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Discussions

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 necessary we have indicated our planned changes to the manuscript. Given the reviewers comments, we intend to: âĂć 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; âĂć Provide a more complete discussion of the soil physical processes important in our analysis – again adding needed information in the introduction and discussion sections; âĂć 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 #2:

This paper presents some progress on the centrifuge technique to separate soil water held at different bindings strengths into the potential stable isotopic pools that may exist in soils. I think this study has some good contributions to offer, but I also think it needs some improvement before I can endorse its publication in HESS.

General comments:

(1) I found the analysis and discussion of the results to be quite “thin”. By that, I mean that there is not an especially in depth or nuanced explanation and discussion of many components throughout. Specific examples follow, but in general, I suggest that the senior authors of the manuscript return to it with a more discriminating eye and identify

where it can be “deepened”.

The authors base the rational for conducting the study on making progress on identifying the potential soil water reservoirs (isotopic or otherwise) that underpin the Ecohydrologic separation, or “Two Water Worlds” (TWW) hypothesis. However, there is only the most minor discussion of this concept in the introduction, and then the authors return to it throughout the results and discussion citing how their findings apply to TWW. This is problematic because the reader doesn’t have any firm understating of TWW or how the authors are interpreting TWW (because interps vary). I suggest there be a fuller discussion of TWW and how this study specifically contributes to investigating it in the introduction. Because HESS has an open review process, subsequent reviewers have the advantage of seeing previous reviewer’s comments. That is the case here, and while I do not intend to “pile on” the authors, I do support Reviewer #1’s comments, especially in regards to the mixing analysis (see my specific comments below).

Response: We very much appreciate this comment as we think that it is important to clearly define the benefits this method may have for studies exploring the mechanisms causing ecohydrologic separation, beyond simply reporting its existence.

Planned changes: The introduction will be revised to include more background on the role of soil physics when discussing mechanisms influencing soil water transport that would generate observed patterns consistent with the Two Water Worlds hypothesis and the interpretation that we are trying to address. To clarify, we interpret the Two Water Worlds hypothesis similar to that in lines 33-36 where we refer to the original introduction of the hypothesis by Brooks et al., 2010 and include updated verbiage by Brantley et al., 2017 that plants are accessing matrix water that is incompletely mixed with isotopically distinct mobile soil water. This interpretation will be highlighted more as we will include more detailed definitions of matrix water and mobile water in reference to the ranges of soil matric potentials at which these “pools” are defined by the literature we cited (please see response to referee #2 specific comment L138 for more on these definitions). In addition, we will explicitly state that the observations mentioned

in lines 33-36 support the Two Water Worlds hypothesis. We will also provide context to Two Water Worlds/ecohydrologic separation studies which have relied on methods discussed in introduction (particularly near lines 57-58). In addition, there will be a new paragraph in the discussion that highlights what our findings mean for interpreting the TWW hypothesis. Please also see response to referee #1 general comment 3, where we mention a new conceptual model diagram that will be referenced when discussing the mechanisms of water mixing between different sized pores and tension fractions in relation to our study and two water worlds hypothesis.

Specific Comments:

L44: Need a brief explanation of what in situ equilibration is and some references of papers using either of these methods.

Response: Thanks for your suggestion and we agree that adding a reference and more details here will help the reader of this article.

Planned changes: We will refer to (Oerter and Bowen, 2017) in a statement highlighting how in situ direct equilibration utilizes field-based water vapor laser spectroscopy with the assumption that most mobile soil water is in isotopic equilibrium with soil water vapor.

L100: These waters aren’t all that different in isotope compositions. Nota Bene: Kona Deep drinking water is about 0 ‰ in _18O and _2H and is available on Amazon.

Response: We appreciate this comment and agree that a greater isotopic difference between waters could be a fascinating avenue for future studies exploring the processes of water mixing/self-diffusion in soil. For the purposes of this study the differences between “heavy” and “light” waters provided us with initial conditions at “0 hours” where the effluents from each tension range (low, mid, and high) did not overlap. In addition, these differences were closer to what might be expected in natural field settings in environments that receive seasonal precipitation as snow in winter and rain in summer.

