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Hydrology and Earth System Sciences
Discussions

Interactive comment on “X Water Worlds and how to investigate them: A review and future perspective on *in situ* measurements of water stable isotopes in soils and plants” *by* Matthias Beyer and Maren Dubbert

Youri Rothfuss (Referee)

y.rothfuss@fz-juelich.de

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I am reviewing the manuscript entitled “X Water Worlds and how to investigate them: A review and future perspective on in situ measurements of water stable isotopes in soils and plants” by Matthias Beyer and Maren Dubbert under discussion for subsequent review in HESS.

First, I have to state for the record that I have collaborated with Dr. Maren Dubbert, which is why I show my identity here. I only accepted to review their manuscript because (1) of its format (review), which is much less subject to controversy than it would be for a research article and because (2) I have never heard of the manuscript until the editor Christine Stumpp contacted me. The authors will see that I provide a number of tough but fair comments!

The manuscript is an exhaustive and timely review on the subject of online non-destructive analysis of soil and plant water isotopic compositions. It is well written, easy to understand (at least to me) and well structured, exception made of Part 2.2, which does not fit the scope of the paper, i.e., the “current status of in situ measurements of water stable isotopes in soils and plants”. (I suggest removing it in my specific comments). Also I leave to the editor to decide if the authors should extensively make reference to their own unpublished/non peer reviewed work for proving their point.

My first general comment is the following: the methods that we employ can only be as good as the understanding that we have of the processes in play. For this we have physically-based models, that, despite their limitations, compile our knowledge and propose possible explanations of (isotopic) observations. The “in situ” methods – I argue later that they should be renamed “online” method – induce a paradigm change in isotopic analysis and leave us with much more information to process. Effort in linking the data stream to existing isotope-enabled models is therefore crucial and should have its own section here, rather than mentioned now and then throughout the manuscript. I wrote together with Mathieu Javaux a paper on the specific subject of model-to-data exchange for the specific case of root water uptake analysis (Rothfuss and Javaux, 2017).

My second general comment is that, in my opinion, the two-water-worlds (TWW) hypothesis is not the development trigger of such techniques. I don’t see these methods as a way to validate the hypothesis. I know that the TWW attracts a lot of attention therefore should be evocated in the main text but not named in the title, especially since you only mention it in the introduction. Furthermore my opinion is that we cannot investigate these water worlds (or pools, even though the link between these two concepts is not obvious) on basis of water stable isotopic measurements: using them makes the analysis biased, as we implicitly recognize that these different worlds/pools exist. There are other (e.g., geophysical, combined tracer) techniques that work on different premises and should be used towards a proper characterization of these pools/worlds.

My third and last comment is about spatial (vertical and lateral) discretization and representativeness of the online methods. They still poorly compare with those of the destructive sampling approaches. What do we do in the field with these highly resolved and long-term isotope compositions data series if the information is only relevant at the square meter-scale or for this particular plant individual?

Looking forward to a revised manuscript!

Cheers -Youri Rothfuss

Technical comments:

Title: you do not measure the water stable isotopes, rather their isotopic compositions.

Abtract

L10. "involving water stable isotopic measurements”

L11. “e.g.”, not “i.e.”

L15. “in the soil-vegetation-atmosphere continuum” (or e.g. “at the soil-atmosphere interface” etc.)

L17. Mention and explain shortly before what for you constitutes a “water pool”.

L17. Reformulate: you mean certainly “spatial variability and temporal dynamics of the water isotopic composition in terrestrial ecosystems”.

L18ff. “in situ” is a vague term… destructive as well as non-destructive sampling are always done in situ. On the other hand, the measurements are performed on-line vs off-line. Consider using another terminology throughout the MS, e.g. the aforementioned

“on-line”

L19. “disentangle” is used twice in the abstract. Find alternate term here maybe…

L21. “water stable isotopic compositions”.

L21-28. Should be one single paragraph.

L24. An interface cannot be threefold. You are talking of a continuum here. They are many interfaces present within a continuum and in this particular case three, i.e., the soil-root, soil-atmosphere, and plant-atmosphere interfaces.

