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Hydrology and Earth System Sciences
Discussions



# *Interactive comment on* "Determining the stable isotope composition of pore water from saturated and unsaturated zone core: improvements to the direct vapor equilibration laser spectroscopy method" *by* M. J. Hendry et al.

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## Genral comments

The manuscript presents the improvements for the relatively new method of direct vapor equilibration laser spectroscopy. These improvements result from experiences, which were gained in the last years by the presenting research group. The method evaluations cover comparisons with mechanical squeezing and piezometer samples, possibilities of contamination by drilling, minimum required water in the geologic/soil



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sample, gas sampling bags and possible effects on the analysis, and contamination of the analysis by hydrocarbons. The issues presented in the manuscript are of high relevance, since the evaluated method is widely used. However, a comparison with the very often used cryogenic extraction (West et al., 2006) is still missing. Nevertheless, the paper addresses relevant scientific questions within the scope of HESS, since the presented improvements are novel and will ensure a proper application of the direct vapor equilibration laser spectroscopy.

The paper is well written and structured with treating one after another all of the issues that the study addresses. A summary completes the manuscript, while conclusions come relatively short. The figures would be much easier to understand if legend were provided.

I propose a publication of the manuscript in HESS, after minor changes that I address in the following specific comments.

**Specific comments**

6243 ln 18: Consider referring to West et al. (2006) for the cryogenic extraction, since the accuracies are better for the newly developed cryogenic extraction methods (see also the comment to 6244 ln23).

6243 ln 22/23: Another alternative is microwave-distillation (Munksgaard et al., 2014).

6244 ln23: Reference to newer studies that show higher accuracies: e.g. West et al. (2006), Orolowski et al. (2013), Koeniger et al. (2011).

6247 ln 7: How do you explain the offset in the second sandy layer between piezometer samples on the on one hand and DVE-LS and squeezing on the other hand?

6251 ln 10-12: “In contrast, mean temperatures measured in the dry core samples were nine times greater than the mean in the piezometers.” Since the temperature is given in °C, which is a relative scale, I don’t think “nine times greater” is the correct term here.



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6252 ln 15-19: At which depth did you find the isotopically enriched pore waters in the unsaturated zone? Can you make sure that the samples did not experience the natural process of evaporation fractionation in the topsoil? Plotting the d-excess over the depth would help indicating a possible natural origin of the isotopic signal due to evaporation. Could you see a relation between measured temperature in the soil samples of the dry sonic coring and the d-excess?

6254 ln 23: Did you check water losses within the first 10 days of storage? Freezer bags filled with 250 – 300 g soil have shown to lose 1 g of water (loss of ca. 0.4 %) in 10 days. (see poster by Herbstritt et al. (2014): http://www.hydro.uni-freiburg.de/publ/pubpics/post229)

6256 ln 17-19: Why is an average loss of 0.26 $\pm$ 0.18 g with the IsoPaks considerable, but an average loss of 0.27 $\pm$ 0.03 g with the silver pouches negligible?

6257 ln 7: Why do you not discuss the prices of the apparently best bags like mylar, black bags, and silver pouches? Maybe state clearer that black bags (and maybe also mylar bags) are not suitable because of the carbon contamination.

6257 ln 22: You list beside the CuO quartz oxidation tube two other methods that you tested to remove hydrocarbons. However, you do not discuss the other two. I would expect a discussion, why the reverse flow Nafion scrubber and the activated carbon tube is not recommended.

6257 ln 25: I am not sure if citing a conference paper is the best solution here (https://gsa.confex.com/gsa/2014AM/finalprogram/abstract_246284.htm). Why not extending this section instead, since Pratt is coauthor? This would give the reader a better overview of the issue.

6257 ln 26: In the abstract by Pratt et al. (2014), they write about C1-C6, but you talk about C1-C5.

6258 ln 9: The section 5 on “Minimum water content required for DVE-LS analyses of



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core samples" is missing in the summary.

**Technical corrections**

6246 ln 22: ma.s.l.? I guess it is BG

6263 ln 12: "fine-grained" instead of "find-grained"

6263 ln 13: doi: 10.1306/031104740736

6263 ln 13: "research methods papers" gives the impression that this is the subtitle. However, it is the classification within the journal. Consider erasing.

Figures: I generally prefer a legend for the indication of the symbols in figures.

Figure 1: "High-resolution profiles vs. elevation above sea level"? I guess it is BG

Figure 1: The fact that the yellow shaded areas represent sandy parts could be stated in the caption. What does the broken line at about 14 m BG indicate?

Figure 2: Why do you plot the solid and open stars that "represent isotopically-spiked drill waters for coreholes for samples trimmed in the field and laboratory, respectively", although the subplot (a) represents trimmed in the field and (b) trimmed in the laboratory. I find it inconsistent to plot the stars in both plots.

Figure 5 and Figure 6: Why plural in "The location of the water table is identified by inverted triangles."? I only see one inverted triangle.

Figure 11: Consider giving the water loss in [%] instead of [g] to have a relative measure. In addition, a figure where the relative deviation from the test pore water is given as a function of the water loss [%] would indicate a threshold of water losses that results in a deviation of the isotopic analysis that is bigger than the standard errors.

**References**

Koeniger P, Marshall JD, Link T, Mulch A. 2011. An inexpensive, fast, and reliable method for vacuum extraction of soil and plant water for stable isotope analyses by

mass spectrometry. Rapid Communications in Mass Spectrometry 25: 3041–3048.

Munksgaard NC, Cheesman AW, Wurster CM, Cernusak LA, Bird MI. 2014. Microwave extraction–isotope ratio infrared spectroscopy (ME-IRIS): a novel technique for rapid extraction and in-line analysis of $\delta$18O and $\delta$2H values of water in plants, soils and insects. Rapid Communications in Mass Spectrometry 28: 2151–2161.

Orlowski N, Frede H, Brüggemann N, Breuer L. 2013. Validation and application of a cryogenic vacuum extraction system for soil and plant water extraction for isotope analysis. Journal of Sensors and Sensor Systems 2: 179–193.

West AG, Goldsmith GR, Brooks PD, Dawson TE. 2010. Discrepancies between isotope ratio infrared spectroscopy and isotope ratio mass spectrometry for the stable isotope analysis of plant and soil waters. Rapid Communications in Mass Spectrometry 24: 1948–1954.

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Interactive comment on Hydrol. Earth Syst. Sci. Discuss., 12, 6241, 2015.