Dear Dr. Orlowski,

Thank you very much for handling our manuscript entitled “Evaporating water is different from bulk soil water in δ^2H and $\delta^{18}O$ and implication for evaporation calculation”. Corrections have been made and the detailed response to each comment from the reviewer is provided below. We tracked all the corrections within the revised manuscript and noted the new line numbers in this document where the corrections can be found in the revised manuscript.

We are looking forward to receiving your positive news.

Sincerely,

Hongxiu Wang
Jingjing Jin
Buli Cui
Bingcheng Si
Xiaojun Ma
Mingyi Wen

Comments from Editor

The reviewer suggested some more minor revisions, which I would encourage you to follow. I think you did a great job with your revisions.

Response: Thanks for your positive comments. We did some revisions based on the suggestions from the reviewer, and the detailed response to each comment is provided below.

Comments from Reviewer:

Main comment:

The authors have done a solid job of revising the manuscript for clarity, especially in terms of presentation and methodology. The manuscript now reads much better and many of the key findings are now more clearly conveyed. I think that the manuscript is nearly ready for publication but there are few important (and hopefully quickly addressable) points to consider from the soil physics perspective, as I detail below. These should, however, these should only be minor revisions.

Response: Thanks for your positive comments and helpful suggestions. We did our best to enhance the soil physics perspective, including the infiltration processes, the boundary conditions, and the bypass flow occurrence in our experimental site.

Specific comments

Page 2, Line 49: "is no longer connected" should be "is hydraulically disconnected"

Response: Done. Thanks.

Page 3, Line 63: "pre-event" don't you mean "event"

Response: The sentence was modified as P3 L64-65: "Furthermore, water in small pores and large pores may differ in isotopic compositions. As is well-known, pre-event soil water occupies the smallest pores."

Page 3, Lines 65-80 (section starting with "…when small pores…"):

This a bit vague and does not appear to be totally correct.

Small pores being filled with water (and/or) and event water being "large" are not necessarily prerequisites for preferential flow.

You could easily have near-positive or positive pore water pressures near the soil surface displacing/filling water in small pores (without requiring all of the water to be channeled into preferential flow paths). But, then you could also have water from the soil matrix (smaller pores) mechanically displacing water in preferential flow paths (larger pores). In the former scenario pre-event "small" pore water could feasibly stay in the matrix, whereas in the later, the matrix water would presumably enter into preferential flow paths, with the potential to contribute heavily to evaporation (based on your three stage descriptions). See these papers:

Sklash, M., Beven, K., Gilman, K. & Darling, W. J. H. P. Isotope studies of pipeflow at Plynlimon, 465 Wales, UK. 10, 921-944 (1996).

Levy, B. S. & Germann, P. F. J. J. o. c. h. Kinematic wave approximation to solute transport along 559 preferred flow paths in soils. 3, 263-276 (1988).

Klaus, J., Zehe, E., Elsner, M., Külls, C. & McDonnell, J. Macropore flow of old water revisited: 460 experimental insights from a tile-drained hillslope. Hydrology and Earth System Sciences 17, 103-461 118 (2013).

Similarly, event water being "large" does not necessarily bear much relevance to the flow partitioning. The amount, in combination with intensity, is much more relevant as you could have a large rain event that is slowly infiltrating (low intensity) and conducive to matrix flow.

Rainfall intensity is particularly important because it may mean the difference between detecting similar or distinctly different water in matrix versus preferential flow paths.

See the general point:

Kumar, A., Kanwar, R. S., and Hallberg, G. R.: Separating preferential
and matrix flows using subsurface tile flow data, J. Environ
Sci. Heal. A, 32, 1711–1729, 1997.

Also see how this idea is applied more recently using stable isotopes of water at hillslope:

Klaus, J., Zehe, E., Elsner, M., Külls, C. & McDonnell, J. Macropore flow of old water revisited: 460 experimental insights from a tile-drained hillslope. Hydrology and Earth System Sciences 17, 103-461 118 (2013).

…and at the soil column scale, which details that these distinct pore scale separations may require extreme rainfall events (e.g.,50 y storm) and well-developed soil structure:

Radolinski, J., Pangle, L., Klaus, J. & Stewart, R. D. J. H. P. Testing the ‘two water worlds’ hypothesis under variable preferential flow conditions. Hydrological Processes 35, e14252 (2021).

I think the authors just need to be a little more explicit in their soil physical description/discussion. The 3-stage evaporation description reads better and makes much more sense now, which is very helpful. However, it may really benefit the manuscript to tighten-up the discussion of boundary conditions and how that influences mixing and/or the source of evaporation in soils.

