Hydrol. Earth Syst. Sci. Discuss.,
https://doi.org/10.5194/hess-2018-538-SC1, 2018

Hydrology and Earth System Sciences
Open Access
Discussions

# *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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Received and published: 13 November 2018

General comments:

In their manuscript, Jimenez–Rodriguez et al. describe a method to collect discrete water vapor samples for subsequent analysis on a laser-based water stable isotope analyzer. For this purpose, they investigated in a three-step experiment (a) the minimum air sample volume required for meaningful data acquisition based on the system response time and the ideal aggregation time period, (b) the consistency of isotope data from continuous sampling of unique sources, and (c) the utility of commercially available polyethylene bags for the collection of discrete vapor samples from remote

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locations. Conservative collection and storage of large numbers of discrete vapor samples at reasonable costs has been a challenge so far. This is mainly due to the lack of suitable sampling containers that would minimize the risk of samples being compromised during handling and storage due to their small reservoir size and resulting high susceptibility to contamination via exchange with ambient atmospheres. A solution of this issue would significantly expand the potential of the increasingly popular laser-based water stable isotope analyzers which is well within the scope of HESS.

However, there appear to be severe misinterpretations of the presented data. Unfortunately, the authors did not compare their sample bag results with data from alternatives of water vapor stable isotope measurements they would have considered trustworthy. The differences between direct laboratory air measurements and bag-sampled air from the same location (Sample D) are remarkable (Table 1) but ignored in the manuscript. The differences between data from bag-sampled air and cold traps are attributed to the alleged failure of the latter. But then why are the authors showing these data? Comparison of vapor concentrations during sampling and during measurements would have been helpful but are missing.

Specifically, I would have expected the cold trap data to follow a trend line, similar to an evaporation line, in dual isotope space as a result of the alleged incomplete vapor sampling. This was not the case (Fig. 8). Neither did they plot towards the upper right of the sample bag data as must be the case after enrichment in 18O and 2H taking the allegedly unflawed sample bag data as the origin of this evolution. In my perception, the cold trap data may indeed represent the natural variability of sampled air masses. Sample bag isotope data were quite consistent and, moreover, strongly deviating from the cold trap cluster in dual isotope space. However, even if cold trap data were flawed there is no proof that bag samples were not subject to exchange with each other and or via the ambient atmosphere. Conversely, unintended exchange would well explain the similarity of their vapor isotopic compositions. The statement that the mere difference between isotope signatures of laboratory air vapor and bag-sampled vapor is a “good indication” that no exchange occurred is not justified. And it is proven wrong when some of the bag samples were supposed to represent the very laboratory air.

Polyethylene bags similar to the ones used in this study have been shown to allow for evaporative loss of water resulting in measurable changes of the contained water vapor stable isotopic composition within several days of storage (Hendry et al., 2015, doi: 10.5194/hess-19-4427-2015). This happened despite the enclosed water vapor being in isothermal equilibrium with a markedly bigger liquid water reservoir present in the co-enclosed natural soil sample. The vapor-only reservoirs investigated in this study were several orders of magnitude smaller than a typical soil sample liquid water reservoir (microliters vs. milliliters) and must therefore be expected to reveal measurable changes in their isotopic compositions within mere minutes. This is the reason why commercially available gas sampling bags, e.g. Lindebags, include one layer of diffusion-tight metal foil.

In summary, the authors did not demonstrate that sample bag data do in fact represent what they are claimed to represent. Furthermore, I do not see how a re-interpretation of the presented data would suffice the aim of a reliable method for collecting representative discrete water vapor samples. The first two steps of the described experiment are mainly a repetition of the work of Aemisegger et al. (2012, DOI: 10.5194/amt-5-1491-2012) with insufficient novelty to justify their publication. I therefore regret to say that I recommend rejecting this manuscript. Further, I provide a list of detailed comments below that should help to improve a future manuscript.

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Specific comments and Technical corrections:

Title: alternative to what?

P1-L4: insert “isotopic” before “fractionation”

P1-L5: the quality of the measurement should be characterized because the analyzer will provide continuous data regardless of source. However, only after sufficiently long analysis of a sufficiently large reservoir these data will be e.g. representative, stable, reliable, meaningful, or reasonable. + delete “one” + capacity of what?

