

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

**César Dionisio Jiménez-Rodríguez et al.**

cdjimenezcr@gmail.com

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Thanks for the comments and constructive critics on the section “Specific comments and Technical corrections”. We propose some major changes to improve the manuscript according to your recommendations. Additionally, we would like to clarify some misinterpretations or misunderstandings related to specific sections in the paper:

1) 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.

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Reply: Regarding the LDPE suitability as sample container, we perform an additional experiment. 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 analyzed 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) 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.

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 analyzed. 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

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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.

Consequently, with the finding from the additional experiment, we decided to remove this section from the experiment to be replaced with the additional experiment (Supplemental Material).

3) 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.

Reply: The additional experiment described in the first section shows the differences between direct measurements performed with the WVIA, 3 different types of bags and cryogenic samples (with 2 different pumping rates) collected with the same cold traps design as the experiment. The cryogenic samples provide a completely different isotope signature as a consequence of the incomplete condensation, even with the slow pumping rate. We believe, it is useful to provide all the collected data even if these ones do not behave as expected. Often cryogenic extraction is used as a benchmark, however, we show that even the slow pumping rate is not enough to reach full condensation. The data about vapor concentrations were not added to keep a reduce the number of figures and focus mainly about their performance during the sampling under field conditions. Additionally, considering the results from the additional experiment this section will be removed from the manuscript.

4) 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

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of the sample bag data as must be the case after enrichment in  $^{18}\text{O}$  and  $^2\text{H}$  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.

Reply: Thank you for pointing this out. Based on this comment and your first comment we carried out an extra experiment. Indeed we found that the LDPE bags do not perform well in comparison to our benchmark and the foil bags (MPE). However, the LDPE bags do perform better than the cold traps. The data on this new experiment can be found as a supplement to this reply.

5) In summary, the authors did not demonstrate that sample bag data do in fact rep-

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resent 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.

Reply: We agree that we did not demonstrate that the LDPE bag is a proper sample bag. Hence we altered our scope after we did the additional experiment. Our new scope is to compare different types of collection bags. Although we use partly the methodology of Aemisegger, our study differs from them. The aim of Aemisegger et al. was to demonstrate the application of different analyzers for water vapor sampling, while we focus on the collection bags when direct measurements are not possible (see page 3 line 6-8). We mention the origin of the methodology with the specific references (page 5, line 21), and we use this procedure to determine the shorter time to retrieve a stable measurement from our device.

Reply to Specific Comments: Title: alternative to what? Reply: We propose to change the title to “technical note: comparison of water vapor sampling techniques for stable isotope analysis”

P1-L4: insert “isotopic” before “fractionation” Reply: Done, Thanks.

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?

Reply: We changed the sentence into "The first experiment determined the minimum air sample volume required to obtain stable measurements of  $\delta^2\text{H}$  and  $\delta^{18}\text{O}$  with a laser spectrometer. The second experiment determined the ability to . . ."

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

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Reply: In the final manuscript this sentence is removed

P1-L8: tense: can -> could, allows -> allowed Reply: Done, Thanks.

P1-L11: “resolution”, not “variation” Reply: Done, Thanks.

P1-L11: insert “with” before “the cold traps” Reply: Done, Thanks.

P1-L13: given the following sentences, this must be evapotranspiration, not evaporation. What are the provided references referring to? Reply: In this case, we are considering the definition of evaporation provided by Savenije (2004). Thus evaporation is defined as the sum of transpiration, soil and interception evaporation. The provided references refer to the magnitude of terrestrial evaporation on a global scale.

Savenije, H. H.: The importance of interception and why we should delete the term evapotranspiration from our vocabulary. *Hydrol. Process.*, 18: 1507-1511. doi:10.1002/hyp.5563, 2004.

P1-L16: rephrase to e.g. “: : surfaces. Their partitioning is : :” or “... surfaces with their partitioning being ...” Reply: We changed this sentence into: “... by plant and litter surface. The partitioning of evaporation is a key element to understand... “

P1-L22: incorrect isotope terminology: delta values do not refer to isotopes but to isotope ratios. Please rephrase. Reply: Rephrased to: “The stable isotope ratios of  $\delta^2\text{H}$  : :”

P2-L1: please be more specific: It’s the isotope fractionation factors that depend on temperature. Reply: We added: “: : and signature variation due to fractionation is linked to : :”

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. Reply: Thanks, we

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rephrased as follows: “Physical isotope fractionation is driven by water phase changes and also to a lower extent by diffusion while mixing processes can alter the isotopic composition.”

