds hypothesis, as separate fractions when it really should be considered a continuum (Sprenger et al., 2018).

(4) 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.

Response: We agree that this pressure is not the wilting point for all plants under all soil conditions. We did state in the methods that wilting point and field capacity vary from soil-to-soil and plant-to-plant (line 125).

Planned changes: We will clarify that this is considered the standardized reference value of wilting point used mostly in the agronomic literature and not technically the wilting point for all plants. In addition, as a response to specific comment by referee #2 of line 138 as well as their first general comment, we will add definitions for 'matrix' and 'mobile' water. These definitions from the recent literature of Brantley et al., 2017 use the agronomic wilting point of -1.5 MPa as a reference point.

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(5) 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.

Response: We appreciate this comment and agree that we were not clear about how we expressed accuracy and precision of the isotope ratio measurements. Indeed, accuracy is a measure of how much the mean measured/corrected values of d2H and d18O of the reference water deviate from the known calibrated values of that reference water, while precision is the standard deviation for all measured values of the lab reference water acquired while analyzing the unknown samples.

Planned changes: We will provide additional clarification as "We report the accuracy as the absolute difference between the mean of analyzed lab reference water samples (n=15) and the calibrated value of lab reference water. We reported precision as the standard deviation of all lab reference water samples analyzed (n=15)."

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

Response: Thank you for this comment as this was an error that needed to be addressed since this should be fractional abundance. We used the reference Hayes 2004, which highlights this with equations 5 and 5a on fractional abundance as well as how fractional abundance was and can be used for mass balance equations similar to equation 7 in Hayes 2004.

Planned changes: To help reduce potential confusion, we will change this to isotope ratio because we get the same results when performing two-part mass balance mixing model with isotope ratio as with fractional abundance.

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