L25. This is a given. Consider omitting.

L25-26. “In situ methods for soils are well established”. The literature as well as yourself later say otherwise.

1. Introduction

L45-48. What is always omitted and should be stated here is the water demand vs water availability. Experts on root water uptake processes know that if a plant does not need to extract water that is “easily” accessible, because it e.g., does not transpire enough or is adapted in this regard…it will keep extracting “less available” water. “Easily accessible“ water is also poorer in dissolved oxygen and nutrients and might be the last place to look for water for some species. This should be discussed.

L52. “at the soil-vegetation-atmosphere interface”. See my previous comment.

L55-64. Earlier you are talking of water “worlds” but here of “pools”. They are not the same. This should be discussed as well.

L62-63ff. Edit reference format. It should be “et al.”

L63-64. “As a consequence, a big question arises: Are all source water studies wrong?”: this is a scary statement (!) Also do not say “wrong”, as there is a moral aspect to it. “biased” sounds about right.

1.1 Are ecohydrological source water studies biased? – The need for in situ methods

L70 “low suction tension” :)) Just say low “low tension” or “low soil water tension”

Fig.1. You are missing evaporation! Also phloem-xylem exchange, Péclet effect, and cuticular evaporation could be mentioned. In addition you should use arrows for fluxes rather that for lag time. Anyway, is this (nice) drawing really needed? It is not quite informative, and you don’t make use of it in the text.

L79. “water isotope composition values”

L101. “2 Review: In situ approaches for measuring soil and plant water stable isotope composition”

L102. “2.1 In situ soil water isotope composition depth profiles”

L103-110. Nice §!

L105. δ2H needs definition

L105-106. Take care of the scientific grammar / isotopic terminology: it should read “The determined isotope composition values agreed well with that of the samples extracted from the soil”.

L103-212. “The concepts tested in Herbstritt et al. (2012) therefore can be seen as a baseline for all subsequent in situ soil water isotope studies.”: I would not say this at all. Barbara Herbstritt’s study is not on soil water, but on meteoritic waters. Their membrane as well as their modus operandi were not further used in the “subsequent in situ soil water isotope studies”. This is also the case for Soderberg et al.’s study, which, even though it constitutes the first published work on online soil water vapor measurement, can be seen as an outlier as their method was not further applied. I see that they are two “families” of methods that rely on the same principles: those of Rothfuss et al. (2013) and Volkmann et al. (2014). The first one has seen to date more applications and further developments (Rothfuss et al. 2015; Gangi et al. 2015;

Quade et al. 2018; 2019, Oerter et al. 2017, 2019, Oerter and Bowen, 2017, 2019, Kühnhammer et al. 2019) that the second one (Gaj et al. 2016), certainly for the reason that the probes weren’t at first off-the-shelf products (although Gaj et al. 2016 used already commercially available soil gas probes). We in Jülich personally did not have the idea to use membranes from Barbara Herbstritt’s work, rather from previous applications in soil CO2, N2O, and CH4 sampling [Dinsmore et al., 2009; Hartmann et al., 2011; Neftel et al., 2000]. These studies could be a nice addup to this nice section. Also you are almost up to date: you are missing the following study:

Quade, M., et al. (2019). "In-situ Monitoring of Soil Water Isotopic Composition for Partitioning of Evapotranspiration During One Growing Season of Sugar Beet (Beta vulgaris)." Agricultural and Forest Meteorology 266–267: 53–64.

L158. “directed in”

L158-159. Dry air cannot equilibrate with some isotopic composition. Please reformulate

L169. “combined measurements of δ18O and δ2H” I presumed.

L213-300. Part 2.2 feels not to fit the scope of the paper, i.e., the “current status of in situ measurements of water stable isotopes in soils and plants”. I suggest removing it. I will not distract the reader away from the core of the paper.

