UNIVERSITY OF
SASKATCHEWAN

September 21, 2015

Dr. Stumpp

Re: “Improvements to the direct vapor equilibration laser spectroscopy method.”

Please find attached the author response to the reviewers’ comments of the manuscript ‘Improvements to the direct vapor equilibration laser spectroscopy method’ by M. Jim Hendry, E. Schmeling, L.I. Wassenaar, S.L. Barbour and D Pratt for your consideration. We believe we have addressed all questions raised by the two reviewers of the manuscript.

As requested, we included a detailed response to reviewer’s questions (below). A revised version will be provided once a decision has been made to accept or reject the manuscript.

The comments and questions posed by the reviewers are presented below. To ease the assessment of our responses to the questions posed by the reviewers, the reviewer’s questions are presented in black font and our responses are presented in blue font following the question.

If you have any additional questions, we would be more than happy to address them.

Regards,

Jim

Comments from Reviewer 1 (M. Sprenger):

General 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 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 legends 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 line 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).

Agreed. We will add this reference to the Introduction.

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

Agreed. We will add this alternative method and reference to the Introduction.

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

Agreed. We will add references to the Introduction.

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?

This was a question we pondered since we collected the profile. Although we are confident in the analyses, we have no definitive explanation for this observation. The piezometer was installed at 8.75 m BG in the second sand layer one year after the core samples were collected. Unfortunately we have no additional data from this sand layer to compare to the squeezed and vapour samples at the time of collection. We attribute the differences on values to a rapid change in source water for this shallow aquifer (as evidenced by the sharp isotopic interface across the lower boundary of the sand). We will clarify this in the text.

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.

Agreed. We changed the wording of the sentence to read, “In contrast, mean temperatures measured in the dry core samples were on average 40°C greater than the mean in the piezometers.”

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?

The purpose of presenting these data was to highlight how deep sonic coring of waste rock can be used to establish isotopic profiles and to note the difficulties in using water in the drilling process due to difficulties associated with sample contamination by the drilling fluids. We believe that the question of how these profiles should be interpreted given the expected fractionation is outside the scope of this manuscript. It is, however, the subject of a manuscript we are currently preparing.

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)

A good question. Unfortunately we were unable to measure the water content in the first 10 days of storage because the drilling campaigns were 8-14 days long. By the time we returned to the lab and allowed the samples to equilibrate, the samples had been stored for more than 10 days. We will add a statement to the revised text.

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

There was a typographical error in this line, the IsoPaks had an average loss of 0.26± 0.18 g but the silver pouches had an average loss of 0.027± 0.03 g. We will correct this error in the revised text to read, “In contrast, water loss from the mylar, black bags, and silver pouches over the test period was negligible at 0.02±0.01, 0.05±0.02, and **0.03±0.03 g**, respectively.”

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.

Agreed. We will revise the text add the sentence, “Mylar bags, black bags and silver pouches (USD 41/100 bags, USD 16/100 bags, and USD 24/100 bags) not suitable for the DVE-LS method because of possible volatile organic 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.

Agreed. A discussion will be added. This added text will be: “The method of construction of the Nafion gas scrubber presents inherent errors in the isotopic signature; the water available to pass through the Nafion membrane is trapped in a stacked fashion in the pore space of the membrane and was not possible to strip it from the pore spaces between samples. Further, we encountered a problem with our ability to maintain water flow rates through the membrane that were high enough to support an isotopic measurement in the laser spectrometer (with respect to sample vapour volume and pumping rates). An activated carbon tube was also investigated, while it removed hydrocarbon gas successfully, it also removed water vapour in the sample resulting in erroneous measurement in the laser spectrometer.”

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.

Agreed. We will add a summary from the comment.

6257 ln 26: In the abstract by Pratt et al. (2014), they write about C1-C6, but you talk about C1-C5.
We will alter the text to read, “Only the CuO oven removed 100% of the hydrocarbons at concentrations up to about 5 vol% as C_1-C_6.

6258 ln 9: The section 5 on “Minimum water content required for DVE-LS analyses of core samples” is missing in the summary.

We will add a summary of section 5 to pg 6259 line 10.

Technical corrections
6246 ln 22: ma.s.l.? I guess it is BG
We will change the text to read, “...seasonally ranged from 0.15 to 0.89 m BG.”

6263 ln 12: “fine-grained” instead of “find-grained”
We will correct the typogrpahical error in this line.

6263 ln 13: doi: 10.1306/031104740736

We will add the doi to this reference.

6263 ln 13: “research methods papers” gives the impression that this is the subtitle. However, it is the classification within the journal. Consider erasing.
We will delete the line, “research methods papers.”