P2-L4: delete “whilst” or connect the two sentences Reply: Whilst is replaced by While

P2-L5: “caused by”, not “caused during” Reply: Done, Thanks.

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. Reply: We meant that during evaporation the lighter isotopes move from the source towards the atmosphere, which is a unidirectional flux. We understand the confusion, so we decided to remove this second part of the sentence from the manuscript.

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

P2-L30: please rephrase: the risk is not ISOTOPIC fractionation. This is in fact taken into account. The risk is incomplete sampling. Reply: Thank you for this suggestion. We have changed the sentence accordingly.

P3-L1: please quantify “short” Reply: We added the approximate time period.

P3-L2: improvements regarding what? Reply: We referred to improvements regarding the accuracy of the machine.

P3-L6: “inTO the field” Reply: Done, Thanks.

P3-L7: what are “controlled run temperatures”? + insert “apply” after “restrictions” Reply: It should be: “controlled room temperatures”. Done, Thanks.

P3-L8: insert “isotope” before “fractionation” Reply: Done, Thanks.

P3-L11: insert “isotope” before “fractionation” Reply: Done, Thanks.

P3-L12: signature -> signatures Reply: This sentence was removed from the

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manuscript.

P3-L13: insert “the” before “cold” Reply: This sentence was removed from the manuscript.

P3-L16: please be more specific, e.g. “A LGR (ABB - Los Gatos Research Inc., San Jose, CA, USA) Water Vapor: : :” Reply: We added this extra information to the manuscript.

P3-L16: signature -> signatures Reply: Done, Thanks.

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

P3-L22f: I do not understand this sentence, please rephrase Reply: Rephrase as “In all the measurements, the first MIU inlet was attached to a dried air source. We used this dried air source, which had a distinctly different isotopic signature than the samples, to identify between the different samples of other MIU inlets in the post-processing of the data.”

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 Reply: This “dried air source” is different from the one used by the WVISS (DAS). Our dried air (not dry) source corresponds to a flux of air not fully dried to provide a different isotope signature during the measurements.

P3-L24f: I do not understand this sentence, please rephrase Reply: We changed the sentence into: “This dried air source was achieved by conveying laboratory air through a 2 L borosilicate bottle that was filled with 1.5 kg of silica gel to dry the laboratory air to a concentration lower than 5000 ppm”

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? Reply: These standard deviation values are rec-



ommended by Kurita et al (2012) as good measurements during the evaluation of laser spectrometers.

P4-L1: signature -> signatures Reply: Done. Thanks.

P4-L3: analyses, not analysis + what kind of analyses? + tests, not test Reply: Thanks for the recommendation. We refer to all the data analysis. We add “data” in the text.

P4-L6: isotope signatures are expressed in delta values, not just in heavy isotopes + “are” or “were” before “expressed” Reply: The  $\delta$  notation is missing here.

P4-L7f: please describe the calibration procedure and the correction – if necessary – of drift and vapor concentration effects during liquid water analyses Reply: We added the following sentence: “The correction and calibration of the isotope signatures of liquid samples were performed with the software LIMS 10.083 (2015)”

P4-L8: please define the abbreviation “IWA”. Is this the “WVIA”? Reply: Corrected, it should be WVIA. Thanks.

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 Reply: We decided to follow the same procedure as Steen-Larsen et al. (2013,2014) and Rambo et al. (2011) because they use similar equipment as we do.

P4-L19: please provide more details on “automatically” + “a” means only one. How many different waters were used for this step? Reply: The WVISS has a software package that provides an automatic calibration according to the settings established by the user. This device allows the use of only one water standard. This water is mentioned on Page 4-line20. We added this information.

P4-L21: I do not understand “water molecule concentrations depending on the air sample concentrations” Reply: This has to do with the specific settings of the device.

The device uses a pump with a specific voltage that allows different water concentration to be injected into the WVIA. So, with the known water signature the device will provide a constant air flow to allow the change of water concentrations (ppm) depending on the isotope water signature. We added this information in the manuscript.

P4-L22: is -> was Reply: Done. Thanks.

P4-L24: are -> were Reply: Done. Thanks.

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 Reply: Thanks for the recommendation. We changed alpha into “ $\varphi$ ”.

P4-L27: value -> values + is -> were Reply: Done. Thanks.

P5-L8: was, not were Reply: Done. Thanks.

P5-L12: “run” -> “was run” or better “was conducted” Reply: Done. Thanks.

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

P5-L18: insert “statistical” or equivalent before “analysis” Reply: Done. Thanks.