Response: Thanks for your fruitful suggestions. The infiltration processes were modified on P3 L64-87 : "Furthermore, water in small pores and large pores may differ in isotopic compositions. As is well-known, pre-event soil water occupies the smallest pores. Depending on the rainfall amount and intensity, an event water may have three pathways. First, a subsequent small event water fills the empty small soil pores. Second, event water with small rates, but long duration, may also displace the pre-existing, saturated smaller pores with slow flow velocity (Beven and Germann, 1982; Brooks et al., 2010; Klaus et al., 2013; Sklash et al., 1996); in cases that the water flow into a relatively impermeable layer, the pre-event water in smaller pores may be forced into large pores, due to the underlining hydraulic barriers (Si et al., 2017). Third, when the event water is large and intense, the event water preferentially enters large pores, bypassing the saturated small pores with large flow velocity (Beven and Germann, 1982; Booltink and Bouma, 1991; Kumar et al., 1997; Levy and Germann 1988; Radolinski et al., 2021; Sprenger and Allen, 2020). Because the exchange rate between these two flow domains is small (Šimůnek and van Genuchten 2008), small pores will lock the signature of first filling water. As the flow velocity is determined by the soil pore size, larger pores have greater hydraulic conductivity, and consequently water residing in larger pores flows faster and thus drains first. Conversely, water residing in small pores drains last (Gerke and Van Genuchten, 1993; Phillips, 2010; Van Genuchten, 1980). Therefore, soil water in smaller pores has a longer residence time or memory (Sprenger et al., 2019b), while water in large pores geneally have a short memory. This differing memory between large pore and smaller pores, due to the sequence of water infiltration and drainage, could introduce variability in the isotopic composition between soil pore spaces. Additionally, due to seasonal, temperature, and amount effects of local precipitation events, there is strong temporal variation in the isotopic composition of precipitation (Kendall and McDonnell, 2012). As a result, precipitation events, differing in isotopic compositions, could recharge different soil pores, which may yield isotopic heterogeneities in soil pore spaces (Brooks et al., 2010; Goldsmith et al., 2012; Good et al., 2015). Isotopically, small-pore water may be similar to old precipitation, with large-pore water resembling new precipitation (Sprenger et al., 2019a; Sprenger et al., 2019b)."

And the soil boundary conditions are discussed on P22 L456-470: "For large and intense precipitation events, event water preferentially infiltrates into the empty large pores because of their high hydraulic conductivity. The infiltrated water may partially or fully transfer to the surrounding empty smaller pores, thus bypassing the small soil pores that are filled with pre-event water at the point of water entry and along the infiltration pathway (Beven and Germann, 1982; Booltink and Bouma, 1991; Šimůnek and van

Genuchten, 2008; Weiler and Naef, 2003; Zhang et al., 2019). The bypass flow occurs universally (Lin 2010) and has also been reported in our experimental site, the Chinese Loess Plateau (Xiang et al., 2018; Zhang et al., 2019). In our experiment, the precipitation event on July 24, 2016, was 31 mm with the intensity of 10.3 mm h^{-1}, and the irrigation event on August 26, 2016, was 30 mm with the intensity of 30 mm h^{-1}, and both were sufficient to initiate bypass flow (> 10 mm h^{-1}; Beven and Germann 1982; Kumar et al., 1997). The pre-event soil water content was close to residual water content (Section 3.1), indicating that small pores were prefilled with pre-event water. Thus, it is reasonable to assume that the new water filled large pores, and medium pores were likely filled by a mixture of pre-event and event water. Therefore, water in large pores was similar to the event water and water in the small pores was close to the pre-event water, i.e., old event water (Brooks et al., 2010; Sprenger et al., 2019a)."

The source of the evaporation water is discussed on P22-23 L471-484: "On the other hand, at the end of the evaporation period, lc-excess of 0–5-cm soil at 24 DAP, which had a lower soil water content than in Period II, was still the smallest compared with deeper soil (Fig. 6d). Therefore, the evaporation front was in the surface soil during both periods. Accordingly, the evaporation in our experiment was in evaporation stage I or II, as indicated in the Introduction. During evaporation stages I and II, small-pore water does not evaporate (Or and Lehmann, 2019; Zhang et al., 2015), and larger-pore water is the primary source of water for evaporation (Lehmann and Or, 2009; Or et al., 2013).

