

## ***Interactive comment on “In-situ unsaturated zone stable water isotope ( $^2\text{H}$ and $^{18}\text{O}$ ) measurements in semi-arid environments using tunable off-axis integrated cavity output spectroscopy” by M. Gaj et al.***

**Anonymous Referee #2**

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In their manuscript entitled “In-situ unsaturated zone stable water isotope ( $^2\text{H}$  and  $^{18}\text{O}$ ) measurements in semi-arid environments using tunable off-axis integrated cavity output spectroscopy”, Gaj and colleagues present a membrane-based method for sampling soil water vapor for indirect determination of soil liquid water isotope compositions. This study follows from previous laboratory and field successful validation attempts and resembles that of Volkmann and Weiler published in 2014 in HESS while having the distinct advantage of using commercially-available soil gas probes instead of custom-built ones.

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The manuscript is in general well written and easy to follow – approximations with the isotope slang put aside. The experimental setup could use some detailing. This study is a relevant read falling within the scientific scope of HESS and of great interest for the eco-/hydrological communities. I have however some doubts as to the method employed to answer its central objective, i.e., the comparison between in-situ and destructive methodologies. The discussion also remains too descriptive and qualitative.

### **GENERAL COMMENTS**

1/ As the authors state in their manuscript's introduction, on-line non-destructive isotopic methods need to be compared with what constitutes the norm, i.e., cryogenic extraction of water and off-line isotopic analysis. This comparison appears to be the central objective of the study. However the experimental conditions under which the authors attempt validating their new method, i.e., field conditions, cannot allow such a comparison. Spatial heterogeneity of soil surface water content in the field is well known and observed. Why should it be otherwise for stable isotopic compositions? Dynamics of isotopic compositions in dry soil surface layers should also exist, especially where day/night variations of atmospheric temperature/relative humidity are strong (which is the generally case in semi-arid environments). In the Discussion the authors come also to the same conclusions to explain the observed discrepancies, especially in the upper part of the soil profile. So why comparing in the first place? Logically, one should sample a representative volume of soil around the gas probe shortly after gas uptake for a proper comparison, but mostly, one should do it under controlled conditions where at least spatial heterogeneity is reduced. It is not clear to the reader which method is “right” and which one is “wrong” here, or which method should be used “here” and which one “there”.

2/ P6120L6: “Further unique is the type of automatization which allows a laboratory like operation”. This is not true (see Volkmann and Weiler, 2014; Rothfuss et al., 2015). Furthermore, it is not clear how well the system works automatically as the announced “High spatial and temporal resolution” (P6116L5) in the Introduction is supported by 12

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profiles "only".

3/ P6127L5-16. Values for accuracy are really high, even after drift and span corrections... To this reviewer, it can only mean that these 6 repetitions exceed what the soil can offer water vapor at thermodynamic equilibrium. Isotopic compositions would be ultimately impacted. Is there a trend from repetition 1 to 6 for each measurement cycle, and depending on water content? With respect to this, the authors should illustrate with an example of a measurement's cycle.

#### SPECIFIC COMMENTS

#### INTRODUCTION

P6116L17-20 The entire sentence should be rewritten: 1/ "stable water isotopes" is an awkward expression...one has the impression that isotopes of "stable water" are in question. Replace with "water stable isotopes". 2/ "stable water isotopes (e.g. deuterium, 2H and oxygen-18, 18O)" should read: "hydrogen and oxygen stable isotopes in water (e.g., deuterium, 2H and oxygen-18, 18O)". 3/ "a linear relationship between 2H and 18O on a global scale..." is not correct. Please replaced with "a linear relationship between water 2H and 18O isotopic compositions on a global scale..."

Additionally, it is not clear to me what means... "the areal input through precipitation which shows..."

P6117L3. "General isotopic composition". Be more precise, i.e., what does "general" mean here?

P6118L10. Consider replacing "intensively" with "actively"

P6118L19. Consider replacing "intense" with "intensive"

P6119L13-15. "Measurements were performed with a cavity-ring-down spectrometer (CRDS) (L1102-I, Picarro, CA, USA) calibrated with liquid water injections using a vaporizer unit" This is not true; I think they used custom-built soil water vapor standards.

