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Hydrology and Earth System Sciences
Discussions

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

Anonymous Referee #1

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General comments

In their manuscript entitled 'An alternative water vapor sampling technique for stable isotope analysis' the authors aim at developing a field vapor sampling method for later water stable isotope analysis of the samples in the laboratory using an OA-ICOS laser-based isotope analyzer (LGR, WVIA 912). They present isotope data from two laboratory experiments and one field sampling campaign. Overall, the manuscript is well structured. However, the language is somewhat imprecise and needs to be improved.

In general, I appreciate the authors' contribution to the field of isotope hydrology and their attempt to establish a water vapor sampling technique for isotope analysis. Since

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water vapor sampling for isotope analysis with laser-based analyzers is currently receiving increased attention with several issues still being unsolved, this contribution appears to be of interest for the readers of Hydrology and Earth System Sciences. However, I think that some questions still need to be addressed, as some assumptions are not correct and the conclusions that were drawn thereof are inadmissible. Also many of the results are discussed rather briefly.

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

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.

Specific comments

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

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in the isotopic composition (memory effect) but information on the response time is given more or less in the instruments specifications (user manual) already.

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? Also, “dried” laboratory air with a vapor concentration of around 5000 ppm isn’t really “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? 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.

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. 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?

References:

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