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”? Reply: We changed the sentence into; “This statistical analysis determines the time interval from where the moving average value is only coming from the white noise of the laser and not by the memory effect of the previous sample. Additionally, the analysis evaluates. . .”

P5-L23: insert “it” before “is” Reply: Done. Thanks.

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

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and its discussion should appear first, as your first decision (i.e. the 1-min aggregation time) is based on it. Reply: Yes, the Allan deviation does reach the minimum value after the aggregation time of 600 seconds. And we are referring to figure 5, however, the figure location will be solved with the final typesetting.

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.

Reply: Aemisegger et al. (2012) determine the minimum time required to have reliable measurements from an outdoor system (direct measurements from the atmosphere). In our case, we follow the same procedure to determine the minimum time required for an indoor system with less variations. In our case, the variability depends on the memory effect and dead volume along the tubing. We perform the experiment in this way to determine if smaller sampling times will trigger changes in isotope signatures due to the no reduction of the memory effect along the tubing. Longer volumes of air guarantee the reduction, but small volumes won't allow the reduction of the memory effect.

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. Reply: Response to this can be found in the previous section on General Comments.

P6-L6ff: such paragraphs should be written in past tense Reply: Done. Thanks.

P6-L11: it has -> with Reply: Done. Thanks.

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

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Done. I do mean connector.

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

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?

Reply: The device has an internal calibration for 10K ppm. However, it is necessary to perform the calibration proposed by Steen-Larsen et al. (2013,2014) and Rambo et al. (2011) due to the internal drift of the WVIA.

P7-L8: statistical -> statistically significant Reply: Done. Thanks.

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

P8-L7: an -> a Reply: Done. Thanks.

P8-L11: were -> was Reply: Done. Thanks.

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? Reply: This is a typo on the manuscript. The bottle is 2.5 L. Thanks for the observation.

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)

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Reply: It was 6 mm of outer diameter and we follow the description giving by Gröning et al (2012).

P8-L18: simultaneously to the cold trap or to each other? Reply: It should be “simultaneously to the cold trap”. Thanks for the suggestion.

P8-L19: why not 24? (4 h \* 6 samples/h = 24 samples) Reply: Yes, it is 24 samples.

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

Reply: Done. Thanks.

P8-L23: delete “a” Reply: Done. Thanks.

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

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? Reply: Yes, but it is necessary to perform the calibration because of the WVIA drift as it was mentioned previously on the section 2.2.2. We changed ‘analysis’ for ‘calibration’.

P9-Figure 3: this figure should appear in the method section. Throughout the manuscript, all figures should appear near their description. Reply: This issue depends on the Latex processor and can be solved during typesetting.

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

P9-L11: please start new sentence (“However,: : :”) + I do not understand “some averages with non stable measurements” Reply: We refer to those measurements with a standard deviation bigger than the defined thresholds. We clarified this in the manuscript.

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

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the right order Reply: This issue depends on the Latex processor and can be solved during typesetting.

P10-Figure 4: see comment on P6-Figure 1 Reply: Done. Thanks.

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 + Reply: In the Allan Deviation graph, we have to see the stable line on the plot and not the Standard Deviation, because the procedure to estimate those ones is completely different. "moving", not "mobile". Reply: Thanks, Done.

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? Reply: Here, we are specifying the minimum volume required to provide a reliable measurement with the standard deviation thresholds established for both isotopes. Additionally, the reason for providing a "dried air" (not dry air) was to provide a different isotope signature between measurements to determine the memory effect of a different sample.

Further, the smaller the vapor reservoir, the higher its susceptibility to contamination Reply: The definition of a minimum air volume required provides information about the type of sampling bag is needed. So, the user can determine later on according with their project restrictions the volume to be sampled in the field.

+ delete "to carry out 300 s of continuous measurements" as you provided this number in the previous sentence already. Reply: Thanks for the recommendation.

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 Reply: We just want to confirm the aggregation time

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

P11-L6: whose capacity? Reply: This should be "ability".

P11-L8: signature -> signatures + insert “those of” after “from” Reply: Done. Thanks.

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. Reply: This issue about the LDPE bags suitability for sampling in the field is discussed on the supplemental experiment. We have to conclude that the LDPE is indeed not suitable for collecting water vapor for longer than 1 day. Therefore we removed experiment 3 from the manuscript.

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

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

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 Reply: Thanks for the recommendation.

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P11-L13: showed -> observed Reply: Done. Thanks.

P11-L14: is this the within-sample or the between-sample deviation? Reply: This is between samples. Thanks.