Figures: I generally prefer a legend for the indication of the symbols in figures.
We believe that this is a personal preference decision. We commonly present the materials in the figures in the manner used in the manuscript to minimize clutter on the figure. As such we prefer to leave the figures as they are. If it is, however, the journal requirements for such legends to be present on the figures, we will change them.

Figure 1: “High-resolution profiles vs. elevation above sea level”? I guess it is BG
We will change the text to read, “High-resolution profiles vs. meters below ground.”

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?
We will state that yellow shaded areas represent sand layers.

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.
We will retain the solid stars in Figure 2(a), as this represents the drill mud used during this drilling campaign. We will also retain the open stars on Figure 2(b) because this drill mud was used during the second drilling campaign.

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.
We will change the text to read, “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.

We will modify the figure to water loss in % rather than grams. We will also add Figure 11(d), which will be water loss (%) vs. deviation from isotope standard value.

Comments from Reviewer 2 (anonymous):

General Comments:

I have completed my review of this manuscript and recommend publishing it in its current form. I seldom have such clear recommendations, but this ms makes a very good contribution to the community of researchers focusing on porewaters in aquitards.

The methods that the authors have tested here will be very useful to a number of researchers, and so this publication is very timely. The writing and organization is excellent. The ms suffers from no grammatical or typographical errors that I could find, and there are a few recommendations that I can make to improve the ms. The authors might consider the following points and questions, although subsequent changes are not critical.

Specific Comments:

1. What are crystal clear bags? Is this a trademarked product or a general description?
   Yes, these are a trademarked product made by Pacific Bags Inc. We will add a TM symbol beside all references to the crystal clear bags.

2. In previous studies I understand that the Ziploc bags are double sealed, i.e. sealed in a second Ziploc. Was this the case here?
   Yes, these bags were also double sealed inside a large-sized Ziploc bag. We will add this for clarification in the section.

3. Were septum-fitted containers such as Exetainers or IsoJars considered?
   We did not consider Exetainers. We did consider IsoJars for an unrelated experiment, however, there was not enough headspace in the IsoJars when connected to the Picarro for the amount of time it takes to obtain a measurement; the vacuum in the jars increased and they collapsed.

4. Picarro makes an accessory oven to combust organics during vapour injection. Was this device considered?
   No. This oven is attached in-line between a vaporizer and the analyzer for liquid water analyses. We are unsure whether it can be used to analyze the vapour directly from the Ziploc bag into the analyzer. Testing is required.

5. Figure 9: this is the reservoir effect on the residual water in the sample after loss to equilibrium of vapor in the headspace. Perhaps this could be clarified.
   Agreed. We will add this clarification point to the revised manuscript.

Comments from the Editor (Christine Stumpp):

General Comments:

Two reviewers thoroughly evaluated the manuscript. Below, I briefly summarize the main comments:

1) give explanation for differences in isotope values in second sandy layer (Figure 1)

Reviewer #1 raised this question and it is addressed above. This was a question we pondered since we collected the profile. Although we are confident in the analyses, we have no definitive explanation for this observation. The piezometer was installed at 8.75 m BG in the second sand layer one year after the core samples were collected. Unfortunately we have no additional data from this sand layer to compare to the squeezed and vapour samples at the time of collection. However, we attribute the difference to a rapid change in source water for this shallow aquifer (as evidenced by the sharp isotopic interface across the lower boundary of the sand). We will clarify this in the text.

2) more specific details about used bags and procedure for carbon removal required

Details related to the bags tested were addressed in reviewer comments. Specifically:

1) the fact that the Ziploc bags were sealed inside large-sized Ziploc bags will be added to the text.
2) Information about the cost of the silver foil pouches, mylar bags and black bags will be added to section 7.
3) Comments regarding exetainers and IsoJars were addressed in the anonymous reviewers comment section.

In addition, the following text will be added to address the carbon removal method:

The method of construction of the Nafion gas scrubber presents inherent errors in the isotopic signature; the water available to pass through the Nafion membrane is trapped in a stacked fashion in the pore space of the membrane and was not possible to strip it from the pore spaces between samples. Further, we encountered a problem with our ability to maintain water flow rates through the membrane that were high enough to support an isotopic measurement in the laser spectrometer (with respect to sample vapour volume and pumping rates). An activated carbon tube was also investigated, while it removed hydrocarbon gas successfully, it also removed water vapour in the sample resulting in erroneous measurement in the laser spectrometer.

3) include main points of required minimum water content in summary

We will add a brief comment on this important aspect to the summary and conclusions that will include the need for a minimum of 3 g of water in a 1 L sample bag and alternately increasing the sample (and bag) size.

4) minor technical corrections required

In addition to the reviewer comments, I have some minor additional comments which should be addressed when revising the manuscript:

1) p6243, ln7-10: All the advantages of core samples are mentioned, but it is also worth mentioning that cores give time integrative information. This is probably sufficient in systems like aquitards and some specific research questions. However, when temporal information is required or dynamics are studied (e.g. unsaturated zone), either core

samples have to be taken more often (and then heterogeneities might be crucial) or traditional water sampling methods are more beneficial.

