

Dear Reviewer,

Thank you very much for your valuable suggestions on our manuscript entitled “Evaporating water is different from bulk soil water in $\delta^2\text{H}$ and $\delta^{18}\text{O}$ ”. We hope we have the opportunity to modify our manuscript for better presentation and interpretation according to your advice. We also did some corrections based on your recommendations and the detailed response to each comment is provided below.

We are looking forward to receiving your feedback.

Sincerely,

Hongxiu Wang

Jingjing Jin

Bingcheng Si

Xiaojun Ma

Mingyi Wen

The “Technical note: Evaporating water is different from bulk soil water in $\text{d}2\text{H}$ and $\text{d}18\text{O}$ ” describes an experiment to elucidate hysteresis of water isotopic signals during evaporation. The process described is known, but the experiment nicely shows the concept and the implication for deriving evaporative loss from isotopic signals. It is, however, a pity that the difference in $\text{d}18\text{O}$ was not high enough to result in significant differences in evaporative loss. In this context, it would be beneficial to add more hypothetical calculations under which conditions (difference pre-event/event water) and soils this process might be important. The latter would strengthen the conclusions. In general, it would have been beneficial to have information on soil texture and eventually matric potential.

Another point that is not addressed yet is that evaporation of heavier water than bulk water evaporation loss cannot be calculated. The authors should comment on whether such replacement of heavier isotope occurs under natural conditions and which effect it could have to calculate evaporative loss for natural

isotope abundances. Another main point concerns the description of the calculations. The equation and variables used should be introduced sequentially. The Figures are appropriate and relevant literature cited. However, the manuscript should be corrected by a native speaker (particularly the first part until Discussion). Finally, the title should be adapted since evaporating water is per se different from bulk soil water, and as such, the title does not reflect the process you seek to investigate.

Response: Thanks for your suggestions. We added the discussion on P21 L432-442 : “The differences, in Period II, was 1.99 ‰ for $\delta^{18}\text{O}$. Nevertheless, the difference in $\delta^{18}\text{O}$ of EW and BW is too small to make a difference on the calculated evaporative water loss. However, by increasing the difference value with 0.01 increment from 1.99 ‰ to 3.40 ‰, there will be a significant difference in the calculated evaporative water loss. The magnitude of isotopic difference of EW and BW is related to the amount of evaporation-insulated small pores water, the amount of event water, and the isotopic difference of event water and pre-event water. Moreover, the maximum amount of evaporation-insulated small pores water is dependent on soil texture, the higher clay content, the greater water amount in small pores (Van Genuchten, 1980). The clay content of our studied soil is 0.24 g g^{-1} . Therefore, more attention is needed when dealing with high clay content soil, and when the event water amount and the difference in isotopic composition between event water and pre-event soil water are large.

On the other hand, more precise analysis is needed when the event water is more enriched in heavy isotopes than pre-event soil water as showed by our $\delta^2\text{H}$ result in Period II. However, the more enriched precipitation than soil water is rarely happened in nature. Commonly, soil water suffers from evaporation and has more heavy isotopes than precipitation. Nevertheless, when the sub-cloud evaporation effect in precipitation is strong (Salamalikis et al., 2016), the precipitation will contain more heavy isotopes than old precipitation i.e. pre-event soil water, then more attention is needed under this condition.” **And we modified our title** “The different isotopic compositions in evaporating water and bulk soil water did not make a difference in estimated evaporative water loss”

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.

Salamalikis, V., Argiriou, A. A., and Dotsika, E.: Isotopic modeling of the sub-cloud evaporation effect in precipitation, *Sci. Total Environ.*, 544, 1059-1072, doi: 10.1016/j.scitotenv.2015.11.072, 2016.

L26 Please make clear that this is not a general statement but specific to the conditions of your experiment.

Response: Done. The small isotopic difference was added on P1 L27-29 : “We also compared soil evaporation losses derived from water isotopes of EW and BW. With a small magnitude of isotopic difference in EW and BW, the evaporation losses did not differ significantly ($p>0.05$)”

L28 Which important implications?

