

# ***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.***

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Anonymous Referee #2 Received and published: 21 July 2015 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

Full Screen / Esc

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Discussion Paper



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. 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.

Authors response: Dear Referee2, we appreciate the revision of our manuscript and your comments that supported a fruitful discussion on unsaturated zone isotope field and laboratory methods. Compared to other studies we used a liquid water vapor analyzer. The advantage of this device is the short warm up period; the disadvantage is a lack of temperature compensation. In addition, this device is not measuring continuously which was an additional challenge for the setup compared to other studies (Rothfuss et al., 2010; Volkmann & Weiler, (2014)). The current principle behind the in-situ methods is the equilibration between water vapor and soil water. It should be noted that beside commercially available soil gas probes and a different analyzer applied in a remote area, another difference between previous validation attempts and the present study is the comparison to a laboratory water extraction method. A comparison between the two introduced methods appears to be reasonable because soil water will be extracted completely (at least for sand). Additionally, fractionation between liquid water and water vapor can either be affected by soil physical or chemical properties, as well as environmental conditions. Hence we, argue that multi-methodical validation attempts, from an isotope point of view, i.e. between equilibration and extraction methods will become more important, for both field and laboratory experiments, especially for soils with an increased content of silt and clay and in arid zone hydrology. There-with, the central hypothesis that both methods lead to the same result can be rejected. Further research is needed to identify the driving processes in the upper part of the soil column to improve soil water balance approaches in arid zone hydrology.

## 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".

### ANSWER:

We agree that a methodical comparison under field conditions has some uncertainties and has a different quality as a comparison under laboratory conditions. However, the comparison shows good agreement for most data points as shown in figure 4. Soil water is completely extracted from fine sand using the cryogenic vacuum extraction method. Though, it is a good benchmark for an indirect determination of soil water isotope composition using the in-situ measurement under field conditions. In our opinion it is straight forward to apply such a system directly in the field, rather than doing extensive laboratory testing. A comparison under laboratory conditions as suggested

**HESSD**

12, C3136–C3144, 2015

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Comment

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Interactive Discussion

Discussion Paper



by the reviewer won't give you information about the robustness of your system under field conditions. If you do measurements in remote areas which are only accessible with a four wheel drive vehicle it can be necessary to unmount your analyzer each time you want to measure at a different spot. Hence you need to give the analyzer at least 1 to 2 hours to warm up, for our particular setting (i.e. climate conditions, type of analyzer, etc...). We agree that heterogeneity of soil surface water content. This is especially the case if the soil is recently wetted or in an intermediate state of soil moisture. Both extremes the very dry and the very wet state show lower variability. As you stated this is already well known and many research has been done to account for the heterogeneity of soil moisture (i.e. Western et al., 2004). The driving processes for soil moisture distribution and isotope distribution in soils can be different. For instance, water vapor transport might cause a change in isotope composition due to evaporation and condensation without introducing a net flux of moisture in the soil column. However, this will depend on the considered time scale. Effects such as vapor transport and/or biological processes might discriminate between isotopologues causing even more variability as only caused by soil physical properties. A decision on whether one method is better than the other depend on the question to answer. Therefore it might be recommendable to provide different approaches for the determination of soil water isotopes (i.e. in-situ, cryogenic extraction or others) to account for different water pools and states (i.e. vapor and water) and fractionation factors of soil water. The latter depends also on the calibration procedure of an in-situ system. Finally there is no study applying an in-situ system in a semi-arid remote area that we are aware of. In addition, nobody compared this methodology to an extraction method to verify their applicability other than with another equilibration method, which would logically lead to similar results. Multi methodical approaches will become more important if soils other than with sandy texture are of interest. The limits and potentials with this regard will be discussed in more detail in the final manuscript.

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).

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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 profiles “only”.

ANSWER: If the Laser spectrometer is able to measure in continuous mode (such as Picarro or the newer models of LGR) it is only necessary to control the air inlet using valves with any kind of control device (see Volkmann and Weiler, 2014; Rothfuss et al., 2015). In contrast to previous studies we used an OA-ICOS DLT-100 device of Los Gatos Research, which is a liquid water isotope analyzer. As you know it is not possible to measure continuously with this device. The measurement cycle is explained in our paper (6124L24-L29). If you want to measure several samples automatically you must maintain the communication via the RS-232 interface. Otherwise you can only use the manual injection mode or the spectrometer will complain about a missing laboratory auto sampler. However with our configuration a laptop, microcontroller or any other device having a serial connection and a python shell can be connected to a laser spectrometer. Then it can be used as it would be run with liquid injections. In addition the common correction templates can be used and each measurement can be treated as it would be a liquid sample injected by an auto sampler. This for us means a laboratory like operation. To our knowledge this was not done before and hence is rather unique. From a technical point of view the reliability of the system depends upon each used component (i.e. valves, computer, interface etc). The Bottleneck of the system in terms of maintenance are the membrane probes, air supply and standard container. The membrane pores might clog in fine textured soils and need to be cleaned; the dry air supply is limited on the size of tank provided. It is recommendable to refresh the standards in the containers at least every two days to avoid misleading results. However, this will depend on the size of the container and the water content of the prepared standard.