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P6120L3. Regarding Objective 1/ It is not clear to the reader why it is so important to measure water stable isotopic profiles in semi-arid environments. Could you elaborate on this?

#### STUDY SITE AND METHODS

P6121L16-17. Consider replacing "between the 9 and 15 June 2014 and the second between 15 and 22 November 2014" with "between June 9th and 15th, 2014 and the second between November 15th and 22nd, 2014"

P6122L3-12. Particule size determination is not further used in this study. I suggest not going into details with the procedure. You might report the results in the text and not show Figure 3.

P6122L22-24. Replace "Isotope values are expressed as parts per thousand in  $\delta$ -notation (e.g. 18O and 2H) and are normalized to the international scale using Eq. (1)" with the following sentence: "18O/16O and 2H/1H isotope ratios and reported on the international " $\delta$ " scale and expressed in parts per thousand"

P6122L25. The factor "1000" is not part of the  $\delta$  definition. (see IAEA technical reports and excellent paper of Coplen, 2011). A  $\delta$  value is still a ratio and expressed in ‰ for commodity reasons only.

P6122L26 – P6123L3. This sentence is not clear: isotope ratios are reported on the VSMOW scale solely, no? One has the impression that they are also compared to those of SLAP.

Consider rewriting the sentence: "where  $R_{sample}$  (–) denotes the isotope ratio ... to VSMOW and SLAP, respectively" with: "where  $R_{sample}$  (–) denotes the 18O/16O isotope ratio (respectively 2H/1H) of a water sample and  $R_{standard}$  (–) those of the Vienna Standard Mean Ocean Water (VSMOW)".

P6123L5. Replace "by.van Geldern..." with "by van Geldern..."

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P6123L6-8. "Accuracies for long-term quality check standards are better than 0.2 and 0.8 ‰ for water samples, but an additional error for sandy soil extractions has to be taken into account which is better than 0.8 and 4 ‰ for  $^{18}\text{O}$  and  $^2\text{H}$ , respectively". 1/ Can you define "quality check" and 2/ how were the "additional errors for sandy soil extractions" determined??

P6123L18-21. Unnecessary detail. Consider erasing.

P6124L2. "Swagelok®" instead of "Swagelok®". It goes as well for "WEBA bags" (P6124L11) (specify firm, city and country of origin, I couldn't find it on the web)

P6124L10-21. This § is rather unclear. What are these standards? Soil water standards solutions? From where to where were they "transported in WEBA bags". Please elaborate on this.

## RESULTS

General remark: I'd keep with paste sense.

P6125L5. I suggest "June 15th, 2014" (goes for the rest of the manuscript)

P6125L18-19. Replace "and are exponentially decline down to 50 cm" with "and exponentially decline down to 50 cm"

P6125L19-20. I wonder what is the interest of calculating a deuterium excess value for soil water that is strongly impacted by evaporation? What gives the obtained value in that case?

P6126L20.  $\delta$  values cannot be "enriched/depleted" but are "higher/lower than"

P6126L24-27. Sentence could use some rearrangement, I suggest something like that: "There was a good agreement between in-situ and cryogenically obtained isotope measurements for both isotope depth profiles of the first campaign between 15 and 50 cm (RMSE= 3.9 and 9.2 ‰ for  $^{18}\text{O}$  and  $^2\text{H}$ , resp.). However, higher values were observed in situ at shallower depth (RMSE= 7.0 and 43.4 ‰ for  $^{18}\text{O}$  and  $^2\text{H}$ , resp.)."

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P6128L16-18. Belongs to "STUDY SITE AND METHODS".

P6128L17-P6129L2. It would have been even better to show all three profiles for each transect instead of giving mean values and sd.

## DISCUSSION

P6129L4-15. This § is filled with much too general statements, e.g., 1/ which advantages, what improvements and with respect to what? 2/ by "...transport of water vapor...not yet fully understood", do you mean evaporation? I'd say this is well understood from a theoretical point of view – i.e., implemented in physical models – only very difficult measuring.

P6129L23-24. What about natural soils with high salt and/or clay contents and their consequence to possible fractionation of soil water isotopes as point out by Oerter et al., 2014? This could lead to possible deviation between extracted and in-situ results...