Response: We modified the sentence on P1-2 L29-32 : “Our results have important implications for quantifying evaporation processes with water stable isotopes. We hope our study stimulate more researches on the effect of soil water isotopic partitioning in pore space to soil evaporation under different soil conditions and other eco-hydrological processes.”

L41 “occupied” seems not the right term in this context.

Response: We used “filled” instead of “occupied”. The detailed information was on P2 L46-48 : “When larger soil pores are filled by water, water in small pores does not participate in evaporation (Or and Lehmann, 2019; Zhang et al., 2015).”

Or, D. and Lehmann, P.: Surface evaporative capacitance: How soil type and rainfall characteristics affect global-scale surface evaporation, *Water Resour. Res.*, 55, 519-539, doi:10.1029/2018WR024050, 2019.

Zhang, C., Li, L., and Lockington, D.: A physically based surface resistance model for evaporation from bare soils, *Water Resour. Res.*, 51, 1084-1111, doi:10.1002/2014wr015490, 2015.

L45 Please rephrase the sentence.

Response: We rephrased the sentence on P2 L50-513 : “With the progressive reduction of water in larger pores, the evaporation rate decreases gradually.”

L54 Large pores instead of pore.

Response: Done.

L37-59 This section should be moved to the methods.

Response: Thanks very much for your suggestion. We really appreciate your help. However, in order to have a good logic in the introduction section, we have to keep the evaporation processes in the introduction section. Combining the evaporation process and infiltration process, we raised our scientific question, which is evaporating water should has different isotopic composition from bulk soil

water. Moreover, we hope we can have the opportunity to have a further discussion on it with you.

Thanks.

L82-84 This should be moved to the method section.

Response: Thanks for the suggestion. Done.

L84 Rephrase: This study may help to

Response: Thanks. The sentence was rephrased on P3 L87-88 : “This study may help to improve our understanding to the process of soil evaporation and the ecohydrological water cycle.”

L98 Add values or signature in the sentence.

Response: Done. The values were added in P4 L99-101 : “The field was irrigated 30 mm of mixed tap water ($\delta^2\text{H} = -61.11 \text{ ‰}$, $\delta^{18}\text{O} = -9.42 \text{ ‰}$) and deuterium enriched water (the ^2H concentration was 99.96 %, $\delta^2\text{H} = 1.60 \times 10^{10} \text{ ‰}$, Cambridge Isotope Laboratories, Inc.) on 2016/8/26.”

L107 “secondary” evaporation

Response: Done.

L129-130 It is not clear whether the authors refer in this sentence to their own findings (in this case I would move the sentence to the results) or if there refer to other studies (in this case they should be cited). Moreover, the structure of the sentence is not clear and should be corrected.

Response: It is referred to other studies. I separated the citations of the next sentence to two parts. The detailed information was added on P6 L141-146 : “However, in terms of isotopic compositions, the extracted water is depleted in heavy isotope than the reference water and the depletion is related with soil clay contents and water contents due to incomplete soil water extraction (Orlowski et al., 2016; Orlowski et al., 2013). In order to extract all of the water from our soil samples with the clay content of 0.24 g g^{-1} , higher temperature ($>200 \text{ °C}$) is suggested to be used for soil water extractions (Gaj et al., 2017a; Gaj et al., 2017b; Orlowski et al., 2018).”

Orlowski, N., Breuer, L., and McDonnell, J. J.: Critical issues with cryogenic extraction of soil water for stable isotope analysis, *Ecohydrology*, 9, 1-5, doi:10.1002/eco.1722, 2016.

Orlowski, N., Frede, H. G., Brüggemann, N., and Breuer, L.: Validation and application of a cryogenic vacuum extraction system for soil and plant water extraction for isotope analysis, *J. Sens. Sens. Syst.*, 2, 179-193, doi:10.5194/jsss-2-179-2013, 2013.