Planned changes: We will add a short statement, when introducing the waters used in the experiment within methods section, that these waters where chosen due to the differences and relative isotopic values being similar to isotopic values and differences for precipitation input expected in temperate environments that receive snow in winter and rain in summer. Within the discussion, we will suggest future studies to consider greater isotopic difference in applied waters as the difference in proportion of isotopologues may dictate the rate of self-diffusion. In addition, our planned addition to discussion about time-dependent mixing model (covered in more detail in response to referee #1 general comment 3) will include how our model does not include mass differences between fractions of extracted waters and the degree to which they interact and equilibrate over time.

L107: The abstract claims that the light water was enough volume to fill only the smallest pores. The procedure described here seems very arbitrary. How do you have any confidence or measure of what soil pores where filled and to what extent?

Response: We appreciate your comment and agree that this detail is more of an assumption.

Planned changes: We will change the verbiage used in abstract to highlight that the "light" water was held under high matric potential by the soil before fully wetted with "heavy" water. We will also add clarification when introducing the experimental design in the methods section 2.1 by explaining that the "light" water applied first to the soil is held under high matric potential being the only water within the soil after removing nearly all other water via oven drying the soil (Adams et al., 2019). We will further explain that we cannot confirm the location of the "light" water within the soil, but that it is likely residing as a thin layer around soil particles and/or within the smallest pores of the perturbed soil due to the adhesion properties of soil particles and the high capillary tension enacted by the smallest pores within the soil. This will work off of the planned

additions to the introduction for the role of soil physics in relation to our study (covered in more detail in response to referee #2 general comment 1).

L118: Are you sure this was the extraction temp? Did you use boiling water? Laramie is pretty high elevation and thus water has a low boiling point.

Response: We appreciate your concerns as the elevation of Laramie would play a factor if we were using boiling water baths for extraction. However, the extraction system at the UW Stable Isotope Facility uses electric heating coils and direct temperature measurements of each extraction vessel using thermistors, thus we are certain of these reported temperatures.

Planned changes: We will add clarification in the methods section about how temperature is controlled and measured using our extraction apparatus.

L122: 95% is still not ALL of the water.

Response: We appreciate your comment and agree that 95% is not all of the water. We were following the guidelines and observations presented in West et al., 2006 where the isotopic signature did not change more than the limitations of instrument accuracy in measuring the stable isotope ratios of water extracted between 95% vs 100%. The majority of our samples had 100% extraction efficiency and the lowest percentage extracted was actually 99%.

Planned changes: We will change this statement to "greater than 99%". In addition, we plan to have additional statement on limitations of CVD and its relation to our study that is covered in more detail in response to referee #2 specific comment L140.

L127: You use the Two Water Worlds terminology here, but you haven't ever really discussed it in any detail in the introduction. I suggest you do so, to help contextualize the rest of the paper.

Response: We appreciate this comment and agree. Please note our response to this concern from referee #2 for planned changes in the introduction, methods, and discussion (see responses to referee #2's first general comment and specific comment L138).

L136: Three and four hours seems like a long time! On what basis did you choose these times?

Response: We agree these times are long and can be shortened as mentioned in the discussion. These times were used from a preliminary study that determined the time necessary to reach equilibrium for the centrifuge speeds (RPMs) used at which no more water eluted at the given speed. As mentioned in the discussion (line 290-291), these times could be shortened via the support of literature that was found after the preliminary study and lab procedure had taken place.

L138: You never really discuss what is tightly or highly bound, or what the potential mechanisms for this soil water are. There are many aspects to this, from soil pore size, to soil mineralogy, etc. This is a main concept of your paper, but you never give readers any background or basis of understanding how you are using this terminology and "boundness" concepts.