2.3 In situ measurements of plant xylem water isotopes

L312. “can be observed”

L312-313, 316ff etc. “xylem water isotope compositions”

L317-318. Define IRIS and IRMS, and “BSquare-weighted M-regression”

L320. Use ‰

L321-349. I am not sure that you should review non-published literature…I leave that to the editor to decide.

L337 (goes as well for at L338). “δ18O xylem isotopic composition values were lower than those of the source water”

L349. This table is central to your review and should be moved from the SI to the main text and named Table 1! It should be mentioned at the beginning of section 2, so that the readers can consult it while reading.

L350. “3 Setup, Calibration and Validation of in situ measurements of soil and plant water isotope compositions”

L354. “for sampling the water vapor”

L355-358. Exactly my specific comment from before on section 2.2 (+see my general comment)

3.1 Materials and approaches for sampling soil water vapor

L362-363. Only Volkmann and Weiler (2014) built probes in the pure sense. The rest of the authors (apart from Gaj et al., 2016) basically just cut sections of the gas-permeable tubing and took care that it was water tight when installed in the soil and properly connected to the sampling lines.

L365. “Self-made” is not appropriate. You mean tubing vs membranes inside sensor.

L367-392. This part echoes my comment from before regarding text at L103-212. I suggest a bit of streamlining and incorporating the one part (L103-212) into the other (L367-392) or vice versa.

Two comments here:

1- soil vapor is not necessarily water saturated for a soil liquid-water vapor equilibrium to be reached. Isotopic equilibrium happens between the two phases at relative humidity < 1 at high soil water tension.

2- there is no (and should not be!) overpressure inside the tubing, otherwise you push the dry air inside the soil and disturb the vapor-liquid coupled state. For this the sampling lines downstream of vapor collection should be kept as short as possible to minimize resistance to air flow and of course an open-split. But even with long collection lines, the increase of pressure is/should not be observed. You have, on the other hand an overflow (rather than overpressure).

L380. “access tube just before the analyzer inlet”: the technical accepted term is “open-split”

L385-390. What is the point of having a slightly easier system to implement/use if in the end it might not provide reliable data? My opinion: make a decision as this will influence the readers and potential future users.

L390-391. You said this already above. Consider erasing.

3.2 Saturation of water vapor, condensation and dilution

L400-410. A bit of reorganizing would help: you need to distinguish between condensation prior sampling starts from condensation during measurements. To get rid of the first problem, you should do iii) and to avoid the second kind of problem you should do points i) and ii).

Ideally you need (i) a three way valve after collection point and before dilution and (ii) a two way “normally open” valve between dilution point and open-split. This former allows you to:

1) flush the liquid water out of the gas-permeable tubing and out of the downstream sampling line prior measurement [valve is turned on and act as open-split]

2) flush the content of the gas-permeable tubing to the laser-spectrometer [valve is turned off]

3) flush the sampling line after dilution point and to the laser spectrometer open-split

once sampling is complete to lower the water vapor mixing ratio in it and avoid condensation problems in between measurement phases [valve is turned off and act as open-split]. Valve (ii) is then closed to keep the sampling line dry and the laser spectrometer samples from its own open-split.

Finally for increased security, you shall heat the sampling lines from the soil/trunk surface to dilution point.

This could be incorporated into Figure 7.

L420. “Correction for water vapor concentration dependency of the laser spectrometer isotopic composition raw readings”

L426. “3.3.1 Soil water vapor isotope standards”

L427. Not only with the same medium but thanks to the exact same method: the standard water vapor has to be collected in the same manner as that of the soil, i.e.:

(i) pass through the walls of the same membrane product coming from the same production batch (e.g., tubing of the same age, thus having the same permeability to water vapor), be exposed to equivalent environment (pH, chemical conductivity of the soil solution).

(ii) at an equivalent flow rate as for the samples

Also not to forget: a soil is not only characterized by its natural texture, but also structure, so the soil water vapor standards should ideally have the same structure on top of the same texture as the investigated soil. In relation to this: in my group we however did not see an effect of soil water content on raw isotopic readings. In Quade et al. (2018), we argue that what Oerter et al. (2017) see is due – at least partly – to the fact that they test the membrane on unstructured soils.