Gaj, M., Kaufhold, S., Koeniger, P., Beyer, M., Weiler, M., and Himmelsbach, T.: Mineral mediated isotope fractionation of soil water, *Rapid Commun. Mass Spectrom.*, 31, 269-280, doi:10.1002/rcm.7787, 2017a.

Gaj, M., Kaufhold, S., and McDonnell, J. J.: Potential limitation of cryogenic vacuum extractions and spiked experiments, *Rapid Commun. Mass Spectrom.*, 31, 821-823, doi: 10.1002/rcm.7850, 2017b.
Orlowski, N., Breuer, L., Angeli, N., Boeckx, P., Brumbt, C., Cook, C. S., ... and McDonnell, J. J.: Interlaboratory comparison of cryogenic water extraction systems for stable isotope analysis of soil water, *Hydrol Earth Syst Sci*, 22, 3619-3637, doi:10.5194/hess-22-3619-2018, 2018.

L131: When are higher temperature needed? In case of higher clay content. This is not clear from the sentence. Could you provide soil texture information?

Response: Done. The soil texture information was added on P6 L144-146 : “In order to extract all of the water from our soil samples with the clay content of 0.24 g g⁻¹, higher temperature (>200 °C) is suggested to be used for soil water extractions (Gaj et al., 2017a; Gaj et al., 2017b; Orlowski et al., 2018).”

Gaj, M., Kaufhold, S., Koeniger, P., Beyer, M., Weiler, M., and Himmelsbach, T.: Mineral mediated isotope fractionation of soil water, *Rapid Commun. Mass Spectrom.*, 31, 269-280, doi:10.1002/rcm.7787, 2017a.

Gaj, M., Kaufhold, S., and McDonnell, J. J.: Potential limitation of cryogenic vacuum extractions and spiked experiments, *Rapid Commun. Mass Spectrom.*, 31, 821-823, doi: 10.1002/rcm.7850, 2017b.
Orlowski, N., Breuer, L., Angeli, N., Boeckx, P., Brumbt, C., Cook, C. S., ... and McDonnell, J. J.: Interlaboratory comparison of cryogenic water extraction systems for stable isotope analysis of soil water, *Hydrol Earth Syst Sci*, 22, 3619-3637, doi:10.5194/hess-22-3619-2018, 2018.

L147: “sub samples”

Response: Done.

L159 Use the present tense for referring to Tables and Figures.

Response: Done.

L167- : Why did you change the soil of the lysimeters. The reason is not apparent.

Response: The reason to change the soil of the lysimeters was added on P7 L184-185 : “Further, in order to keep better representative of the field soil, the soil of the inside lysimeter was changed every four days.”

L222-228: Here, the introduction of the variables and equations is mixed up and difficult to follow.

Please introduce each equation with its variables from top to bottom since this is an important aspect of your study.

Response: Thanks for pointing out our mistakes. We rewrote the introduction of the variables and equations and the detailed information can be found on P10 L232-250 : “The evaporative water losses were estimated using Eqs. (10-16) (Hamilton et al., 2005; Skrzypek et al., 2015; Sprenger et al., 2017), which is based on bulk soil water isotope balance and Craig-Gordon model.

$$f = 1 - \left[\frac{\delta_{BW} - \delta^*}{\delta_I - \delta^*} \right]^{\frac{1}{m}}, \quad (10)$$

where f represents the ratio of evaporative water loss to the total water source; δ_{BW} is the isotopic signal of 0-5 cm bulk soil water; δ_I is defined as the isotopic signal of the original water source by calculating the intercept between the evaporation line of the 0-5 cm bulk soil water isotope data in Period I in the dual-isotope plot and the LMWL (Fig. 3); m and δ^* are described below.