Response: We appreciate this comment and agree that more details should be included on what the tightly bound or matrix water is within the soil.

Planned Changes: With the planned revisions to the introduction for Two Water Worlds and definitions of mobile and matrix water, we will include details on how soil holds onto water at different tensions depending on volumetric wetness and the relation of pore size (likely around line 47 where soil water retention curves are mentioned). Mobile and matrix water will be defined similarly as done by Brantley et al., 2017 where mobile water freely drains or flows under the force of gravity and matrix water is involves hygroscopic and capillary water that does not freely drain or flow under the force of gravity due to the tension enacted by pores and adhesive forces between water molecules and soil particles. We agree "tightly bound fraction of soil water" is not best terminology for this line (line 138) and we will adjust to "a fraction of water held under high tension that

is comprised of capillary and hydroscopic soil water that is rarely directly compared to more mobile waters." Hygroscopic and capillary waters will be defined similar to Brantley et al., 2017 definitions that reference agronomic wilting point as -1.5 MPa: - hydroscopic water is soil water held at high tensions, greater than agronomically defined wilting point, within soil and resides primarily as thin films around soil particles due to strong adhesive forces between water molecules and soil particles - capillary water is soil water held within pore spaces and does not flow freely under the force of gravity and can be held at tensions greater than agronomic wilting point depending on the size of the pore. At high tensions it forms bridges between hygroscopic water films on adjacent soil particles With planned additions covered in response to referee #1 general comment 3, we will explain how these waters are part of a continuum and not discrete fractions of soil water (Sprenger et al., 2018).

L140: Again, are you sure it was ALL of the water left. Or was it 95%? I dont mean to be tedious here, and there are limits to CVD, but that is prwcisely my point. Even CVD at 100 C wont get all the water out that is in interlayers spaces in clays, etc. Are more nuanced discussion is needed (maybe it comes later in the discussion), and at least some acknowledgement of the study's potential limitations is needed. I will look for that as I read. . .

Response: We really appreciate this comment as we think including more details will help tie our work to other recent work on this topic. Planned changes: We will include a statement acknowledging that CVD at 100°C and oven drying soil at 104°C both do not respectively retrieve or remove all of the water from soil as shown by Adams et al., 2019. We will highlight that for the purposes of this study the amount of hydroscopic water that is not retrievable is such a small amount and is likely similar in isotopic composition of the local tap water used for "light" water. Thus, it would have very minimal influence on our results.

L142: I think you should move up the details about the centrifuge and inserts. It hard to envision what you did until you tell us about the inserts.

Response: Thanks for the comment. We agree that some description of the inserts would help at this point.

Planned changes: We will move line 142-149 into the methods section 2.2 after describing the soil and waters used (line 104).

L149: Good that you accounted for evap during the procedure. I assume it was done at room temp, but I could easily see temp being higher inside the centrifuge, especially for 3 to 4 hours. Did you measure this?

Response: We appreciate this comment and see the need for additional details here for readers.

Planned changes: We will include a statement describing that centrifugation was performed with the cooling function on for the Sorvall RC 5B Plus centrifuge and that the internal temperature for the 3-4 hours never exceeded 25°C.

L167: What is atomic fraction? Do you mean isotope ratios (not in delta format)? Or do you mean mixing fraction?

Response: Thank you for this comment as this term was also a concern of referee #1. Please see our detailed response and planned changes to referee #1 general comment 6.

L178: Is this 1% the total mass (water + soil) or just water? If it was total mass, then a decent amount of water lost to evap (and a big shift in isotope ratios) could be contained in the 1% number. I suggest a sensitivity analysis be done to quantify (in isotope terms) what the effects of this much water loss would actually be. It may seem tedious and unnecessary, but with this much handllng of the wet soil, I could easily see evaporation being a bigger factor in isotope results than a casual view would expect.

Response: We appreciate your comment and agree that some clarification is needed. Line 178 refers to 1% mass uncertainty of water, not water + soil. This is why we discounted the impacts of evaporative fractionation on our results.

