Hydrology and Earth System Sciences

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Discussions

Interactive comment on "Long-term and high frequency non-destructive monitoring of water stable isotope profiles in an evaporating soil column" *by* Y. Rothfuss et al.

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Dear Referee #2, thanks a lot for your review of our manuscript. You will find our answers to your general and specific comments below.

The paper presents continuous time series of temperature, soil moisture and its isotopic composition in several depth of an evaporating soil column in the laboratory. This is a really nice data set. The build-up seems well done, the observational chain is sensible and the presented data seems to be of high quality.

The paper has two flaws in my opinion: 1. there is almost no discussion, only results

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and 2. it is overselling evidence for prove. I-1) Regarding point 1: This is such nice data so I am really missing the discussion. For example, it is reported that the upper soil layers exhibit different lines in d18O-dD space. But no explanation is given why. There are already no meteoric water lines in the plots to compare.

ANSWER: meteoric water lines will be incorporated in the plots

I-2) What would you expect if you think about evaporation lines? Gat has shown that the observed evaporation line is a combination of several evaporation lines at different temperatures. Could you do something similar? I-3) I think that figure 7 does not add anything to the manuscript. I-4) Another point of discussion could be the value of the kinetic fractionation factor. One has E and VPD so one gets the conductance. One has also theta at the soil surface and the atmospheric conditions. So you can estimate the enrichment at the evaporating front and hence can deduce the equilibrium fractionation that fits best. Are Mathieu and Bariac right, what seems to be suggested by recent studies? Or is it completely wrong because it neglects the resistance in the soil for the evaporation? I guess evaporation E was deduced from the change of the soil moisture profile. This was not explained in the manuscript. So if you can do that, can you then also get the isotopic composition of the evaporation from the change in the isotope profile? And if so, what for do I need the evaporating front?

ANSWER: The reviewer is right that the data could be further discussed to retrieve information on kinetic fractionation factors. In the revised version of the manuscript, we show that simulated values of evaporation line slopes obtained for 10 consecutive days of isotopic data and using the expression proposed by Gat (1971, #1) (based on the Craig and Gordon model, 1965 #2) lead to a good estimation of the measured slopes ($R^2 = 0.76$; $p<0.001$). For this kinetic fractionation factors were computed using vapor diffusivities ratios from Merlivat (1978, #3) and n exponent from Mathieu and Bariac (1996, #4). Surface soil moisture was calculated from data above the evaporation front whereas the isotope compositions in the liquid phase at the evaporation front as estimated in §4.3. Determining the evaporation isotope composition from changes in

the isotope profile is a great idea which unfortunately cannot be validated here as we do not measure the evaporation isotope compositions. Nevertheless in the revised manuscript, the authors will provide time series of evaporation isotope compositions calculated using Craig and Gordon model with Mathieu and Bariac formulations for n exponent. Note that evaporation rate was deduced from changes in mass measured by a weighing balance (P3898L20-21). Finally, the authors would like to keep Figure 7 as it illustrates with a dual-isotope approach the increasing link between atmosphere and soil surface water vapors.

#1 Gat, J.: Comments on the Stable Isotope Method in Regional Groundwater Investigations, Water Resour. Res., DOI: 10.1029/WR007i004p00980, 1971

#2 Craig, H., and Gordon, L. I.: Deuterium and oxygen 18 variations in the ocean and marine atmosphere, Stable Isotopes in Oceanographic Studies and Paleotemperatures, Spoleto, Italy, 1965, 9-130, 1965.

#3 Merlivat, L.: Molecular Diffusivities of $H_2^{16}O$, $HD^{16}O$, and $H_2^{18}O$ in Gases, J Chem Phys, DOI: 10.1063/1.436884, 1978

#4 Mathieu, R., and Bariac, T.: A numerical model for the simulation of stable isotope profiles in drying soils, J Geophys Res-Atmos, DOI: 10.1029/96jd00223, 1996

I-3) I was also wondering if you can deduce soil moisture from the humidity in the tubes? I could not find a word about it in Rothfuss et al. (2013) but some sentence in this manuscript made me think that it should be possible.

