Evaporating water is different from bulk soil water in $\delta^{2}H$ and $\delta^{18}O$

**Summary:**

Wang et al. sought to determine the contribution of bulk water from cryogenic extraction to evaporation water using stable isotopes of water. The team used a clever and practical method to collect evaporated water in a corn field and compared this to extracted bulk water throughout the growing season. Additionally, the authors applied a deuterium labeled irrigation to improve endmember resolution. Following the label, the evaporation and bulk water appears to decrease in $2H$ through time in similar overall values, whereas the $18O$ signature increases through time with significant differences between these two sampling domains. The authors interpret this to mean that, in this system, evaporation shows a strong preference for new water residing in large pores and that the source of evaporation differs from that of cryogenically extracted bulk water.

**General Comment**

I think that both the aim and the results of this study are relevant and interesting. These kind of experiments are severely lacking in modern hydrological sciences, and are needed to force the field to think openly about flow and mixing assumptions. However, there are numerous instances where the presentation and interpretation of the results make it difficult to judge the merit of the experiment, overall. I detail these discrepancies below. I think most of the necessary analyses have been conducted but I find it hard to accept without a substantial change to the current presentation and interpretations.

**Specific Comments**
- **Introduction to Evaporation Dynamics**

Lines 40-51: This section is a bit unclear. How exactly are the initial evaporation phases preferentially expressing larger pores? Yes, the larger pores connecting the deeper (more positive pore water pressure) source water to the near-surface may require higher contribution from higher conductivity ("larger") pores to sustain evaporation. However, it is unclear if the source of water vapor at the evaporation front is distinctly associated with larger pores, as smaller pores are dominated by stronger capillary forces (capillary > gravity + viscous forces) that maintain the gradient that links surface evaporation to deeper layers.

I think that this section needs to be made clearer which appears to be a critical point of the manuscript. I suggest providing a more detailed link to the literature, especially as these references (e.g., Ohr and Lehman + Zhang et al) do not make such obvious pore-scale distinctions.

- **Figures and Presentation**

Generally, it is difficult for the reader to interpret results from most of these figures. The labels of the figures are sporadic with non-intuitive descriptions in figure captions. Having to flip back and forth between plots and timelines to attribute dates with important time periods does not help (maybe get rid of dates, use time, and intuitive descriptors for each key time period?). Overall the quality of figures is often lacking. The exception is figure 8 which is well done. Please see my specific comments below (and attached file).

Also regarding the fractional evaporation:

Line 325: This gets a bit confusing.

1) how are you expressing the fraction of evaporated water source from both pools if equation 10 requires input from bulk water (i.e., this should work for just BW)?

2) why are you only comparing EW vs BW for 18O in period 2 and not 2H (or period 1)?

3) Why make all of these sporadic comparisons and list one panel as not available.
These points really detract from the meaning meant to be conveyed here.

**Interpretation and Explanations**

Here are some key points:

Line 361: This is quite puzzling. How could you expect a difference in detected source in 18O between evaporation and bulk water, when the there is such a stronger end member separation in 2H? ~ 80 delta 2H per mil divided by instrument precision 0.2 = 400 units of detection versus almost no separation for 18O.

If this finding is indeed true, I think its worth discussing how you would see this in one isotopic signature (2H) and not 18O. Is it possible that that the instrument precision of 2H was greatly reduced after the label (e.g., drift and memory effects) whereas we see a more correct version of 18O during phase 2? Would you have any data to calculate the precision of the analysis throughout the study period to confirm?

Lines 373-375: Here is where the soil physics perspective matters. As you mention in your introduction (Lines 53-54) when tighter pores are filled with water (e.g., field capacity or wetter) the likelihood of preferential flow increases, as high porewater pressures force more water into large pores. However, under dry conditions (e.g., your irrigation event on 8/22) infiltrating water will initially fill these small pores, due to high matrix flux potential or a strong potential gradient between wetting front and dry soil. As the infiltration event proceeds, hydraulic length increases (e.g., depth of wetting front) driving down the infiltration rate (low gradient), the pore water pressures increase such that the air-entry pressure of large pores is exceeded, and then macropore or preferential flow ensues. Under the later phase gravitational forces exceed capillary "pull" into he matrix, increasing the likelihood of dual domain flow and separation between small and large pores.