P1-L7: I know “under . . . conditions” but not “under. . .set up”. Please rephrase.

P1-L8: tense: can -> could, allows -> allowed

P1-L11: “resolution”, not “variation”

P1-L11: insert “with” before “the cold traps”

P1-L13: given the following sentences, this must be evapotranspiration, not evaporation. What are the provided references referring to?

P1-L16: rephrase to e.g. “. . .surfaces. Their partitioning is. . .” or “... surfaces with their partitioning being ...”

P1-L22: incorrect isotope terminology: delta values do not refer to isotopes but to isotope ratios. Please rephrase.

P2-L1: please be more specific: It’s the isotope fractionation factors that depend on temperature.

P2-L1f: rephrase to e.g.: “Physical isotope fractionation is driven by water phase change and also to a lower extent by diffusion.” Mixing is a conservative process and does not cause fractionation although it does in fact produce a different isotopic composition in the case of two distinct reservoirs being mixed.

P2-L4: delete “whilst” or connect the two sentences

P2-L5: “caused by”, not “caused during”

P2-L7: “unidirectional”? E.g. net evaporation or net condensation is the result of a mismatch between the absolute evaporation flux and the absolute condensation flux. This makes it highly bidirectional.

P2-L20: start new sentence: “However,. . .”

P2-L30: please rephrase: the risk is not ISOTOPIC fractionation. This is in fact taken into account. The risk is incomplete sampling.

P3-L1: please quantify “short”

P3-L2: improvements regarding what?

P3-L6: “inTO the field”

P3-L7: what are “controlled run temperatures”? + insert “apply” after “restrictions”

P3-L8: insert “isotope” before “fractionation”

P3-L11: insert “isotope” before “fractionation”

P3-L12: signature -> signatures

P3-L13: insert “the” before “cold”

P3-L16: please be more specific, e.g. “A LGR (ABB - Los Gatos Research Inc., San Jose, CA, USA) Water Vapor. . .”

P3-L16: signature -> signatures

P3-L18: colloquial language, please rephrase, e.g. “with measurements of liquid water standards of known isotopic composition. . .”

P3-L22f: I do not understand this sentence, please rephrase

P3-L24: 5000ppm? Dried air should have no more than a few hundred ppm remaining vapor mixing ratio. Please comment on the high number you encountered

P3-L24f: I do not understand this sentence, please rephrase

P3-L30: please specify what makes these standard deviations meaningful. For example, are they sufficient to discriminate samples that represent the natural variation of isotope ratios on typical timescales?

P4-L1: signature -> signatures

P4-L3: analyses, not analysis + what kind of analyses? + tests, not test

P4-L6: isotope signatures are expressed in delta values, not just in heavy isotopes + “are” or “were” before “expressed”

P4-L7f: please describe the calibration procedure and the correction – if necessary – of drift and vapor concentration effects during liquid water analyses

P4-L8: please define the abbreviation “IWA”. Is this the “WVIA”?

P4-L15 (and throughout the manuscript): this is a correction, not a calibration, usually resulting in a normalization of raw isotope data to a reasonable water vapor mixing ratio (see e.g. Schmidt et al., 2010, DOI: 10.1002/rcm.4813 or Johnson et al., 2011, DOI: 10.1002/rcm.4894 for more details). Please state why you chose to do differently

P4-L19: please provide more details on “automatically” + “a” means only one. How many different waters were used for this step?

P4-L21: I do not understand “water molecule concentrations depending on the air sample concentrations”

P4-L22: is -> was

P4-L24: are -> were

P4-L24f: add here that these were calculated using equations 2 & 3 + I suggest to not use the symbol alpha as it represents fractionation rather than correction factors in isotope contexts

P4-L27: value -> values + is -> were

P5-L8: was, not were

P5-L12: “run” -> “was run” or better “was conducted”

P5-L16f: this statement should be placed after the description how one minute was determined as ideal aggregation time period.

P5-L18: insert “statistical” or equivalent before “analysis”

P5-L19: isn’t it the standard deviation of the moving average that is governed (not driven – sloppy jargon)? + why not connect the two sentences with “and” as they both start with “This analysis”?

P5-L23: insert “it” before “is”

P5-L25: the Allan deviation plots I know have minima at the respective aggregation time. + Are you referring to Figure 5 here? If so, please state. Furthermore, this figure and its discussion should appear first, as your first decision (i.e. the 1-min aggregation time) is based on it.