ANSWER: It could be theoretically feasible from mass balance calculations. However one would need the soil water vapor output flow rate value, which was not measured. Only input flow rate was set which could differ, especially under dry conditions, with soil water vapor output flow rate.

II-1) Regarding point 2: The study is an application of the method developed earlier and presented in Rothfuss et al. (2013). But the abstract states: "In this study, we

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present a new non-destructive method ..." The enrichment at the evaporating front is well known, often observed and explained at least since Barnes and Allison (1984). But the abstract states: "we could also show for the first time the increasing influence of the isotopically depleted ambient water vapour on the isotopically enriched liquid water close to the soil surface (i.e., atmospheric invasion)."

ANSWER: This is true that Barnes and Allison (1983a, 1983b, and 1984) measured and modelled the depth of the evaporation front, however at permanent and isotopic steady states. Their measured isotopic profiles are unique solutions obtained for given and constant atmospheric conditions (as well as with unique values for soil physical properties such as tortuosity). In the present study, we documented for the first time the dynamics of the evaporation front from our isotopic data with a daily temporal resolution. This will be specified as such in the conclusion. Moreover in contrast with e.g., Barnes and Allison studies, the daily estimation of evaporation front is inferred not from the maximum steady state soil water isotope compositions but from maximum isotopic gradients.

II-2) The same in the conclusions. It is stated, for example, "it could capture sudden variations following a simulated intense rain event." It is true that the method reacted to the watering. No attempt was done, though, to quantify if the observed change in isotopes fits to the isotopic water balance.

ANSWER: No attempt was indeed made to quantify if the isotopic water balance corresponded well with the addition of water. However, similarly to our answer to your comment I-4) the isotope composition of Evaporation flux is needed to close this isotopic water balance. This was not available during the experiment.

II-3) Also "followed quantitatively the progressive isotope enrichment" was not proven. The authors took the calibration done in another medium; at least it sounded different to the sand in Rothfuss et al. (2013). I have always wondered about the physics behind the calibration curve. For example, why is the observed offset not the equilibrium

fractionation at 0 degC? So to me it was not proven that the same calibration curve is valid for different soils. There could be a dependency of the soil, which was also hinted in section 4.1.

ANSWER: The method was calibrated with pure quartz sand with very similar pore size distribution and density, and with no organic matter. It is true that other natural soils having high clay and/or salt content(s) might need other calibrations. This is not the case in the present study. Note, that we correct these calibrated readings with those of the two laboratory standards, which account for soil properties as well as aging of the tubings etc. Why Rothfuss et al. (2013) could not simply keep the equilibrium fractionation values measured by Majoube (1971) (or from any other authors for that matter) has to do with how the soil vapor phase in actively sampled.

III-1) I have a few other questions and comments: The method for determining the evaporating front is very flawed. I would have at least fitted some kind of spline to determine the front. Otherwise you are limited to the resolution of your measurements. But in any case, the evaporating front does not have to be the maximum. This depends on the atmospheric value. It can be even seen in the measurements presented in deuterium on DoE 100-150: The profile is pretty vertical in the upper soil while the front is already a few cm down the soil. It is not the maximum of the curve but rather the point of a discontinuity in the first derivative that indicates the evaporating front.

ANSWER: The gradients were simply calculated using a linear approximation of the composition profiles between two observation depths. We did not use splines because the non-monotonous change of the isotope compositions with depth could lead to considerable uncertainties. The reviewer makes the correct remark that the depth of the evaporation front does not necessarily corresponds with the depth where the observed isotope compositions are the largest. If the maximum isotope compositions are used to define the depth of the evaporation front, then the invasion of the evaporation front in the porous medium is predicted at later times. Secondly, the two different isotopes then lead to considerable differences in the prediction of the depth of the evaporation