The main point here is that dry conditions would likely facilitate preferential wetting of smaller pores due to strong capillary forces during initial infiltration. Thus, dry conditions could result in greater continuity between small and large pores. Having said this, preferential flow is known to happen under dry conditions too (especially in cracks) yet these conditions could really reduce the separation between the two pore domains. Note also that your introduction covers this process of preferential filling of small pores under dry conditions on Lines 52-53.

Please consider this point in your interpretation.
Lines 381-382: Again, why exactly do you assume the small pores to only express old water? The average water content before irrigation was quite low (~0.15 in the upper 10 cm).

These 25 mm of irrigation could have filled ~7-10 cm of upper soil assuming a uniform wetting front and a conservative porosity of 0.45. Thus the signature of infiltrating water alone could have muted the pre-event evaporation water source by >70%.

Lines 388-393: See my comments about these stages in the introduction.

Lines 420-421: This is not consistent with Brooks et al. Brooks et al suggested that transpiration water and bulk soil were similar and that smaller pores with high residence time supplied this Ecohydrological flux.

**Specific comments:**

Line 10: This reads like you are referring to the pool of water as being larger. "soil water from larger pores" is more clear and direct.

Line 16: maybe distinguish this as "natural precipitation.." to be clear

Line 26: "...evaporation losses from .." from what?

Line: 27: "implicationS" (plural)

Line 28: "process" Remove or make plural.

Line 36: I do not think that these two previous sentences could be considered a full paragraph.

Lines 38-40: Why is this specific distinction relevant?

Lines 39-40: This sentence does not make sense as written. Also, it is not clear what you are trying to convey. Maybe you mean "minimum?"

Line 41: See earlier comment. Rephrase to water in smaller pores (or something like this). Please revise this throughout the manuscript.

Line 45: Try to be clear with this term "depleted," as this is also a study of water isotopes (e.g., isotopic depletion). Maybe choose a different word (e.g., drained).

Lines 46-47: "capillary pumping" is never used in Or and Lehman (2019). This point is also unclear. Please specify.

Line 60: use "infiltration" not "invasion"

Line 71: "partitionING"
Okay, I think that the authors have used this small versus large pores enough to warrant a more specific reference. I suggest giving a more specific example of small versus large pores, especially here where vacuum pressure matters.

Lines 77-78: Good point.

Lines 84: "improve our understanding" works better? Does not make sense as written.

Lines 133-135: Are these equations provided anywhere? Is the manuscript available for review. This seems to be an important detail.

Lines 156-158: What exactly was measured here and what was calculated? Please state explicitly here and in the Supplemental file.

Lines 170-176: Looks like you have 2 paragraphs with 2 sentences and no transition? Please fix this.

Line 175: Should use "instrument" not "machine."

Lines 201-202: Is it also possible that the plastic film itself can fractionate condensed water molecules? This point might be worth clarifying/considering at this stage.

Line 246: "mean values.." of what exactly?

Figure 4, Lines 258-259: This is very confusing. It looks like there are 4 periods. I suggest shading these two areas with different colors or something similar.

Line 260: So the pink circles indicate when you compared bulk water versus evaporation water? Please clarify. Also were there no similar comparisons in Period 2?

Line 363: What is the porosity?

Line 265: Water contents can "jump"? :). please revise.

Line 266: Note that "Figure 4c" is not so clearly distinguished in the Figure. Would it be possible to move the letters e.g., "(a), "(b)" to the left-hand side and increase the font size? Also, please refer to these sections directly in the figure captions.

Line 270: remove "was"

Line 277: "Therefore" ??

Line 278: "relatively" should be "relative"

Line 282: "resulting in.." this sentence has been cut off.

Line 290: BW 18O also increased? Looks like there is a missing section??

Line 292: still describing period 2? Specify

Line 306: Can you clarify why the period 1 EW and BW values are not shown together here? It looks like they would indicate a different source water for EW (minus one outlier)

Line 321: I would really suggest getting rid of the dates here and using some intuitive representation in time (e.g., before irrigation, after irrigation, early period 1 etc..) It is difficult for the reader to discern what the various times mean and their relevance is not
mentioned in the Figure 6 caption.

Line 342: "preferentially evaporated" is more grammatical correct.

Line 354: "...THE evaporation period."

Line 362: difference in what? Please also specify for clarity.

Line 365: "partitionING"

Line 372: "...in larger pores than in small.."

Line 408: difference did not make a difference?

Please also see my specific comments in the attached pdf, if needed.

Please also note the supplement to this comment: 