L453-459. You should mention of course the work of Markus Schmidt and colleagues, however do not display their equations as they are specific to their instrument. Also

they used one of the very first L1102i (number 8 if I remember correctly :) and Picarro® (and this goes for other companies) have since greatly reduced the linear response of their instruments to water vapor activity.

What you should write, on the other hand, is a short description on how these dependencies should be investigated using, e.g. the aforementioned soil water vapor isotopic standards at different dilution rates.

3.3.3 Other corrections (mineral mediated fractionation, organic contamination, carrier gas and biogenic matrix effects)

L469-470. This relates to artificial unstructured soil mixtures. . .see my previous comment. We are dealing with. . .soils, so structure (bulk density for instance) might play a significant role!

L475-487. If this apply to soil and plant water online measurements, the associated effect on raw isotopic composition readings should be orders of magnitude lower than for extracted water after inverse sublimation of for evaporated water following pyrolysis. . . You could mention that this has not been investigated but you don’t need to review the literature that deals with VOC contamination on liquid samples (out of scope).

In addition: what about the material out of which the sampling lines are made of and about their isotope effects? (there is also a dynamic adsorption-desorption equilibrium happening in them) Which one should we take - plastic or metal? Which kind of plastic, which kind of metal??

3.3.4 Drift correction

L494. Split “Conversion of vapor to liquid values” from “3.3.4 Drift correction”. These are unrelated things.

L497-498. You can omit the book of Clark and Fritz (this goes as well for at L122): the (peer-reviewed) works of the great Juske Horita and Mustafa Majoube are enough :)

These equations refer then to another state of equilibrium, namely “static equilibrium”. What we deal with here during purping is dynamic quasi isotopic-equilibrium. Rothfuss et al. (2013) showed that the purging and/or the PP material had an isotopic effect for 1H2H16O. And it is up to now the only real calibration available. These equations should be preferred over those of JH and MM or to the very least mentioned.

3.4 Validation –comparing apples and pears?

L538. Oerter et al. (2017) does not “propose a novel, innovative way of calibrating in situ data of soil water isotopes”. You refer to Oerter and Bowen (2019), certainly.

L545-560. There is a good chance that such regression analyses will add more uncertainty to the measurements when not performed carefully.

Points (i)-(ii) omit the importance of the soil structure on soil water vapor flow. A note: the addition of water to a dry soil does not ensure a homogeneous soil water content.

Points (v)-(vi) apply to deconstructed soil samples, see previous comments

4 Summary and Outlook

L586-587. “we spare modelling approaches in this review, but refer to recent developments,. . .”: see my general comment.

L618-621. In my opinion, this is not the way to go. It is much better to prepare different standards in an appropriate manner (repacked at the same field density) reflecting the different textures encountered in the field, so accounting for e.g. the effect of hydration and isotopic fractionation around clay particles.

It has to be proven if, indeed SWC plays a role when the soil is structured: my group has never seen such an effect (see Rothfuss et al. 2013, 2015; Quade et al. 2018; Kühnhammer et al. 2019) with compacted soil: this should mentioned/discussed.

L649-653. Rothfuss et al. (2013) did this. . .also do not cite a paper under review (Marshall et al. 2019).

L664-661. This is a very good idea! However the terminology used in a bit funky: the relative humidity is the ratio of actual to saturated water vapor pressures (not water vapor concentration) in the original definition. Also you certainly mean water vapor dry mixing ratio, which is typically expressed in vol-ppm. Why should the relative humidity be higher than 0.9 specifically? Look at the Kelvin equation and you’ll see that for soil pF=7, relative humidity should yield to 0.97.

L671. Define compartments

L674. This only applies to trees, right..?

L689-693. Why would you say that? Scientist from other field might say otherwise. . .you can say, on the other hand, that online non-destructive methods are more complex to install/implement than destructive sampling ones. But as long as we do not make complex things complicated, we are on the safe side :)!

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