front. For Deuterium, the compositions in the upper two observation depths are almost equal to each other for most of the times so that it is hardly possible to derive the evaporation depth from the maximal composition measurement. However, the temporal evolution of the vertical gradients in isotope composition is more consistent for the two isotopes. It can also be argued that below the evaporation front, the gradient is positive and decreases with depth. Above the evaporation front, atmosphere water vapor with lower isotope compositions intrudes in the porous medium. This reduces in a first phase the increase of isotope compositions which results from isotope enrichment at the evaporation front. Only after a certain time, the intrusion of atmosphere vapor will result in a decrease in isotope compositions above the evaporation front. But, the intrusion of atmosphere water vapor which slows down the increase in compositions has an effect on the vertical isotope composition gradients above the evaporation front: they start to decrease and become smaller than the isotope composition gradients below the evaporation front before the compositions start decreasing with time. A more in depth investigation of the behavior of the composition gradients with time and depth will be carried out in a follow-up study with detailed numerical simulations using the isotope-enabled SVAT SiSPAT-Isotope.

III-2) Why is there no decrease in water content in the lowest layer. It seems like standing at 0.3x and not moving for 300 days. This is impossible with a porous glass plate at the bottom. And quite contrary to Merz et al. (2014). Did you really have a porous plate on the bottom? If not, this is the reason why you do not see stage I evaporation.

ANSWER: The reason why water content was almost constant for 300 days from -0.3 m depth down to the bottom of the column is explained by the fact that the soil column was sealed directly below the porous glass plate (2-way valve was in closed position, P3898L19-20). Nevertheless, even if the 2-way valve was maintained opened during the experiment, the properties of the porous plate would not allow drainage or evaporation of water. The porous glass plate has an air entry value of 0.87 m

(computed from the pore size distribution), which is larger than the maximum possible water column length (i.e., 0.6 m, when soil is saturated at the very beginning of the experiment).

III-3) So there in an argument in section 4.3 that the resistance increases with increased wind speed and this is why there is no stage I evaporation. This is unphysical. The exact opposite is true and also measured very often, even in the same institute.

ANSWER: We meant that the transfer resistance increases with decreasing water content in relative terms more for a thin (high wind velocity) than for a thick (low wind velocity) boundary layer. This does not mean that the transfer resistance for a fully wet surface is higher for a high than for a low wind velocity. In the revised text, the following §(P3905L11-15): "This indicates greater wind velocity in the air layer above the soil column due to the laboratory ventilation system which would lead to a decrease in evaporation rate during stage I due to an increased transfer resistance in the boundary layer above the drying porous medium as observed and modelled by Shahraeeni et al. (2012)." was reformulated as: "This indicates greater wind velocity in the air layer above the soil column due to the laboratory ventilation. For higher wind velocities, the boundary layer above the drying medium is thinner and the transfer resistance for vapor transfer lower than for lower wind velocities. But, for thinner boundary layers, the evaporation rate depends stronger on the spatial configuration of the vapor field above the partially wet evaporating surface. Evaporation rate decrease (and the transfer resistance in the boundary layer increase) with decreasing surface water content more for higher than for lower wind velocities (Shahraeeni et al., 2012)."

III-4) The discussion about the atmospheric water vapour is strange. What does it mean: "These values were significantly lower than the calculated ratio of the equilibrium fractionation for 1H2H16O and 1H218O that characterises meteoric water bodies, which should have ranged between 8.32 (DoE 200–250) and 8.47 (DoE 0–50) at the measured laboratory air temperatures." Atmospheric air is long-range transport. It has nothing to do with "the measured laboratory air temperatures". Why does it has to be in

equilibrium with some meteoric water bodies? What are these bodies? Did you check the weather patterns? Could have been air from the East instead from the West as normal.

ANSWER: Indeed! This is a mistake and this has been corrected in the revised version of the manuscript where instead of laboratory air temperature, local daily mean air temperatures were taken into account for calculating ranges of temperature-dependent meteoric water lines slopes.

III-5) Last but not least, the manuscript uses very often 'isotope' where it should be the adjective 'isotopic' such as in isotopic composition.

ANSWER: Following T.B. Coplen (Guidelines and recommended terms for expression of stable-isotope-ratio and gas-ratio measurement results, RCMS, 2011), both 'isotope' and 'isotopic' apply. When e.g., looking at the reference list of this manuscript, 'isotope' is preferred no less than 10 times over 'isotopic'.

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Interactive comment on Hydrol. Earth Syst. Sci. Discuss., 12, 3893, 2015.

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