

## ***Interactive comment on “Technical note: an alternative water vapor sampling technique for stable isotope analysis” by César Dionisio Jiménez-Rodríguez et al.***

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We would like to thank the reviewer for his/her valuable comments on our manuscript. We appreciate that the reviewer acknowledges the interest and relevance of our study. Nonetheless, the reviewer indicated some issues which we will clarify point-by-point:

1) One essential point is missing in this study: there is no evidence that one can rely on the air-tightness of the bags. Are the selected bags really appropriate for collecting discrete vapor samples? The magnitude of weight loss of moist samples through the wall of different containers and bag types has been shown previously (Herbstritt et al., 2014). The assumption that the deviation of the laboratory air from the collected air

C1

samples is ‘. . . good indication that there is no mixing. . .’ is not verified. What would the isotopic composition of the sampled vapor look like after a few days or weeks of storage? Maybe you can’t trust the PE bags and the difference in D-Ex between sample A and samples B/C is not due to the different sampling sites one day before but due to evaporation through the wall of the sampling bag?

Reply: We agree that this was missing, so following the comments and recommendations from both reviewers and Mr. Gralher, we developed an extra experiment aiming to clarify the performance of the LDPE sampling bags. The full experiment is available as an appendix to this reply and as a proposal to add its results to this manuscript. In this extra experiment we compared the consistency of air stored in our LDPE-bag to two commercial air-sampling bags: Tedlar and Foil bags. We collected air samples and stored them in these different types of bags on ‘day 0’ and analysed the samples 1,2,9, 16 and 17 days after collection. The bag samples were also compared to direct measurements of the laboratory air by the WVIA. Additionally, we also weighted the bags to check the conservation of mass.

As the main result, we confirm the low reliability of the LDPE bags when compared to the foil bags and direct measurements with the WVIA. However, the performance of the LDPE is better than the performance of the cold traps. We also found that not only our LDPE bag was affected by the ambient laboratory air, but also the other 2 bags likely due to the water vapor transmission rate of the different materials (Tock, 1983). This confirms the pattern described by Herbstritt et al. (2014) who depicted the effect of water mass loss by diffusion through the wall of different sampling materials for the determination of stable isotope signatures of soil pore water under equilibrium conditions. This experiment and its results are added as supplemental material to the reply to the reviewers.

2) Further, it is not discussed why sample D (= sampled laboratory air) does not match the directly analyzed laboratory air (Table 1). A simple test for the reliability of the sampling bags could be to fill the potential sample containers with dry gas (< 1000

C2

ppm) and check the vapor concentration from time to time over the course of several days or weeks.

Reply: Thank you for pointing out this issue. In fact, this interpretation is a misunderstanding from our methods where it was not clearly explained that the sampling date in the laboratory is not the same as when the samples were analysed. Hence 'sample D' and 'laboratory' should not have a similar isotopic value per se. In method section 2.2.4, page 7, line 3 we omitted to mention that Sample D was collected one week before the measurement at the laboratory. We added the "laboratory" sample as a background validation during analysis to show the "Laboratory" as a proof of that no laboratory air was leaking and/or mixing within the inlet used to convey the air from the sampling bag to the Multiport Inlet Unit. We agreed that we haven't mentioned the time difference between the sample collection and sample analysis.

Due to the lack of this essential information and the missing proof of the sample bags' reliability, the manuscript cannot be recommended as a reference for operators of this technique and therefore should be rejected.

Reply to Specific Comments

1) In my opinion, Experiment 1 and 2 are quite similar to the work of Kurita et al., 2012 and Aemisegger et al., 2012. It is true that response times (Exp. 1) may differ due to the setup, i.e. the dead volume of tubings etc. and due to the between-sample differences in the isotopic composition (memory effect) but information on the response time is given more or less in the instruments specifications (user manual) already.

Replay: The aim of experiment 1 was set as "The first experiment (Section 2.2.3) aimed to determine the minimum air volume required to obtain measurements of 2H and 18O with standard deviations lower than 1.5‰ and 0.30‰ respectively to ensure reliable measurements (Kurita et al., 2012)." We cited Kurita et al. (2012) as the source of our target accuracy for individual samples, whilst the methodology of the experiment 1 aims to describe the time required for the specific conditions of our device.

C3

This is important for all users in order to define the specific time required to get a stable signature depending on the tubing length of their laboratory setup, as it is mentioned later on by the same reviewer: "It is true that response times (Exp. 1) may differ due to the setup, i.e. the dead volume of tubings etc. and due to the between-sample differences in the isotopic composition (memory effect) but information on the response time is given more or less in the instruments specifications (user manual) already". Therefore, we decided to provide a practical way to determine the required volume considering the specific device and setup used.

In respect to Aemisegger et al. (2012), we state in Section 2.2.3 that we are following the Aemisegger et al.'s methodology. This one was applied to check whether the minimum volume defined in the previous section of the same experiment is driven by the device's white noise or not: "This analysis determines the time interval from where the moving average is driven by the laser white noise and not by the memory effect of the previous sample. This analysis evaluates the difference between consecutive measurements ( $y_i$  and  $y_{i+1}$ ) aggregated at the same time interval ( $\tau$ ) and averaged over the total number of measurements ( $n$ ) (Aemisegger et al., 2012; Allan, 1966)".

2) Some clarifications of details in the method sections would be necessary, as some important information was skipped e.g. how were the vapor concentrations of the vapor standards generated?

