Reply to anonymous referee #2

In blue we copied the comments of the reviewer, in black our replies.

The study of Jiménez-Rodríguez et al. examines different ways of sampling and storing atmospheric water vapor for water stable isotope analysis in the lab. Their technical note is very well written and the photos and technical drawings provided inthe Supplementary are very helpful and support the description of the experimentsin a very concise way. In addition to questions raised by referee 1, I have a few more questions and suggestions on improving the manuscript that you can find in the uploaded pdf file.

The authors thank the reviewer for his/her additional remarks aiming to improve the manuscript. Following his/her suggestions, we provide a reply for each of them:

Comment 1. Page 1, Line 1: Water vapour samples from which hydrological component?
Reply: we changed for:

"Atmospheric water vapor samples are key elements …"

Comment 2. Page 1, Line 1: From where? The soil, open water body...? Be more specific.
Reply: we changed for:

"… to describe the different elements of the evaporation process (e.g, plant transpiration, soil evaporation and the evaporation of intercepted water on wet surfaces) thanks to …"

Comment 3. Page 2, Line 28: "has" instead of "have"
Reply: Done.

Comment 4. Page 3, Line 3: add ","
Reply: Done.

Comment 5. Page 3, Line 3: "sampling bag's"
Reply: we changed the sentence changing "storage units" for "sampling bags"

Comment 6. Page 3, Line 4: The "aim of the research" needs a few more sentences.
Reply: we improved the "aim of the research" as follows:

"The aim of this work is to evaluate different sampling procedures to collect atmospheric water vapor and analyze the stable water isotopes. This experiment tested whether the stored mass of vapor remained unchanged as well as whether the isotope signature of the stored air samples remain consistent in time. We included three sampling bags to determine their suitability for sampling, storing and analyzing water vapor isotopes. The results were compared against a set of cryogenic samples and direct measurements performed with a cavity output spectrometer."

Comment 7. Page 3, Line 19: Identify what?
Reply: we used this distinctive isotope signature to identify each of the individual samples. We updated the sentence as follows:

"… compared to the samples. It was used to identify the measurements of each individual sample with the order of the MIU inlets during the post-processing of the data. The altered …"

Comment 8. Page 3, Line 21: "modify" instead of "modified"
Reply: Done.

Comment 9. Page 3, Line 21: add "water vapor"
Reply: Done.

Comment 10. Page 3, Line 25:Did you also test longer measuring times?
Reply: We did not test different measuring times, since after 120 s the isotopic signal did not change.

Comment 11. Page 5, Line 2: Wrong sentence structure.
Reply: We restructure the sentence to be more readable as follows:

"…sample concentrations. This correction was carried out during the water vapor sampling and the posterior measurement of the samples. The correction procedure was performed every time the MIU start a new round of measurements. The raw signatures …"

Comment 12. Page 5, Line 4: Tenses
Reply: We corrected the tenses as follows: "were" for "are".

Comment 13. Page 5, Line 15-16: This sentence should go at the end of the introduction, too.
Reply: Thanks for the recommendation. We followed your suggestion adding it to improve the aim of the research.

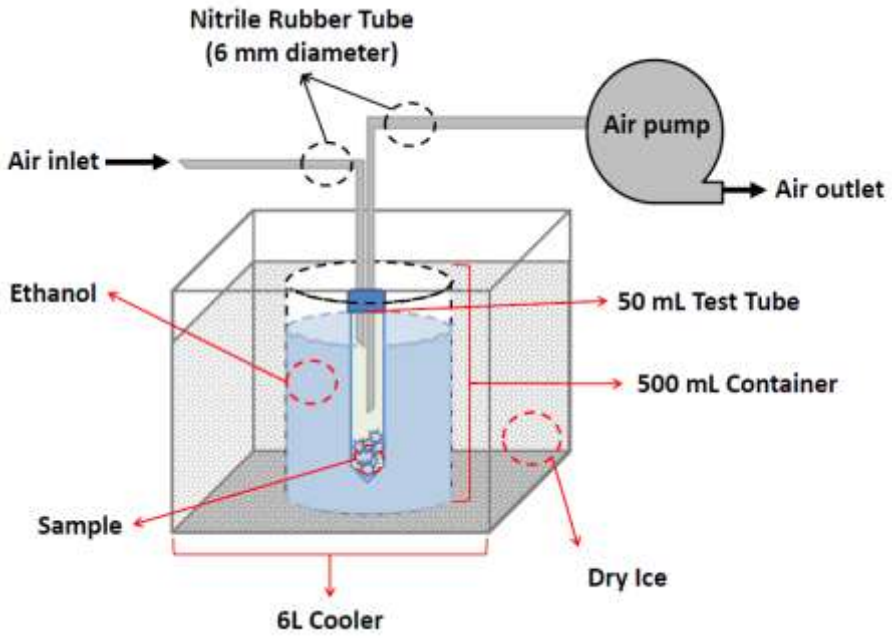
Comment 14. Page 5, Line 18: "to" instead of "with"
Reply: Done.