P6-Figure 1: I do not understand why this effort was necessary. Why wasn’t it sufficient to (perform and) look at the 600 s interval to retrieve the desired information? And isn’t this information already provided in Aemisegger et al. (2012, DOI: 10.5194/amt-5-1491-2012) or could have been concluded from the injection frequency and valve operation pattern of routine liquid water analyses performed on such analyzers? Similar objections apply for the aggregation time.

P6-L5: why were polyethylene bags selected despite being aware of the findings of Hendry et al. (2015, doi: 10.5194/hess-19-4427-2015)? See general comments for details.

P6-L6ff: such paragraphs should be written in past tense

P6-L11: it has -> with

P6-L12: insert “for” before “the tight” + what do you mean by “movement”?

P7-L1: “Air samples were collected manually...”

P7-L6: why didn’t you normalize all measurements to e.g. 10k ppm i.e. calculate the raw isotope numbers the analyzer would have shown if the vapor concentration had been 10k ppm (see e.g. Schmidt et al., 2010, DOI: 10.1002/rcm.4813 or Johnson et al., 2011, DOI: 10.1002/rcm.4894 for details), prior to calibration?

P7-L8: statistical -> statistically significant

P7-L11: commonly, the deuterium excess is indicated by the lower case letter d (in italics)

P8-L7: an -> a

P8-L11: were -> was

P8-L13: it would be important to read that the tubes reached the bottom of the bottles in a way that only the minimized inner cross section area of the tubes allowed for the interfacial exchange between sampled water and ambient atmosphere. Were they installed that way? 15 cm sounds a little short for 5-L bottles. And 9 mm sounds a little wide for this purpose. How would this affect your LMWL?

P8-L14: 6mm inner or outer diameter? Both of which appear quite a lot. + “reduce the vapour exchange“ -> “facilitate pressure compensation while at the same time minimizing loss via vapor diffusion” or equivalent. Pressure compensation is necessary once the inlet tube is submersed into the sampled water which should happen as soon as possible (see previous comment)

P8-L18: simultaneously to the cold trap or to each other?

P8-L19: why not 24? (4 h * 6 samples/h = 24 samples)

P8-L21: please rephrase and start new sentence (the frozen vapor was not closed nor did it collect...), e.g. “The liquid water sample were immediately transferred into...”

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P8-L23: delete “a”

P8-L25: “the” not “its”, because vapor was measured, not vapor condensation or sampling bags

P8-L25f: I do not understand this statement. Wasn’t the concentration at which the samples were analyzed just the one present inside the bags?

P9-Figure 3: this figure should appear in the method section. Throughout the manuscript, all figures should appear near their description.

P9-L8: insert “probably” before “because”, as this is your speculation

P9-L11: please start new sentence (“However,. . .”) + I do not understand “some averages with non stable measurements”

P9-L12: please make sure that figures and their description and discussion appear in the right order

P10-Figure 4: see comment on P6-Figure 1

P10-Figure 5: I am unable to find 0.3‰ or 1.5‰ on the vertical axis, thus I am unable to see what aggregation time is sufficient to reach these standard deviations + the numbers on the vertical axis are not evenly spaced + the label of the horizontal axis should be "aggregation time" or equivalent + this figure and its discussion should appear before any figure featuring 1-min-means because those were chosen based on this analysis of the Allan deviation + “moving”, not “mobile”

P10-L1: aren’t 450 mL calculated quite tightly? What if you have two strongly differing successive samples and the memory effect causes the readings from the second sample to not have stabilized after 240s leaving not enough time for a 1-min-average before the bag is empty? Further, the smaller the vapor reservoir, the higher its susceptibility to contamination + delete “to carry out 300 s of continuous measurements” as you provided this number in the previous sentence already

P11-L2: I do not understand why this step was necessary. Do you have indication that small vapor reservoirs such as your sampling bags would reveal significant variations? If so please elaborate on this also in the introduction

P11-L4: insert “probably” before “because”, as this is your speculation

P11-L6: whose capacity?