Replay: In Section 2.1 Instrumentation it states that: "A Water Vapor Isotope Analyzer (WVIA; model 912) was used to determine the isotope signature of water vapor samples, with the support of a LGR Water Vapor Isotope Standard Source (WVISS; model 908-0004-9002) employed to provide a controllable flow of water vapor with a known liquid standard measurement for an absolute calibration of raw measurements". Additionally, the methodology of each experiment describes the specific water vapor concentrations used for the calibration.

3) Also, "dried" laboratory air with a vapor concentration of around 5000 ppm isn't really

C4

“dry”; it rather seems to be quite high compared to the produced vapor standards of 4600 ppm, 6500 ppm and 8350 ppm. Was the produced “dry” air used to dilute the produced vapor standards?

Replay: Actually, we used the term “dried” instead of dry because we did not completely dry the air on purpose. In the Section 2.2.3 Experiment 1: Response Time, we mention the following: “In order to identify the memory effect from a previous analysis, ambient air from the laboratory and dried air were measured alternately with the same time intervals (Fig.1)”. This shows that the idea of alternating the target sample with dried air from the laboratory was to provide a completely different isotope signature before the target sample. In this way, we were able to determine the precise moment when the signature recorded by the WVIA has no memory effect anymore of the previous sample. Additionally, the “dried air” collected with the MIU is different from dry air required for the WVISS.

Consequently, we propose to add the following sentence on page 3, line 21 (Section 2.1) to clarify the difference between the dried air for the MIU and the dry air source for the WVISS:

“The dry air needed for the WVISS was provided by the Dry Air Source (DAS) device from LGR.”

We hope that this will clarify that the “dried air” used on the first inlet of the MIU is completely different than the dry air required for the dilution of the water standard source (DAS).

4) Furthermore, in Experiment 2, the memory effect is not reduced by the “dried” air. In this case, it would have been rather reduced by analyzing the samples subsequently, as their isotopic composition is quite similar.

Replay: This is a misunderstanding of the following sentence: “The variation provided by the source of dried air in between samples allows to identify among individual sam-

C5

ples and to observe the capacity to reduce the memory effect from the previous air sample”. In this case, we refer to the capacity of the first 2 min of measurements to get rid of the memory effect from the isotopic signature provided by the dried air.

5) The cold trap samples appear to be enriched in d2H relative to the bag sample data, but in the case of incomplete condensation, I would expect that both isotope ratios are affected. This is not the case for d18O. Obviously, the cold trap data show higher variabilities than the vapor samples but seem to correspond more or less to the precipitation (liquid) sample at the respective day whereas bag sample data don't.

Replay: According to the results from the additional experiment performed, we decided to remove this experiment from the manuscript.

6) Why is there no difference along the sampled profile in the vapor bags (Exp. 3)? Did the authors expect to see different isotopic compositions in the vertical profile or why was this setup chosen? Would it be possible that the isotope data of the sampled vapor were flawed by diffusive exchange through the bags' wall with ambient air prior to analysis?

Replay: We were expecting to see differences among heights as a consequence of transpiration from the canopy. After the additional experiment we carried out, we agree with the reviewer about the diffusive exchange through the bag's wall. However, the additional experiment showed that cold traps differ strongly from the direct measurements with the WVIA and the error between cold traps and benchmark are bigger than the LDPE bags.

#### References

Aemisegger, F., Sturm, P., Graf, P., Sodemann, H., Pfahl, S., Knohl, A., and Wernli, H. Measuring variations of d18O and d2H in atmospheric water vapour using two commercial laser-based spectrometers: an instrument characterisation study, *Atmospheric Measurement Techniques*, 5, 1491–1511, <https://doi.org/10.5194/amt-5-1491->

C6

2012, 2012.

Allan, D.: Statistics of atomic frequency standards, *Proceedings of the IEEE*, 54, 221–230, <https://doi.org/10.1109/PROC.1966.4634>, 1966.

Herbstritt, B., Limprecht, M., Gralher, B., Weiler, M.: Effects of soil properties on the apparent water-vapor isotope equilibrium fractionation: Implications for the headspace equilibrium method [poster presentation], UNI Freiburg. Available at: <http://www.hydro.uni-freiburg.de/publ/pubpics/post229>, 2014.

Kurita, N., Newman, B. D., Araguas-Araguas, L. J., and Aggarwal, P.: Evaluation of continuous water vapor D and <sup>18</sup>O measurements by off-axis integrated cavity output spectroscopy, *Atmospheric Measurement Techniques*, 5, 2069–2080. , <https://doi.org/10.5194/amt-5-2069-2012>, 2012

Orlowski, N., Pratt, D. L., and McDonnell, J. J.: Intercomparison of soil pore water extraction methods for stable isotope analysis. *Hydrol. Process.*, 30: 3434–3449. , <https://doi.org/10.1002/hyp.10870>, 2016

Tock, R. W.: Permeabilities and water vapor transmission rates for commercial polymer films. *Advances in Polymer Technology: Journal of the Polymer Processing Institute*, 3(3), 223-231. <https://doi.org/10.1002/adv.1983.060030304>, 1983.

Wassenaar, L. I., Ahmad, M., Aggarwal, P., Duren, M., Pölsenstein, L., Araguas, L. and Kurttas, T.: Worldwide proficiency test for routine analysis of  $\delta^2\text{H}$  and  $\delta^{18}\text{O}$  in water by isotope ratio mass spectrometry and laser absorption spectroscopy. *Rapid Commun. Mass Spectrom.*, 26: 1641-1648. , <https://doi.org/10.1002/rcm.6270>, 2012.

Please also note the supplement to this comment:

<https://www.hydrol-earth-syst-sci-discuss.net/hess-2018-538/hess-2018-538-AC1-supplement.pdf>

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