Planned changes: We will clarify the statement to be 1% mass uncertainty of water.

L217: You state that the BSE waters were not significantly different from the applied waters, but in Figure 3 upper left panel they sure look different to me. It seems that you were not getting back what you put in. This seems problematic.

Response: Thanks for the comment and this is a valid concern. We tried to highlight that this difference is not considered significant, but BSElight water was used for mass balance mixing model due to the shift in values that is in the direction that is typical of fractionation due to evaporation (Allison et al., 1983). This evaporation is likely due to water being applied the low relative humidity of local atmosphere in Laramie, WY since the application by hand of "light" water exposed a lot of surface area of soil to dry atmosphere.

Planned changes: We will add statement in the results that the BSElight isotopic values indicate that likely some evaporative fractionation took place during the application of "light" water recently oven dried soil that had high amount of surface area exposed to dry local atmosphere. Although this changed the isotopic value of water in soil before application of heavy water, the light waters applied and BSElight extracted waters were not significantly different when considered groups ($p > 0.05$). We will also plan to add ellipses around data points for each group to highlight the multivariate normal distribution of these values at the 95% confidence interval to emphasize that there is overlap between the various waters being investigated.

L218 / Figure 3: Suggest adding A -F labels to the panels in Figure 3. Also, the x-axis labels and ticks seem inadequate.

Response: We appreciate this comment and agree that panel labels and more x-axis labels will help display data.

Planned changes: We will add A-F labels and a description in the figure caption for Figure 3. We will add more ticks on the x-axis labels for d18O for Figure 3.

L222: I suggest keeping the applied water points in all panels in Figure 3 for easier comparison. Perhaps make them dashed outline or ghosted or something to show them but not distract form the time series data.

Response: Thank you for the suggestion as adding the applied waters to all panes would help show how the isotopic signatures of each low-, mid- and high-tension effluents change over time in relation to applied waters.

Planned changes: Points for light and heavy applied waters as well as BSE waters will be added and included in all panels of Figure 3.

L227: So basically, after enough time, all the waters extracted by any means all converged upon the Heavy water signature. And the heavy water signature is the one that you soaked the sample in, but only put a little of the light water in the same samples?

Response: Thanks for bringing up this point. Yes, we inundated the sample in heavy water and applied a relatively small amount of the light water to each sample. Due to the much larger proportion of heavy water applied compared to light water, the data do appear to converge mostly towards the heavy water. So no, they did not converge on heavy water isotope signature in any way inconsistent with mass balance mixing.

Planned changes: We believe by applying the changes mentioned above (in responses and changes to specific comments of referee #2 L217, L218, and L222) that we will help clarify these details. In addition, we will describe in the results that over time the isotopic signatures converged upon the mixture of the two applied waters that has similar isotopic composition of extracted BSElight+heavy and is affected by the large proportion of heavy water applied compared to light water applied, consistent with expectations of mass balance mixing. In the discussion, we will highlight that changing the amount of water applied first and second should be explored in future studies to further understand the degree that antecedent moisture conditions and isotopic ratios created by application of the first water affect the mixing of second applied water and the power of statistical tests.

L231: So, the conclusion is that the samples were all well mixed? OR something else? Because the dont look well mixed to me, especially not until dy 3 or later. Am I missing the point? If so, please explain better.

Response: We appreciate your concerns and hope that by addressing your comment in the previous points (specific comments L217, L218, L222, L227) we can clarify the work. However, we will include some changes to make this section of the results more explicit.

Planned changes: We will add a statement to this part of the results section to explicitly state that these values suggest all water was accounted for in extraction processes and that minimal, if any, fractionation occurred due to evaporation.

L243: How do you evaluate the mixing results if you dont actually known how much of each type of water you put into the soil? Seems to me that with so much more heavy water than light, you are not really evaluating mixing, but more like the time to equilibrium, wherein the heavy water signal just overwhelmed the light because there was so much more of it.

