Reply to anonymous referee #1

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

With the development of water isotopes measurements using the laser spectrometer, real-time measurements of water vapor isotopes can be realized. However, the real time measurements of water vapor isotopes need a constant power supply and the deployment of the laser spectrometer in the field is not cheap. Instead, it is more convenient and cheaper to collect air samples in the field for later analysis in the laboratory with a mass or laser spectroscopy. However, the applicability of the sample storage unit needs to be tested. This study airs to test the applicability of different sampling techniques, which can give a guide for scientists who'll collect air samples for isotopic measurements. The paper is well written and has a good readability. It deserves to be published and I have a few suggestions for improving this paper.

The authors want to thank the reviewer for his/her suggestions on our manuscript. We welcome the reviewer interest and relevance acknowledgement of the study. The reviewer provided a series of suggestions to improve the manuscript that we want to address point-by-point:

Line 20-21 in page 3, why to modify the laboratory air to a concentration lower than 4000 ppm? To my knowledge, the laser spectroscopy generally has lower measurement accuracy for low vapor concentration (for example, <2000 ppm).

Reply:

The idea behind adding an altered air source during the sampling is to be able to differentiate between samples during the laboratory procedure and post-processing of the data. This helped to carry out the data analysis because after the air passed by the drying element, the $\delta^{2}H$ and $\delta^{18}O$ signatures will change drastically. To clarify this, we proposed to improve the lines 18 and 19 of page 3 as follows:

"… post-processing of the data. **The data obtained from this inlet was not used during the analysis as it was used only as a distinction mark between samples**. The altered air …"

Line 1-13 in page 5, how do you establish the relationship (equation 2 or 3) between isotopic ratio and vapor concentration? Because you mentioned in line 12-13 of page 3 'The WVISS was set to run the automatic pump with the following voltages 3.0V, 2.0V, 1.5V and 1.0V to provide a controlled water vapor concentration (ppm) during the calibration of each set of samples.', did you establish the relationship using four data points? If yes, the number of data points for establish the relationship between isotopic ratio and vapor concentration is not enough.

Reply:

This relationship was established based on the correction procedure used during similar experiments and devices published by Rambo et al. (2011), Kurita et al. (2012) and Steen-Larsen et al. (2013, 2014). This is mentioned on line 6 of page 5. Despite it is true that the relationship was established using four data points, each data point corresponds to the average of 12 individual measurements performed every 5 s by the laser. The use of this method to correct the isotope measurements is based on the assumption of a linear drift in the humidity-isotope correction (Steen-Larsen et al., 2013).

We proposed to add on page 3, line 13 the following:

"… of each set of samples**, running each voltage for a period of 2 min**. The dry air needed for the …"

And on page 5, line 6 the following:

"… Steen-Larsen et al., 2013, 2014). **Each data point used in equations 2 and 3 corresponds to the last minute of measurements for each voltage, obtaining an average based on 12 individual measurements for both stable isotopes and water vapor concentrations**. The corrected values of each …"

The authors should add a plot in the manuscript for manifesting the relationship between isotopic ratio and vapor concentration.

Reply:

The authors agreed with the suggestion of adding an additional plot to the manuscript showing the relationship of the correction procedure applied. This plot will be added as an appendix to the manuscript as follows:

Adding on page 5, line 4 the following:

"… to the water mixing ratio (ω) in ppm **(see Appendix C)**: "

And the appendix as:

Appendix C: Plots of the Water Vapor Correction Procedure

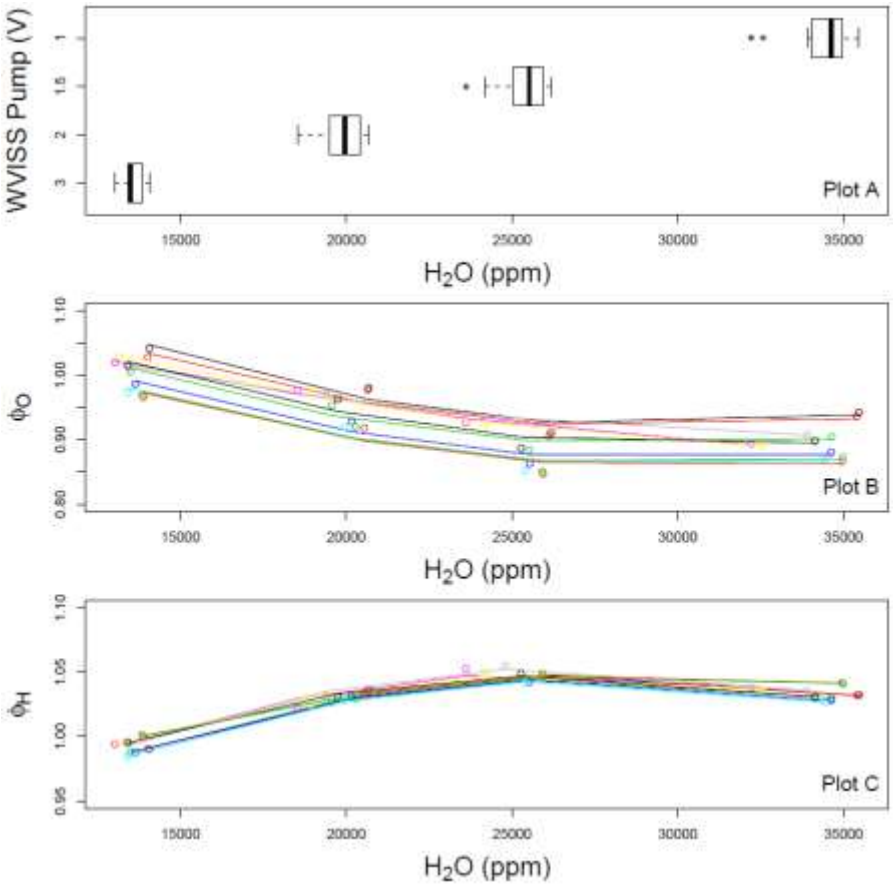

Figure C1. Water vapor correction plots showing the variation of the water vapor concentration (ppm) and the correction factors ϕ_O and ϕ_H. Plot A shows the variation of water vapor concentration in ppm for

each voltage used on the WVISS pump during the correction procedure. Plots B and C show the polynomial relationships between the water vapor concentration and the correction factors ϕ_O and ϕ_H, respectively.

In addition, how did you correct the drift effect of the laser spectrometer? which was not mentioned in the text.

Reply:

The LGR analyser used during this experiment did not experience a significant drift during the measurements due to the little time running on a daily basis (less than six hours every day). Additionally, the model of water isotope analyser (IWA) keeps a "negligible drift" as it is stated by the manufacturer (LGR, 2019).

To clarify this, we proposed to add the following sentence on Page 4, line 10:

"… Steen-Larsen et al., 2013, 2014). **The drift of the used laser spectrometer was negligible, because the measurement period was not longer than 6 hours every day. In addition, the thermal control within the laser chamber provides stable measurements with a negligible drift as it is stated by the manufacturer (LGR, 2019).** The correction of water vapor measurements was …"

In addition to the Water Vapor Transmission Rate (WVTR) of sample bag, other factors such as air tightness of valve or fitting of the sample bag may also have an important influence on the isotopic measurements. Other potential influences should be discussed in the text.

Reply:

The authors followed the suggestion from the reviewer and it was decided to add the following paragraph on page 8, line 1:

"**The tendency of drift towards the signature of the laboratory air could be linked to other factors such as welding quality between bag material and the valve (for MPE and PVF bags), fitting issues between the tubing connecting the sample bags to the MIU unit (all sample bags) or the inlet connection for the LDPE bags. In the case of MPE and PVF bags, the manufacturer states that the bags should not be filled more than 90% of their capacity like we did in the experiment. This practice could lead to the development of fissures between the air valve and the bag material that in the case of PVF bags due to their brittle properties respect to MPE of LDPE bags. An increment on the air pressure within the MPE bags can lead to the detachment of the air valve from the layers in which it is welded. LDPE bags are susceptible to leaking as a consequence of the inlet built with in-house materials that the presence of different joints can induce the filtering of the laboratory air.** "

References

LGR: Los Gatos Research, Inc. Isotopic Water Analyzer (Liquid+Vapor) - Enhanced Performance, https://www.lgrinc.com/analyzers/isotope/isotopic-water-analyzer, visited on: August 27, 2019, 2019.

Kurita, N., Newman, B. D., Araguas-Araguas, L. J., and Aggarwal, P.: Evaluation of continuous water vapor δD and δ 18O measurements by off-axis integrated cavity output spectroscopy, Atmospheric Measurement Techniques, 5, 2069–2080, https://doi.org/10.5194/amt-5-2069-2012, 2012.

Rambo, J., Lai, C.-T., Farlin, J., Schroeder, M., and Bible, K.: On-Site Calibration for High Precision Measurements of Water Vapor Isotope Ratios Using Off-Axis Cavity-Enhanced Absorption Spectroscopy, Journal of Atmospheric and Oceanic Technology, 28, 1448–1457, https://doi.org/10.1175/JTECH-D-11-00053.1, 2011.

Steen-Larsen, H. C., Johnsen, S. J., Masson-Delmotte, V., Stenni, B., Risi, C., Sodemann, H., Balslev-Clausen, D., Blunier, T., Dahl-Jensen, D., Ellehøj, M. D., Falourd, S., Grindsted, A., Gkinis, V., Jouzel, J., Popp, T., Sheldon, S., Simonsen, S. B., Sjolte, J., Steffensen, J. P., Sperlich, P., Sveinbjörnsdóttir, A. E., Vinther, B. M., and White, J. W. C.: Continuous monitoring of summer surface water vapor isotopic composition above the Greenland Ice Sheet, Atmospheric Chemistry and Physics, 13, 4815–4828, https://doi.org/10.5194/acp-13-4815-2013, 2013.

Steen-Larsen, H. C., Sveinbjörnsdottir, A. E., Peters, A. J., Masson-Delmotte, V., Guishard, M. P., Hsiao, G., Jouzel, J., Noone, D., Warren, J. K., and White, J. W. C.: Climatic controls on water vapor deuterium excess in the marine boundary layer of the North Atlantic based on 500 days of in situ, continuous measurements, Atmospheric Chemistry and Physics, 14, 7741–7756, https://doi.org/10.5194/acp-14-7741-2014, 2014.