Therefore, EW is mainly from larger-pore water, similar to the event water in isotopic composition; BW contains EW and evaporation-insulated small-pore water, similar to the pre-event water. Compared with pre-event water, event water takes evaporation precedence. Therefore, the sequence of water in the evaporation layer can be analogically summarized as adhering to a "last-in-first-out" rule. Thus, when isotopic composition in the event water was smaller than that in pre-event BW, such as δ^2H and $\delta^{18}O$ in Period I and $\delta^{18}O$ in Period II, the isotopic composition in EW was smaller than that in BW (Fig. 4). When the event water was enriched in heavy isotopes relative to pre-event BW, such as δ^2H in Period II, EW should be enriched in ^2H compared with BW; however, a more precise analysis is needed."

Beven, K. and Germann, P.: Macropores and water flow in soils, Water Resour. Res., 18, 1311-1325, doi:10.1029/WR018i005p01311, 1982.

Brooks, J. R., Barnard, H. R., Coulombe, R., and McDonnell, J. J.: Ecohydrologic separation of water between trees and streams in a Mediterranean climate, Nat. Geosci., 3, 100-104, doi:10.1038/NGEO722, 2010.

Klaus, J., Zehe, E., Elsner, M., C Külls, and Mcdonnell, J. J.: Macropore flow of old water revisited: experimental insights from a tile-drained hillslope, Hydrol Earth Syst Sci, 17, 103-118, doi:10.5194/hess-17-103-2013, 2013

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Booltink, H. W. G. and Bouma, J.: Physical and morphological characterization of bypass flow in a well-structured clay soil, Soil Sci Soc Am J, 55, 1249-1254, doi:10.2136/sssaj1991.03615995005500050009x, 1991.

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Šimůnek, J. and van Genuchten, M.T.: Modeling Nonequilibrium Flow and Transport Processes Using HYDRUS. Vadose Zone J, 7, 782-797, doi:10.2136/vzj2007.0074, 2008.

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Van Genuchten, M. T.: A closed-form equation for predicting the hydraulic conductivity of unsaturated soils, Soil Sci Soc Am J, 44, 892-898, doi:10.2136/sssaj1980.03615995004400050002x, 1980.

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Weiler, M. and Naef, F.: An experimental tracer study of the role of macropores in infiltration in grassland soils, Hydrol Process, 17, 477-493, doi:10.1002/hyp.1136, 2003.

Zhang, Z., Si, B., Li, H., Li, M.: Quantify piston and preferential water flow in deep soil using cl and soil water profiles in deforested apple orchards on the loess plateau, china. Water, 11, 2183, 2019.

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Xiang, W., Si, B. C., Biswas, A., and Li, Z.: Quantifying dual recharge mechanisms in deep unsaturated zone of chinese loess plateau using stable isotopes, Geoderma, 337, 773-781, doi:10.1016/j.geoderma.2018.10.006, 2018.

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Lehmann, P. and Or, D.: Evaporation and capillary coupling across vertical textural contrasts in porous media, Phys. Rev. E, 80, 046318, doi:10.1103/PhysRevE.80.046318, 2009.

Page 21, Line 446: "see my previous comment about large versus intense events. Please revise through the manuscript.

Response: Done. "Large and intense events" was used.

Page 21, Line 448: Yes. But again, these do not necessarily have to be empty pores as displacement will likely occur simultaneously. (see comments, references, and discussion points that I made above).

Response: The infiltration processes is discussed on P22 L456-470: "For large and intense precipitation events, event water preferentially infiltrates into the empty large pores because of their high hydraulic conductivity. The infiltrated water may partially or fully transfer to the surrounding empty smaller pores, thus bypassing the small soil pores that are filled with pre-event water at the point of water entry and along the infiltration pathway (Beven and Germann, 1982; Booltink and Bouma, 1991; Šimůnek and van Genuchten, 2008; Weiler and Naef, 2003; Zhang et al., 2019). The bypass flow occurs universally (Lin 2010) and has also been reported in our experimental site, the Chinese Loess Plateau (Xiang et al., 2018; Zhang et al., 2019). In our experiment, the precipitation event on July 24, 2016, was 31 mm with the intensity of 10.3 mm h^{-1}, and the irrigation event on August 26, 2016, was 30 mm with the intensity of 30 mm h^{-1}, and both were sufficient to initiate bypass flow (> 10 mm h^{-1}; Beven and Germann 1982; Kumar et al., 1997). The pre-event soil water content was close to residual water content (Section 3.1), indicating that small pores were prefilled with pre-event water. Thus, it is reasonable to assume that the new water filled large pores, and medium pores were likely filled by a mixture of pre-event and event water. Therefore, water in large pores was similar to the event water and water in the small pores was close to the pre-event water, i.e., old event water (Brooks et al., 2010; Sprenger et al., 2019a)."

