

***Interactive comment on* “Technical note: comparison of water vapor sampling techniques for stable isotope analysis” by César Dionisio Jiménez-Rodríguez et al.**

Anonymous Referee #3

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I am reviewing the manuscript of César Dionisio Jiménez–Rodríguez and colleagues, entitled “comparison of water vapor sampling techniques for stable isotope analysis” submitted as technical note and currently under discussion for HESS.

The authors investigated in the laboratory the short to mid-term (1-16 days) reliability of different plastic sampling bags for isotopic analysis of water vapor, as an affordable alternative to the online analysis with laser-based spectrometers. They highlight that only one commercial product (made out of MPE) provided reliable results, independently from storage time. The authors don't say clearly what could have been the cause of the change with time in isotopic composition of the sampled water vapor in the

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two other types of bags, although they show the influence of the laboratory air during measurement. If the bags were not tight, then the influence of the laboratory air would not be restricted to the time of measurement, but would spread from sampling to measurement times (i.e., over the whole storage duration). To me, this points to a tightness problem during measurement. The laser spectrometer seemed to have sampled from a mix of laboratory air and bag air and measured some average-weighted water vapor isotopic composition. This should be thoroughly addressed by the authors.

I also urge the authors to remove the part on cryogenic extraction from the benchmarking, as it was not working well enough during the experiment and is off-topic.

I found the text to be difficult to read at times and generally not well structured. I am afraid it did not undergo sufficient internal review before it was submitted to HESS. I provide the authors with many comments and corrections below.

Technical comments:

Throughout the manuscript: - stick to past tense for things that happened in the past.
- provide unit/dimension for all parameters and variables present in the different equations

Abstract P1L1. The first two sentences read awkward. I propose something like: "The isotopic characterization of water vapor samples can help describing evaporation processes. However the collection of water vapor, which historically involves phase change, may be associated with fractionation in case of incomplete sampling. "The isotope signature of a parcel of air was continuously monitored with a cavity. . ." P1L4-5. You did not sample the same air parcel with different methods simultaneously, rather you sampled from the same air parcel simultaneously with different methods.

1 Introduction

P1L11. The isotopes or isotopologues are the tracers, not their isotopic signatures.

P1L12. "Water stable isotopes..". Also move the deltas to the previous sentence. You

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are not talking about their signatures here.

P1L14. Consider citing a more recent review on plant water use isotopic applications, e.g., Rothfuss and Javaux (2017).

P1L15. Remove "only" from this sentence: sampling precipitation conservatively is not that straightforward actually.

P1L17. Some sample cannot describe evaporation processes, please rephrase.

P1L18-19. "It is formed by water vapor originated from evapotranspiration (plant transpiration and soil evaporation) and of intercepted water..." What about free water surfaces (streams, lakes, etc.)?

P1L20-22. This should be shortened: go straight to keywords evapotranspiration partitioning.

P1L22. "has been..."?. It is still the case and will always be, right?

P2L4-15. This level of detail in this section is not needed. Also it is confusing: at this point, it is not clear anymore what you are referring to "water vapor"; is it the atmospheric water vapor or the evaporated water vapor? Since you are addressing the potential isotopic effects of the sampling bags during/following collection/storage of atmospheric water vapor, this first "technique" is off-topic.

P2L17. "collects"

P2L17-23. These two sentences are hard to read, should be merged and shortened, e.g. the "second method consists in..." (it is the operator who collects); "conveyed at..."; "requires sublimating...". What you need to say is that we have two different classes of measuring techniques: 1- online, direct and continuous and 2- offline. The second technique is then subdivided in two sub classes: a-direct (with sampling bags) and indirect (via sublimation).

P2L20-23. Again, these sentences are hard to read: a sample does not collect itself;

there is no such thing as “heavier isotope signatures”. An isotopic signature does not “occur”. You should write something like: “The collection of water vapor in cold-traps for isotopic analysis is only a reliable technique when recovery rate tends towards 1; an incomplete recovery of water vapor fractionates water stable isotopes following the Rayleigh distillation model”

P2L25-26. We measure the isotopic composition of water vapor, not the “water stable isotopes”. Change “cavity output spectroscopy” to the general term “laser-based spectroscopy”.

P2L31. What is a “storage unit”?

P3L1-3. I think there is a conceptual misunderstanding here: the equilibration bags for soil water vapor are water-tight (due to the hydrophobic nature of the plastic) but let the water vapor diffuse through their walls. The observed problems have not to do with “[liquid] water diffusing through the container wall”

P3L3-4. Why are you referring to “units” here? In the abstract you say “sampling bag”. You should stick to one lexical field/terminology.

2 Methodology

2.1 Instrumentation and Measurements

P3L12. Why is mentioning the voltage of the water pump of interest to the reader? How do they relate to the “controlled water vapor concentration”? Please explain. Also you mean water vapor “mixing ratio”, and not “concentration”.

P3L13. What is a “sample set here”?

P3L17-18. “allows the connection to different sampling devices. . .”. It is “inlet” or “port”? Stick to wording for ease of reading.