P6130L10-17. A much better indicator for the extent of kinetic effects during evaporation of soil water is the so-called evaporation line (Craig et Gordon, 1965) rather than the deuterium excess. In addition, if removing of water vapor would disrupt the thermodynamic conditions prevailing between soil liquid and gas phases, the sampled water vapor would not be enriched but to the contrary depleted at first. It would be only after some time – depending on the uptake rate and initial water content that you would measure isotope values in the sampled gas higher than the initial (equilibrium) values because the soil liquid water parrallely enriches itself with stable isotopes.

P6130L17-26 and P6131L23-24. I think these are the right explanations: differences between in situ and destructive methods stem from the natural spatio-temporal dynamics of water isotopic compositions and the fact that these measurements were not made simultaneously and for comparable soil volumes.

P6131L8-15. This comment seems a bit off-topic here. In addition, you do not have for instance measured water potential profiles or capture the dynamics of xylem water

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isotope composition to support your assumptions. Consider removing.

P6131L24-25.  $\delta$ 2HI values are “higher” than  $\delta$ 2HC

P6131L25-28. How can you say that evaporation takes place so deep in the soil? There is a good chance that after the rain event, even under low water content the soil evaporates from the surface only. For this you should know the residual water content for the sandy soil.

P6131L29- P6132L3. This is not very clear, nor is the reference accessible.

P6132L4-10. Not only kinetic effect plays a role, but also the intrusion of atmosphere water vapor in the upper soil layers as recently published by Rotfuss et al. this year in HESSD. I would avoid only saying that “things are not yet fully understood” (this goes for almost everything no?)

P6132L18-19. . .or maybe also due to the chemical properties of the porous material?

P6133L14-15. Allison et al. (“1983” and not “1984”) analytical equation could not predict such a “displacement” as this study’s experimental conditions met neither isotopic steady state and isothermal conditions.

## CONCLUSION

P6134L2-3. What constituted a possibility (evaporation is induced during sampling) is now a certitude?

P6134L19-20. This very last sentence is somewhat unappropriate and does not fit with the rest of the conclusion (or the manuscript for that matter)

## TABLES

### Table 2

The introduction of the “1000” factor in the definition of  $\delta$  leads to curious labels such as “ $10^3 \delta^{18}\text{O}$ ”. Replace simply with “ $\delta^{18}\text{O} (\text{‰})$ ”. This goes for the Figures as well.

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## FIGURES

### Figure 2

I would have liked a scheme/picture of the prepared standards

### Figures 5

Definition for “GWML”, and the different subscripts are missing from the caption.

Coplen, T.B. (2011), Guidelines and recommended terms for expression of stable isotope-ratio and gas-ratio measurement results. *Rapid Commun. Mass Spectrom.*, 25, 2538–2560, doi:10.1002/rcm.5129

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.

Hu, Z., X. Wen, X. Sun, L. Li, G. Yu, X. Lee, and S. Li (2014), Partitioning of evapotranspiration through oxygen isotopic measurements of water pools and fluxes in a temperate grassland, *J. Geophys. Res. Biogeosci.*, 119, 358–371, doi:10.1002/2013JG002367

Oerter, E., Finstad, K., Schaeffer J., Goldsmith G., Dawson, T., and R. Amundson (2014). Oxygen isotope fractionation effects in soil water via interaction with cations (Mg, Ca, Na, K) adsorbed to phyllosilicate clay minerals. *Journal of Hydrology*, 515:1-9

Rotfuss, Y., Merz, S., Vanderborght, J., Hermes, N., Weuthen, A., Pohlmeier, A., Vereecken, H., and N. Brüggemann (2015), Long-term and high frequency non-destructive monitoring of water stable isotope profiles in an evaporating soil column. *Hydrol. Earth Syst. Sci. Discuss.*, 19, 1–26, 2015. doi:10.5194/hessd-19-1-2015

Volkmann, T. H. M., and Weiler, M. (2014), Continual in situ monitoring of pore water stable isotopes in the subsurface. *Hydrol. Earth Syst. Sc.*, 18, 1819-1833, doi: 10.5194/hess-18-1819-2014, 2014.

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