We agree. We will add text to acknowledge that this method is best applied when the primary goal is spatial variability (vertical) of the stable isotopes of water rather than temporal variability. If temporal variability is of concern at specific locations, recent advances in the real-time sampling of soil vapour (references will be added) may be more appropriate. Interestingly, the fundamental basis for these methods (equilibrium fractionation between the aqueous and vapour phases) remains the same as the method described in this paper.

2) p6244, ln19: Give ranges of analytical precision

We will add the analytical precision of the method to line 19. The analytical precision for the core method is ±0.4‰ for $\delta^{18}O$ and ±2.1‰ for $\delta^{2}H$.

3) p6244/45, ln29/1-3: some very recent studies have been published for<15 m (Sprenger et al. 2015) and <100m (Filippini et al. 2015) Sprenger, M., Volkmann, T.H.M., Blume, T., Weiler, M., 2015. Estimating flow and transport parameters in the unsaturated zone with pore water stable isotopes. Hydrology and Earth System Sciences, 19(6):2617-2635. DOI:10.5194/hess-19-2617-2015 Filippini, M., Stumpp, C., Niejenhuis, I., Richnow, H.H., and Gargini, A., accepted. Evaluation of aquifer recharge and vulnerability in an alluvial lowland using environmental tracers. Journal of Hydrology, doi: 10.1016/j.jhydrol.2015.07.055

We will add these references to line 29 on page 6244 and lines 1-3 on page 6245.

4) p6248, ln6: how many liters of 99% deuterium oxide were used? Just to give the reader an idea on potential costs for such methods

Agreed. The statement will be modified to include "(0.015 mL of D2O per 1 L of water at a cost of USD1/mL of D2O)."

5) p6251, ln12/13: But does the temperature increase also affect the isotopic composition (e.g. due to stronger evaporation during sample preparation)? Not generally, but most of the samples from dry sonic drilling are more enriched compared to wet sonic drilling. Can you get any information from d-Excess depth profiles?

This question was raised by Reviewer #1. Our response to his question was: The purpose of presenting these data was to highlight how deep sonic coring of waste rock can be used to establish isotopic profiles and to note the difficulties in using water in the drilling process due to difficulties associated with sample contamination by the drilling fluids. The question of how these profiles should be interpreted given the expected fractionation is outside the scope of this manuscript. It is, however, the subject of a manuscript we are currently preparing.

6) p6252, ln23: has Barbour et al. (2015) been accepted? Otherwise, remove sentence

This manuscript will be submitted to HESS in the coming weeks. As such, the sentence will be replaced with: A method for correcting these profiles for fractionation associated with core heating and water loss has been developed and will be submitted for consideration in the near future.

7) p6257, ln12/14: references required

Can Cite: Hendry et al 2011b and

Brand, W. A.; Geilmann, H.; Crosson, E. R.; Rella, C. W. Cavity ring-down spectroscopy versus high- temperature conversion isotope ratio mass spectrometry; a case study on δ2H and δ18O of pure water samples and alcohol/water mixtures. Rapid Commun. Mass Spectrom. 2009, 23 (12), 1879−1884.

Schmidt, M.; Maseyk, K.; Lett, C.; Biron, P.; Richard, P.; Bariac, T.; Seibt, U. Reducing and correcting for contamination of ecosystem water stable isotopes measured by isotope ratio infrared spectroscopy. Rapid Commun. Mass Spectrom. 2012, 26 (2), 141−153.

8) p6258, ln16: I would not say that it is in widespread use considering that only a couple of labs worldwide have been doing the analysis to date; certainly, the potential is high to use the method even more frequently in future.

Although we have helped establish laboratories in Australia, Texas, China and Scotland, we agree that it is not yet in widespread usage. We will change the sentence to read, "...developed by Wassenaar et al. (2008) and is becoming more frequently used."

9) p6258, ln25: is the temperature really no issue here?

Correct - this was a mis-statement on our part. Dry sonic drilling can adversely impact measured values as noted in the sentence at the end of the same paragraph. That sentence reads "DVE-LS analyses on core samples collected from thick unsaturated zones using wet and dry sonic methods should be avoided due to contamination by drill water and heating during sonic coring resulting in kinetic fractionation, respectively." To correct this mis-statement, the bracketed text "(e.g., Dry sonic)" will be removed from the line in question.

10) p6259, ln21: this is a general statement and I suggest deleting :and being conducted by our group"

We will delete, "and are being conducted by our group."

11) Figure 6: It would be good having information about temperatures on second y axis

We will add temperature data to a secondary y-axis. Temperature data will also be added to Figure 5.