Comment 15. Page 5, Line 23: Could you please provide the distributor?
Reply: MPE and PVF sampling bags are distributed by "MediSense", while the LDPE bags by "HARDIRON Store". However, the authors do not think this information is relevant for the manuscript considering that the technical information of the samples is already available (Page 5, lines 17 to 24; and the Appendix A).

Comment 16. Page 6, Line 5: Could you please provide the distributor?
Reply: the CPR balloon is distributed by "Praxisdienst" in The Netherlands but the authors do not think this information is relevant for the manuscript. However, we agree that it requires a bit more of technical information. Consequently, we add the following in page 5, line 6:

"… the sample bags. This device has a balloon with a volume of 1.0 L. It is made with sturdy Polyvinyl Chloride (PVC) with a Positive End-Expiratory Pressure (PEEP) valve to release the air when excess of pressure is present. Also, the WVIA …"

Comment 17. Page 6, Line 9: Could you also provide a technical drawing for this setup?
Reply: We add the following image as an Appendix to the manuscript.



Comment 18. Page 6, Line 22: add ","
Reply: Done.

Comment 19. Page 6, Line 25: add "atmospheric"
Reply: Done.

Comment 20. Page 7, Line 3: add "of the"
Reply: Done.

Comment 21. Page 7, Line 6: Do you have data on the initial ppm values of the sampled air?
Reply: Yes, we have the measurements during the sampling period and the measurement of the samples. This is a good point to be added to the manuscript. Consequently, we decided to add the following in the results section in page 7, line 2 as follows:

"Atmospheric water vapor concentration during the collection of samples had a mean value of 17 930 ± 369 ppm. This concentration changes with time during the different days of measurement (Figure 2). Between the measuring days 2 and 9 the water vapor concentration drops from 18000 ppm to less than 14000 ppm, while towards the measuring day 19 it increased with 1000 ppm more. This trend is tightly followed by the PVF sampling bags, followed by the LDPE with a larger difference and the MPE with small variations respect to the atmospheric water vapor concentration of the samples collection. This data shows that all the sampling bags exchange water vapor from and towards the atmosphere with a different degree of magnitude."

Page 7, line 26-27:

"… stable isotope measurements and water vapor concentrations, including the MPE bags. …"

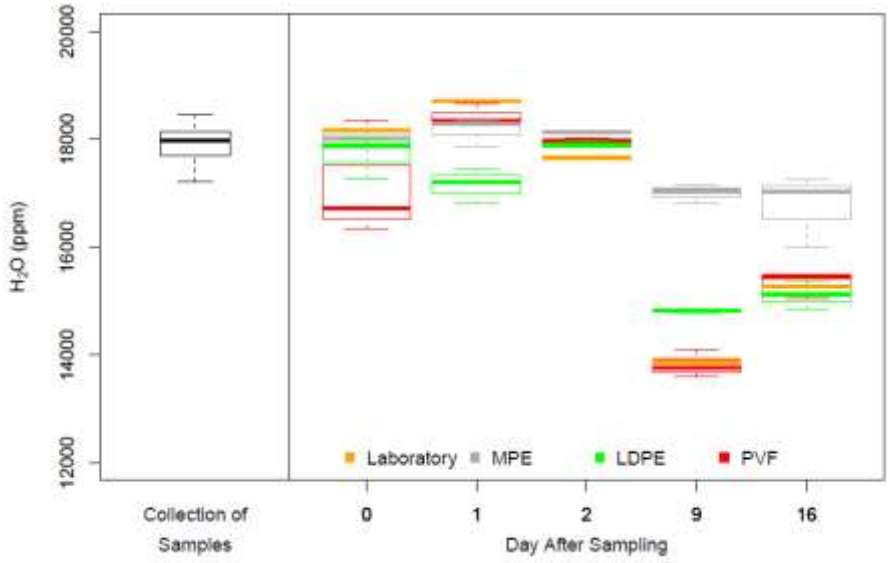


Figure 2. Boxplots describing the concentration of atmospheric water vapor in ppm during the collection of samples and the posterior measurement of samples.

Comment 22. Page 7, Line 16: One single value is not very meaningful. Can you replicate this?

Reply: the authors are aware of the lack of representativity of only one sample. However, the design showed in page 6 lines 7-10 describe the cryogenic sampling. We were expecting to collect three samples for each pumping rate, however the device was not successful to collect enough sample with the lower pumping rate as it is mention in page 7, line 16-18. Despite this step back, we decided to add this sample to include all data collected. To replicate this sample it will be necessary to re-do all the experiment, however as the cryogenic samples collected with the pumping rate of 3 L min^{-1} were suitable for analysis we do not see the need to replicate the 50 mL min^{-1} samples. Also, this provides insights about the difficulties linked with low pumping rates for the collection of atmospheric water vapor.