$$m = \frac{h - \frac{\varepsilon}{1000}}{1 - h + \frac{\varepsilon_k}{1000}}, \quad (11)$$

$$\delta^* = \frac{h * \delta_A + \varepsilon}{h - \frac{\varepsilon}{1000}}, \quad (12)$$

where h is the average ambient air relative humidity over 30 days prior to each soil water sampling (Sprenger et al., 2017); ε is the total enrichment factor; ε_k is the kinetic enrichment factor; δ_A is the ambient vapor isotopic composition.

$$\varepsilon = (1 - \alpha_1^*) * 1000 + \varepsilon_k, \quad (13)$$

$$\varepsilon_k(18O) = 28.5(1 - h), \quad (14)$$

$$\varepsilon_k(2H) = 25.115(1 - h), \quad (15)$$

$$\delta_A = (\delta_{rain} - (\alpha_A^+ - 1) * 1000) / \alpha_A^+, \quad (16)$$

where α_1^* is the equilibrium fractionation factor under the field soil condition (Fig. 1); α_A^+ is the equilibrium fractionation factor in the ambient air; δ_{rain} is the amount weighted isotopic composition in precipitation from 2016/7/11 to 2016/9/16.”

Hamilton, S. K., Bunn, S. E., Thoms, M. C., and Marshall, J. C.: Persistence of aquatic refugia between flow pulses in a dryland river system (Cooper Creek, Australia), *Limnol. Oceanogr.*, 50, 743-754, doi:10.4319/lo.2005.50.3.0743, 2005.

Skrzypek, G., Mydłowski, A., Dogramaci, S., Hedley, P., Gibson, J. J., and Grierson, P. F.: Estimation of evaporative loss based on the stable isotope composition of water using Hydrocalculator, *J. Hydrol.*, 523, 781-789, doi:10.1016/j.jhydrol.2015.02.010, 2015.

Sprenger, M., Tetzlaff, D., and Soulsby, C.: Soil water stable isotopes reveal evaporation dynamics at the soil–plant–atmosphere interface of the critical zone, *Hydrol Earth Syst Sci*, doi:10.5194/hess-21-3839-2017, 2017.

L240: Is the variable n introduced?

Response: Done. The introduction of variable n was added on P11 L261-263 :

$$f = 1 - \left[\frac{\delta_{BW} - \delta^* + n}{\delta_I - \delta^* + n} \right]^{\frac{1}{m}}, \quad (17)$$

where n is an intermediate variable and can be expressed as following,

$$n = \frac{-2.13\alpha_1^*}{h - \frac{\varepsilon}{1000}}, \quad (18)$$

L242. The article is missing: A general linear ...

Response: Done.

L270: Delete “was”.

Response: Done.

L277: What is meant by newly added water? The irrigation water? Please use the same terminology as before.

Response: Thanks. We used event water to describe precipitation event water and irrigation event water. All the manuscript was modified.

L300-306: style: delete some “therefore”

Response: Done.

L414: Could you explain how you estimated the value of 3.52 to result in significant differences.

Response: the method was added on P21 L434-436 : “However, by increasing the difference value with 0.01 increment from 1.99 ‰ to 3.40 ‰, there will be a significant difference in the calculated evaporative water loss.”

L418: Do you mean matric potential?

Response: Yes, you are right. We changed it to matric potential on P21 L449-450 : “While evaporation prefers larger pores water, larger pores water also has relative higher matric potential and therefore, may also be preferred by roots and dominate groundwater recharge (Sprenger et al., 2018)”

Sprenger, M., Tetzlaff, D., Buttle, J., Laudon, H., and Soulsby, C.: Water ages in the critical zone of long-term experimental sites in northern latitudes, Hydrol Earth Syst Sci, doi:10.5194/hess-22-3965-2018, 2018.

L436: Please make clear that this statement refers only to small differences in isotopic signals.

Response: Done. The information was added on P22 L467-470 : “Our results indicate that even isotopic

composition in BW is significantly different from that in EW, the small difference does not affect evaporative water loss calculation. However, more attention is needed when there is a large isotopic difference between event water and pre-event water.”