Beven, K. and Germann, P.: Macropores and water flow in soils, Water Resour. Res., 18, 1311-1325, doi:10.1029/WR018i005p01311, 1982.
Booltink, H. W. G. and Bouma, J.: Physical and morphological characterization of bypass flow in a well-structured clay soil, Soil Sci Soc Am J, 55, 1249-1254, doi:10.2136/sssaj1991.03615995005500050009x, 1991.
Šimůnek, J. and van Genuchten, M.T.: Modeling Nonequilibrium Flow and Transport Processes Using HYDRUS. Vadose Zone J, 7, 782-797, doi:10.2136/vzj2007.0074, 2008.
Weiler, M. and Naef, F.: An experimental tracer study of the role of macropores in infiltration in grassland soils, Hydrol Process, 17, 477-493, doi:10.1002/hyp.1136, 2003.
Zhang, Z., Si, B., Li, H., Li, M.: Quantify piston and preferential water flow in deep soil using cl and soil water profiles in deforested apple orchards on the loess plateau, china. Water, 11, 2183, 2019.
Lin, H.: Linking principles of soil formation and flow regimes, J. Hydrol., 393(1-2), 3-19, doi:10.1016/j.jhydrol.2010.02.013, 2010.
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Kumar, A., Kanwar, R. S., and Hallberg, G. R.: Separating preferential and matrix flows using subsurface tile flow data, J. Environ. Health Sci. Eng., Part A: Environmental Science & Engineering & Toxic & Hazardous Substance Control, doi:10.1080/10934529709376639, 1997
Brooks, J. R., Barnard, H. R., Coulombe, R., and McDonnell, J. J.: Ecohydrologic separation of water between trees and streams in a Mediterranean climate, Nat. Geosci., 3, 100-104, doi:10.1038/NGEO722, 2010.
Sprenger, M., Llorens, P., Cayuela, C., Gallart, F., and Latron, J.: Mechanisms of consistently disconnected soil water pools over (pore) space and time, Hydrol Earth Syst Sci, 23, 1-18, doi:10.5194/hess-2019-143, 2019a.

Page 21, Line 452: “pre-filled with pre-event water”. You were just describing bypass flow when small pores were empty. Now they are filled?

Please clarify.

Response: Yes, pre-event water filled the small soil pores. The reason was added on P22 L465-470 : “The pre-event soil water content was close to residual water content (Section 3.1), indicating that small pores were prefilled with pre-event water. Thus, it is reasonable to assume that the new water filled large pores, and medium pores were likely filled by a mixture of pre-event and event water. Therefore, water in large pores was similar to the event water and water in the small pores was close to the pre-event water, i.e., old event water (Brooks et al., 2010; Sprenger et al., 2019a).”

Brooks, J. R., Barnard, H. R., Coulombe, R., and McDonnell, J. J.: Ecohydrologic separation of water

between trees and streams in a Mediterranean climate, Nat. Geosci., 3, 100-104, doi:10.1038/NGEO722, 2010.
Sprenger, M., Llorens, P., Cayuela, C., Gallart, F., and Latron, J.: Mechanisms of consistently disconnected soil water pools over (pore) space and time, Hydrol Earth Syst Sci, 23, 1-18, doi:10.5194/hess-2019-143, 2019a.

Page 23, Lines, 504 and 506-508: Okay. Again, this does not appear to be strictly correct.

You are mentioning on Line 504 that "larger pore water" is preferred by plants and dominates groundwater recharge.

Then you mention that this is consistent with Brook et al. who categorically distinguish two water worlds as one tightly bound pool of soil water that supplies transpiration and another mobile pool that recharges groundwater and enters streams.

Brook et al., write on page 103: "Our results indicate that for this seasonally dry watershed within the Cascade Mountains of Oregon, soil water is separated into two water worlds: mobile water, which eventually enters the stream, and tightly bound water used by plants."

Please revise.

Response: Thanks very much for your suggestion. We really appreciate it. We revised the text on P24 L521-527: "This is inconsistent with Brooks et al. (2010), who separated soil water into two water worlds: mobile water, which eventually enters the stream, and tightly bound water used by plants. In our study, soil water content was below field capacity and thus according to Brooks et al. (2010), all water in our soil is "tightly bound water", including the large pore water we discussed above. Therefore, in our study, the larger pore water is still under the field capacity, the water that percolates into streams (groundwater) rather slowly and/or is adsorbed by plant roots, which has broad ecohydrological implications."

Brooks, J. R., Barnard, H. R., Coulombe, R., and McDonnell, J. J.: Ecohydrologic separation of water between trees and streams in a Mediterranean climate, Nat. Geosci., 3, 100-104, doi:10.1038/NGEO722, 2010.