P11-L15: why would wind change the isotopic composition? Are you referring to different air parcels being sampled? Reply: Considering the forest matrix where the tower is placed, low wind conditions will allow a stronger signature from the Douglas Fir transpiration. Whilst with stronger wind, the footprint will retrieve isotope signatures from other blocks mixed with the signature from the forest stand under analysis. However, we decided to delete this experiment from the manuscript.

P11-L16: sampling -> sample + per set of sample or per sample? Reply: Done. Thanks.

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.

Reply: We agree that this was unclear. Please have a look at our reply in the general comments where we clarify what we did.

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? The note at the bottom of the table states that lower case letters on the same column are statistically different. Each letter represents a homogeneous group determined with the Tukey test.

P12-L4: delete "or after" or write "or later on that day" Reply: Done. Thanks.

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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.

Reply: Thanks for the recommendation. Unfortunately, we don't have data on the humidity in the laboratory. However, we changed experiment 2 completely by comparing different sample bags in time to a benchmark and the open inlet.

P12-L10: the offset of the equation has the "unit" % Reply: Corrected. Thanks.

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

P12-L12: insert "isotopic signatures" before "water vapor Reply: Done. Thanks.

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

P12-L14: insert "show" before "less variation" Reply: Done. Thanks.

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 Reply: This is explained in the additional experiment.

P12-L15f: the location of atmospheric vapor isotope signatures relative to the LMWL also depend on the slope thereof. Reply: We decided to remove experiment 3

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 Reply: We refer to the cold traps. Considering the issues of incomplete condensation showed with

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the additional experiment. We decided to remove experiment 3

P12-L21: insert “isotope” before “signature” Reply: We decided to remove experiment 3

P12-L22: heavier  $\delta^2\text{H}$  -> higher  $\delta^2\text{H}$  values + incomplete at  $-70\text{ }^\circ\text{C}$ ? What was the remaining vapor pressure at the cold trap outlet? Reply: We decided to remove experiment 3

Assuming that cold trap data might be flawed, why did you present them as a reference for the sample bag data? Reply: We showed this as a comparative experiment. However, we did not expect the issues with the cold traps and neither the LDPE bags. We decided to remove experiment 3

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?

Reply: The enrichment in  $\delta^2\text{H}$  shows the data above the sampling bags. This pattern was seen as well with the additional experiment added as supplemental material to this response. Therefore we decided to remove experiment 3.

P12-L23: delete “it” + replace “is” by “may be”, as this is your speculation and strongly depends on setup properties Reply: We decided to remove experiment 3

P13-Figure 7: I suggest “time of day (hh:mm)” as label of the horizontal axis Reply: We decided to remove experiment 3

P13-L3: all -> the entire + exception from big differences? + is shown -> was observed Reply: We decided to remove experiment 3

P13-L4: “Isotope signature at 34m height from cold traps: : :” -> “Isotope signatures of samples collected at 34 m height via cold traps: : :” Reply: We decided to remove

experiment 3

P13-L4f: what if these data were the true numbers and your bag sample data were flawed? Reply: After the additional experiment, we check the incomplete condensation of the cryogenic samples and the issues from the LDPE bags. We decided to remove experiment 3

P13-L7: enriched in what? Reply: We decided to remove experiment 3

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. Reply: The air flow through the cold traps is specified on section 2.2.5 (3 L min<sup>-1</sup>). We decided to remove experiment 3

Based on this estimate, further interpretations of the sample bags' diffusion-tightness might be possible. Reply: Thanks for the recommendation. We did this in our new experiment 2, which is added as supplementary text to this reply. Based on these results we decided to change our scope and remove experiment 3.

P14-L7: insert "it" after "experiment 2" and "isotope" after "stable" Reply: Done. Thanks.

P14-L7f: please rephrase this sentence Reply: Done. Thanks.

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

P14-L12: please connect the two sentences or rephrase Reply: Done. Thanks.

P14-L14: dew temperature -> dew point Reply: Done. Thanks.

P14-L15: of -> or + insert "the dew point in" before "the field". Reply: Done. Thanks. Do you have a suggestion how to deal with this situation? Reply: Not yet.

P15-Figure 9: proportional to -> indicating Reply: The figure caption states: "propor-

tional to the standard deviation of each sample". However, we decided to remove experiment 3.

Please also note the supplement to this comment:

<https://www.hydrol-earth-syst-sci-discuss.net/hess-2018-538/hess-2018-538-AC3-supplement.pdf>

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Interactive comment on Hydrol. Earth Syst. Sci. Discuss., <https://doi.org/10.5194/hess-2018-538>, 2018.

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Discussion paper