P11-L8: signature -> signatures + insert “those of” after “from”

P11-L8f: I strongly disagree with this statement. From your experimental design and data, there is no way of telling whether your bag samples are or are not a mixture of the original (e.g. flux tower) sample and other sources. This would only have been possible if you had analyzed a distinct air directly and sampled it into bags in parallel, then stored the bags while exposing them to a different ambient atmosphere, then analyzed the bag air, and then compared the results of direct and discrete sample measurements.

P11-L10: statistical -> statistically significant + insert “and” between the two delta expressions

P11-L11: insert “probably” before “the reason”, as this is your speculation

P11-L12: insert “probably” before “because”, as this is your speculation + are you referring to the absolute deviation of your arithmetic mean from the true value (i.e. the accuracy) or are you rather referring to the standard deviation (i.e. the precision)? + on -> of

P11-L13: showed -> observed

P11-L14: is this the within-sample or the between-sample deviation?

P11-L15: why would wind change the isotopic composition? Are you referring to different air parcels being sampled?

P11-L16: sampling -> sample + per set of sample or per sample?

P12-Table 1: shouldn't laboratory air and sample D be consistent? Could it be that the sample bags were stored in a confined space where they exchanged with each other? The consistency among A-D is striking. And so is the discrepancy between laboratory air and sample D. Why was sample D not discussed in the manuscript? This could have been an indication that bag samples represent what they are supposed to represent. In order for a potential consistency of lab air and D to be a proof, conditions as described in comment to P11-L8f would have been necessary + in the figure caption: lower case -> superscript + this needs more details. What exactly is different when a, b, c, or d is displayed?

P12-L4: delete "or after" or write "or later on that day"

P12-L5f: given, that you report the LGR measurements in ppm, can you provide ppm values for the observed humidity as well? This might give the reader a clue whether your sampling was conservative or exchange with ambient air has occurred

P12-L10: the offset of the equation has the "unit" ‰

P12-L11: is located -> plots + "heavier" is too colloquial, please rephrase

P12-L12: insert "isotopic signatures" before "water vapor

P12-L13: "lighter" is too colloquial, please rephrase + insert delta symbols before 2H and 18O

P12-L14: insert "show" before "less variation"

P12-L14f: but shouldn't it be the opposite? Cold trap samples should represent a mixture of six potentially variable bag samples. The similarity among air samples leads me to the conclusion that the originally present natural variation, still revealed to some degree by the cold trap data, got completely lost when all bag samples exchanged with or via a similar atmosphere prior to analysis

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P12-L15f: the location of atmospheric vapor isotope signatures relative to the LMWL also depend on the slope thereof

P12-L17f: aren't these interpretations referring to liquid water? You are showing vapor data. Therefore, you first have to determine where the corresponding liquid water reservoir would plot relative to the LMWL before making these statements

P12-L21: insert "isotope" before "signature"

P12-L22: heavier delta2H -> higher delta2h values + incomplete at -70°C? What was the remaining vapor pressure at the cold trap outlet? Assuming that cold trap data might be flawed, why did you present them as a reference for the sample bag data? Why was it not possible to design the experiment in a way that the reference data set (i.e. cold trap) is trustworthy? Further, wouldn't incomplete condensation result in a trend line extending to the upper right of the sample bag data rather than in a data cloud located towards the upper left? + enrichment of what?

P12-L23: delete "it" + replace "is" by "may be", as this is your speculation and strongly depends on setup properties

P13-Figure 7: I suggest "time of day (hh:mm)" as label of the horizontal axis

P13-L3: all -> the entire + exception from big differences? + is shown -> was observed

P13-L4: "Isotope signature at 34m height from cold traps…" -> "Isotope signatures of samples collected at 34 m height via cold traps…"

P13-L4f: what if these data were the true numbers and your bag sample data were flawed?

P13-L7: enriched in what?

P13-L12: what was the air flow rate through the cold traps? This information would be useful to calculate the minimum humidity (in ppm) during sampling. Based on this estimate, further interpretations of the sample bags' diffusion-tightness might be possible

P14-L7: insert “it” after “experiment 2” and “isotope” after “stable”

P14-L7f: please rephrase this sentence

P14-L10: resolution, not variation + please connect the two sentences or rephrase

P14-L12: please connect the two sentences or rephrase

P14-L14: dew temperature -> dew point

P14-L15: of -> or + insert “the dew point in” before “the field”. Do you have a suggestion how to deal with this situation?

P15-Figure 9: proportional to -> indicating

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