P3L18-21. Why do you need the altered water vapor source?

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P3L23-24. "The first 3 minutes were discarded from the analysis to account for memory of the instrument to the previous sample". Users know that memory effect is due to the turnover rate of the volume ahead and inside the cell of the laser. No need to say this.

P3L24-25. Please revise grammar

Figure 1. I don't think the drawing is necessary. Text is enough to me. Also both liquid and vapor modes are missing the part of the analyzer itself. They should be renamed e.g. vapor and liquid "peripheral devices".

P4L1-5 & Eq. (1). This is also not needed. Also terminology is not correct: "hydrogen and oxygen isotopic ratios are expressed relatively to those of the SMOW" not "Isotope signatures (^2H and ^{18}O) [...] were expressed in respect to the Vienna Standard Mean Ocean Water (VSMOW)". A signature is the relative deviation of some ratio with respect to another, meaning it remains a ratio, only on another scale. So why is a "signature" termed as "relative concentration" when "ratio" isn't? They are all ratio of concentrations.

2.2 Water Vapor Correction

You address here the problem of the nonlinear response of the laser spectrometer to changes of water vapor mixing ratio, which translates into a dependency of the raw isotopic readings to water vapor mixing ratio in the measuring range. This section's text is overall not well structured. Choose your wording carefully and stick with it. It starts with the title: it should read something like "Water vapor isotopic calibration". The isotopic terminology is sometimes not adequate (e.g. "The raw signatures of $\delta^2\text{H}$ and $\delta^{18}\text{O}$ "). I advise you to be as precise as possible and write "water vapor mixing ratio" and not "concentration of water molecules" (does not apply here: the LGR measures water vapor mixing ratio, not concentration) or "ppm concentration" (does not mean anything).

P4L8-10. Revise sentence structure. It is hard to read.

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P4L10-12. Revise sentence as well: how did you measure evaporated standard water at different water vapor mixing ratio? Is it by changing the water pump flow rate (hence the different voltage values mentioned earlier?) or by adapting the dry air flow rate? I understand you did a one-point calibration rather than a two-point (span) calibration? Have you investigated the laser dependency to water vapor mixing ratio at another value of isotopic composition?

Eqs (2-5): they yield to $\delta^{18}\text{O}=\delta^{18}\text{O}_{\text{standard}}$ and $\delta^2\text{H}=\delta^2\text{H}_{\text{standard}}$, so something does not add up here. Please revise. A “good” instrument is characterized by a slow time drift of a, b and c; is this the case?

2.3 Experimental Design

P5L15-16. “. . .the isotope signature of the stored air water vapor samples remains. . .” or the “the water vapor isotope signature of the stored air samples remains. . .”

Points 1.-3. Avoid starting each sentence with “these”

P5L18. “According to the supplier, . . .”

P6L3. Until now, it wasn't clear that the experiment took place in the laboratory. It should be stated early on (abstract + listing of objectives in the introduction). Did you check for complete recovery for the fast (3 L min⁻¹) option by, for, instance measuring the water vapor mixing ratio with the laser spectrometer at the outlet of the trap, or installing a second trap in series to observe if water vapor was collected in it?

P6L8. Was it a simple test tube or something more elaborated (i.e. with an inner collecting wall)? This needs further detail as this greatly impacts the ability of the trap to capture moisture.

2.4 Analysis

This section needs some streamlining: you are unnecessarily repeating yourself (P6L18: “The cross comparison was performed with the Z-score analysis” vs P6L28:

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“The comparison was performed with the Zscore analysis”).

P6L17. Revise sentence, e.g., “you compare the isotopic signature of the samples to that of the benchmark”, not “to the benchmark”.

P6L19. “(Orlowski et al., 2016; Wassenaar et al., 2012), where S is the isotope signature ($\delta^{2}\text{H}$ or $\delta^{18}\text{O}$) of the bags air water vapor and cryogenic water samples, B is the benchmark water vapor isotope signature (WVIA), and μ is the target variability.”

P6L25-26. Here, you are not testing the ability of the association trap+cryogenic bath to fully collect the air moisture, rather you are testing its reproducibility. See my previous comment on P6L3.

3 Results and Discussion

P7L2-3. Revise sentence (“the isotope signature of the benchmark . . . had an isotope signature”)

P7L5-6. Please revise (edit grammar).

P7L15-24 and Fig. 2B. I don’t understand the difference between “cryogenic bath” and “cryogenic test sample”. There is no distinction made in the text here and before. . .but see my general comment: I don’t see how cryogenic water extraction is relevant in your study. Also: use letter “d” for day, or “t” for time, but not “T” (stands for temperature usually).

Rothfuss, Y., and Javaux, M.: Reviews and syntheses: Isotopic approaches to quantify root water uptake and redistribution: a review and comparison of methods, Biogeosci. Disc., 14, 2199-2224, doi:10.5194/bg-14-2199-2017, 2017.

Interactive comment on Hydrol. Earth Syst. Sci. Discuss., <https://doi.org/10.5194/hess-2019-344>, 2019.

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