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

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Discussion Paper



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.

ANSWER: The accuracy is determined using a quality check standard. The offset between the drift and span corrected values and the known value will lead to the accuracy. . Though, it is a standard of known isotopic composition that is treated as an unknown sample. (P6124 L14-17) The accuracy might be affected by either drift that could not be corrected by the drift standard or device specific properties affected by environmental conditions. The accuracy is not related to the repetitions at each depth and hence does not reflect reservoir conditions! In contrast, the analytical precision of each sample is determined from the standard deviation of repetitive measurements. Hence, this value reflects the uncertainty related to the measurement cycle and a potentially exploited reservoir (see table 2). These values are comparable to other in-situ studies (see Volkmann & Weiler (2013)). Besides, the analytical error for soil water extraction in the laboratory especially for very dry soils can be 3 and 5 times higher for  $^{18}\text{O}$  and  $^2\text{H}$  respectively (see Königer et al., 2011). Hence the analytical error is better for the in-situ approach.

### 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,  $^2\text{H}$  and oxygen-18,  $^{18}\text{O}$ )" should read: "hydrogen and oxygen stable isotopes in water (e.g., deuterium,  $^2\text{H}$  and oxygen-18,  $^{18}\text{O}$ )".

3/ "a linear relationship between  $^2\text{H}$  and  $^{18}\text{O}$  on a global scale" is not correct. Please replaced with "a linear relationship between water  $^2\text{H}$  and  $^{18}\text{O}$  isotopic compositions

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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? ANSWER: We changed “General isotopic composition” to “The isotopic composition”

P6118L10. Consider replacing “intensively” with “actively” ANSWER: We changed “intensively” to “actively”

P6118L19. Consider replacing “intense” with “intensive” ANSWER: We changed “intense” to “intensively”

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. ANSWER: (Volkman and Weiler, 2014) used custom built soil water vapor standards. However the statement you are referring says: “All standards were measured at 17,000 ppmv water vapor mixing ratio using the vaporizer unit of the analyzer and an autosampler” [P3749L40] (Rothfuss et al., 2013)

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? ANSWER: Vapor transport processes can be an important variable of the soil water balance especially in arid zones. Small changes in water content can cause high changes in matrix potential. This can have a significant contribution to the soil water balance and might also affect the stable isotope composition of soil water (Soderberg et al., 2012).

## STUDY SITE AND METHODS

P6121L16-17. Consider replacing “between the 9 and 15 June 2014 and the second

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between 15 and 22 November 2014” with “between June 9th and 15th, 2014 and the second between November 15th and 22nd, 2014” ANSWER: We replaced “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. Particulate 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. ANSWER: We will remove the figure and report the results in the text only.

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” ANSWER: We replaced as recommended.

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. ANSWER: We changed as recommended.

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  $R_{\text{sample}}(-)$  denotes the isotope ratio to VSMOW and SLAP, respectively” with: “where  $R_{\text{sample}}(-)$  denotes the 18O/16O isotope ratio (respectively 2H/1H) of a water sample and  $R_{\text{standard}}(-)$  those of the Vienna Standard Mean Ocean Water (VSMOW)”.

ANSWER: We rewrote “where  $R_{\text{sample}}(-)$  denotes the isotope ratio to VSMOW and SLAP, respectively” with: “where  $R_{\text{sample}}(-)$  denotes the 18O/16O isotope ratio (respectively 2H/1H) of a water sample and  $R_{\text{standard}}(-)$  those of the Vienna Standard Mean Ocean Water (VSMOW)”.

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P6123L5. Replace “by.van Geldern” with “by van Geldern” ANSWER:We replaced as recommended.

#### References:

Rothfuss, Y., Vereecken, H., and Brüggemann, N.: Monitoring water stable isotopic composition in soils using gas-permeable tubing and infrared laser absorption spectroscopy, *Water Resour. Res.*, 49 (6), 3747–3755, doi:10.1002/wrcr.20311, 2013.

Volkmann, T. and Weiler, M.: Continual in-situ monitoring of pore water stable isotopes, *Hydrol. Earth Syst. Sci.* (18), 1819–1833, doi:10.5194/hess-18-1819-2014, 2013.

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Western, Andrew W.; Zhou, Sen-Lin; Grayson, Rodger B.; McMahon, Thomas A.; Blöschl, Günter; Wilson, David J. (2004): Spatial correlation of soil moisture in small catchments and its relationship to dominant spatial hydrological processes. *Journal of Hydrology* 286 (1-4), S. 113–134. DOI: 10.1016/j.jhydrol.2003.09.014.

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## HESSD

12, C3136–C3144, 2015

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