Comment 23. Page 7, Line 24: How do you make sure that you trap "all" the conveyed air? What would be a measure for that?

Reply: if we measure the relative humidity of the air on the inlet and at the outlet of the cryogenic bath, we can have a measurement of the specific humidity of the air. Here, we can compare the difference between both flows and determine how efficient the cryogenic bath is. Consequently, we decided to add the following to the manuscript in Page 7, line 24:

"… from the conveyed air. However, as this is an open system that requires a constant flow of air and cannot be closed as the batch distillation (Koeniger *et al*, 2011; Vendramini and Sternberg, 2007), it requires to monitor the atmospheric water vapor concentration before and after the sample collection. This can be achieved measuring the air temperature and relative humidity in both, the inlet and outlet of the cryogenic bath. This information can be used to estimate the specific humidity of the air and evaluate the efficiency of the cryogenic bath. "

Comment 24. Page 7, Line 27: add ","

Reply: Done.

Comment 25. Page 7, Line 30: Again, how high/low were your values during the sampling?

Reply: in our experiment we did not measure the WVTR. The values showed on the manuscript are the reported ones for each material. However, following a previous recommendation of the reviewer (comment 21) we added the water vapor concentration during the sampling and posterior measurement of samples. That specific data showed the variation of the water vapor concentration among samples and measuring days. This, fulfill this request of information about how high/low these values were during sampling, meanwhile the WVTR is a characteristic that "defines the ability of a film to transfer water molecules depending on the relative humidity gradient" (page 7, lines 27-28 of this manuscript).

Comment 26. Page 8, Figure 2: A minimum of at least three samples is required to draw any conclusions.
Reply: see reply in comment 22.

Comment 27. Page 8, Line 9: I would not go so far, since you only have a limited amount of replicates.
Reply: we modify the sentence as follows:

"…sample collection. Atmospheric water vapor sampling with cryogenic baths provides suitable accuracy when the collection efficiency is high. However, this requires a suitable system to monitor the specific humidity of the air at the inlet and outlet of the cryogenic bath. However, there …"

Comment 28. Page 8, Line 11: Can you say something about material costs for the different methods/bags types? Can you say something about practicability of the cryo versus the bag method? Please provide some more suggestions to the reader in terms of selecting an appropriate method.
Reply: Following this suggestion, we decided to add the following in page 7, after line 32:

"The suitability of every sampling method to collect atmospheric water vapor in the field will depend in their accuracy to keep unmodified the mass and isotope signature of every sample (Peters and Yakir, 2010). However, the logistics (e.g, the location, the travel time from and towards the laboratory, basic research infrastructure on the field) and the project budgets play an important role on the selection of the sampling methods. Assuming in this experiment the laboratory equipment (e.g, glassware, output cavity spectrometer, air temperature and relative humidity sensors) and logistics (e.g, all the expenses related to the travel costs to the sampling) as fixed costs, the main difference will rely on the selected sampling method. Carrying out this experiment in Europe in 2019, the MPE and PVF sampling bags have a cost of €12.0 per bag and the LDPE sampling bags of € 0.2 per bag with the disadvantage that each of them can be use only once. On the other hand, collecting 3 samples per hour with the cryogenic bath during 24 hours, the price per sample during one day is € 2. After thawing the sample and storing it properly within borosilicate vials, the sample can be store for longer periods of time. This method requires also the monitoring of the water vapor concentration during the sampling to have an indication of the collection efficiency."

Adding the following in the conclusions:

"MPE sampling bags are the more accurate and more expensive sampling method. The LDPE sampling bag is the cheapest sampling method with the limitation that the samples should be analyzed on the same day of collection. This method gives an additional restriction considering the transport time and susceptibility to exchange water vapor with the surrounding air. Finally, the cryogenic bath has an affordable price per sample if the project collects samples continuously, maximizes the use of the supplies such as the dry ice that tends, and monitor the collection efficiency with the estimation of the specific humidity of the sampled air"

Comment 29. Page 14, Line 5: “an” instead of “a”
Reply: Done.

References

Koeniger, P., Marshall, J. D., Link, T., and Mulch, A.: An inexpensive, fast, and reliable method for vacuum extraction of soil and plant water for stable isotope analyses by mass spectrometry, Rapid Communications in Mass Spectrometry, 25, 3041–3048,https://doi.org/10.1002/rcm.5198, 2011.

Peters, L. I. and Yakir, D.: A rapid method for the sampling of atmospheric water vapour for isotopic analysis, Rapid Communications in Mass Spectrometry, 24, 103–108, https://doi.org/10.1002/rcm.4359, 2010.

Vendramini, P. F. and Sternberg, L. d. S. L.: A faster plant stem-water extraction method, Rapid Communications in Mass Spectrometry, 21,164–168, https://doi.org/10.1002/rcm.2826, 2007.