Response: We appreciate your concerns. We agree in the notion that the samples are moving towards equilibrium (as mentioned in line 240 when starting to discuss mixing results), but inherently this would require mixing of two separate water “bodies” until a state of equilibrium is reached. Therefore, both of these terms relate to the process and our discussion should be clear on our use of the terms. Yes, we estimated volume of light water applied using gravimetric water contents, but we did know how much heavy water was applied due to a direct change in mass measurement.

Planned changes: We plan to add to our results that even though all measurements of water additions were not made directly to get a perfect mass balance, the isotope results make sense in that final isotopic value is a weighted mixture of the light and heavy waters. Due to the much larger proportion of heavy water used compared the small amount of light water used, the isotope values are similar to the heavy water, but are slightly lighter because of the small amount of light water added.

L248: This section reads more like a conclusions paragraph than the start of a discussion. You haven't really supported any of these statements, yet.

Response: Thanks for the comment. We intended here to lay out the structure and direction for the discussion section by highlighting what we feel are the most important take-home points.

L252: What are the proposed mechanisms of mixing? This is hard to determine, because you haven't ever discussed where in soil water is actually held. Is the "mixing" done via diffusion? if so, water self- diffusion in soils is fairly well studied and you could greatly increase the impact of your findings by bringing in some discussion of that work. This seems like an over simplistic analysis of your results, which are a bit fast and loose as it is. No offense intended, just that I am seeking more detail and justification in your measurements and results.

Response: Thanks for the comment. The proposed mechanisms were introduced briefly in the abstract (line 19) and were further discussed later on in the discussion starting line 271. Please see response to referee #2 specific comment L277, which outlines planned changed for more details on self-diffusion.

L266: Are there carbonates in your soil? Easy test with HCl.

Response: Thanks for the suggestion. Indeed, we did test our soil using 1 N HCL and the soil was non-effervescent (i.e. no bubbles formed). In addition, the possible fractionation displayed in d18O data is not explained by isotopic effects due to interaction with carbonates (Meißner et al., 2014) because the shift in isotope values were in the opposite direction than what is predicted due to carbonate interactions.

Planned changes: We will add a statement about our HCl test result in the methods when introducing the soil used in the study, section 2.2.

L270: This is the first time you have acknowledged that your samples have perturbed

soil structure and thus pore sizes. This may be the biggest reason for any isotope effect of any discussed.

Response: We appreciate this comment and agree that the fact that the soil was perturbed needs to be highlighted and acknowledge early in the manuscript. We emphasize however that what we are presenting is a combination approach and we use a fairly artificially disturbed soil for proof of concept. We are unaware of perturbed structure having observed isotope effects on water extracted from soil. We are aware that recent work has highlighted that oven drying soil may change the wettability and surface adhesion of water molecules (Gaj et al., 2019).

Planned changes: We will include a statement in the methods that highlights the fact that soil structure was non-native and perturbed for this study which likely affects the normal distribution of pore sizes. In the planned additional paragraph of the discussion on fractionation effects, we will mention that oven drying the soil may have change the wettability and surface adhesion of water molecules in our study soil (Gaj et al., 2019). We will state that we lacked the capability of identifying these with our lab procedure and that future studies should consider these factors. L277: Finally, the discussion I was yearning for. Can you expand by making some calculations that support these arm waving statements?

Response: Thank you again for your insightful comments. We agree that sharing the equation discussed will help add to the discussion.

Planned changes: We will include the equation for diffusion of solutes in soil that is used for understanding self-diffusion of water within soil as it will be also be useful for helping discuss the conceptual model and details brought up in response to referee #1 general comment 3. We will also demonstrate within the discussion that for a clay soil, the increased porosity affects the tortuosity factor and would therefore affect the rate of diffusion between pores within a clay soil.

L288: Good point on the pore size changing during the spinning.

Response: Thank you!

L290: Yes, shorter spin times!

Response: We agree that this would make the method more realistic for wider applications.

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