

Supplemental Material: Additional Experiment

Objective

Determine the capacity to retrieve similar isotope signatures of air samples collected with different sampling methods for water vapor samples.

Methodology

On the market different sample bags exist to store air samples. In this experiment we test whether these stored air samples remain isotopically consistent in time. We tested the isotopic signature of the air samples stored for a period of 17 days. We tested 3 different types of bags that we all collected on the same day (T_0). Successively we analysed them on the same day (T_0), and after 1, 2, 9, 16, and 17 days after collection (T_1 , T_2 , T_9 , T_{16} , T_{17} , respectively). We compared the results to direct air vapour sampling with the open inlets from the MIU unit on day T_0 , this measurement is our 'benchmark'. Additionally, we also collected liquid samples with two cold traps with different pumping rates on day T_0 . One cold trap experiment was carried out with a fast pumping rate (FPR) and with a slow pumping rate (SPR).

The three types of bags tested are:

- MPE bags: these 1 L bags of methalized polyethylene are manufactured with a five layer structure (Foil Bag; Model: FP-1, Samplebags.eu) and designed to be filled to 90% of its volume capacity. Every bag has a 2-in-1 PTFE fitting for the injection and extraction of the air sample.
- PVF bags: these 1 L bags are composed of polyvinyl fluoride (Tedlar Bag; Model: ITP-1, Samplebags.eu) and designed to be filled to 90% of its volume capacity. Every bag has a 2-in-1 PTFE fitting for the injection and extraction of the air sample.
- LDPE bags: these 1.1 L bags are made of low density polyethylene used for filling packaging spaces. The sampling bags are fabricated with a simple valve made from polyethylene as well.

Both, MPE and PVF bags are designed to be filled to 90 % of its volume capacity and every bag has a 2-in-1 PTFE fitting for the injection and extraction of the air sample. Whilst the LDPE bags are fabricated with a valve made from polyethylene as well. The collection of the samples took 3 hours. Each hour we filled 6 sample bags per bag type and carried out the cryogenic sampling with two cold traps. The cryogenic samples were collected through cold traps built with two different pumping rates: 50 mL min⁻¹ (slow pumping rate) and 3 L min⁻¹ (fast pumping rate). The cold traps were built with a test tube of 50 mL capacity immerse in a container filled with ethanol (100 %) inside a cooler filled with dry ice (-70 °C). The water collected in both test tubes was thaw and transferred to a 1.5 mL vial for its measurement after the experiment with the LWIA. The cryogenic sampling was performed during the 3 hours of sampling, collecting 3 samples with the FPR and only one with the SPR. We also took our benchmark sample by using the open inlet of the WVIA, collecting 8 samples per hour during the 3 hours experiment (24 samples). During the analysis of the sample bags on days T_1 , T_2 , T_9 , T_{16} and T_{17} , we also sampled the laboratory air with one open inlet of the MIU. The samples were analysed and calibrated according to the procedure as described in Section 2.2.1 and Section 2.2.2, using an standard water with an isotope signature of $\delta^{18}\text{O}$: -14.44 ‰ and $\delta^2\text{H}$: -104.09 ‰.

The consistency analysis of the isotopic signatures was performed comparing the isotope signatures obtained from the different samples against the benchmark collected the same day of the sampling (T_0), which corresponds to the direct measurements from the WVIA. The cross comparison was performed with the Z analysis (Equation 1) (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 or cryogenic samples, B is the benchmark isotope signature (WVIA) and μ is the target variability. Differing from Orlowski *et al.* (2016) and Wassenaar *et al.* (2012), the target variability (μ) was established as the isotope range measured with the WVIA during the three hours of measurements of the benchmark ($\delta^2\text{H}$: 2.0 ‰ and $\delta^{18}\text{O}$: 0.4 ‰) considering the transient condition in the laboratory. Thus, we adopted the limits proposed by Orlowski *et al.* (2016) for accurate analysis (Z -score < 2.0), questionable analysis (Z -score: 2.0 – 5.0) and unacceptable analysis (Z -score: > 5.0).

$$Z = \frac{S - B}{\mu}$$

Equation 1



Figure 1. Air sampling bags used to test the consistency among air sampling methods. Silver bag on the left is the MPE bag, the middle transparent bag corresponds to the PVF bag and the transparent bag on the right is the LDPE bags.

3. Results and Discussion

Benchmark isotope signature from the 24 measurements performed during the three hours experiment had an isotope signature of $-15.61 \pm 0.14 \text{ ‰}$ and $-115.12 \pm 0.47 \text{ ‰}$ for $\delta^{18}\text{O}$ and $\delta^2\text{H}$, respectively. All the vapor samples collected with the bags that were measured on the same sampling day (T_0) are located within the accurate region based on the *Z-score* analysis (Figure 2). Contrary to these samples, the liquid samples collected with the cold traps are located on the unacceptable region, showing *Z* values bigger than 5. The SPR is only based on one sample because we were only able to collect 0.1 mL of liquid during the three hours, while the FPR collected 0.25 mL every hour. Both liquid samples show a heavier signature than the benchmark, as a consequence of incomplete condensation. These differences are linked to not perfect collection efficiencies during the cryogenic sampling with the cold traps (Griffis, 2013).

The signature of the laboratory air changed during the course of our measurements. The orange samples marked as “Laboratory” in Figure 2 depict the differences among the days of measurement and the sampling date (T_0). These differences in laboratory air signatures partly influences the measurement results from all the air samples collected with the three types of bags. The MPE samples are the only ones from the experiment with almost all measurements located within the accurate region of the *Z-score* plot (*Z-score* < 2). Despite the accuracy reached with the MPE, the measurements are influenced by the isotope signature of the air within the laboratory. All the measurements after the sampling date with the LDPE and PVF bags are located within the questionable region of the *Z-score* plot (*Z-score*: 2-5), while the PVF samples from T_9 are on the unacceptable region (*Z-score* > 5). These sampling bags are influenced by the isotopic signature of the laboratory air considering its location close to the laboratory signature during the measurements.

Herbstritt *et al.* (2014) 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. They mention the capacity of the layered foil bags (similar material to the MPE bags used in this experiment) to prevent the vapor mass loss during long periods of time. However, the sampling bags design

influences strongly the capacity to retain stable samples. Tock (1983) evaluates the water vapor transmission rate (WVTR) of different polymers films, finding that methalized polyethylene coated materials have the lowest WVTR ($1.55 \text{ g m}^{-2}\text{d}^{-1}$) compared with the LDPE ($23.25 \text{ g m}^{-2}\text{d}^{-1}$) and the PVF ($50.22 \text{ g m}^{-2}\text{d}^{-1}$). The WVTR defines the capacity of a film to transfer water molecules depending on the relative humidity gradient (Kumaran, 1998). Thus, the WVTR of each material provides insights about the variation of the stable isotope measurements, including the MPE bags. It is important to remark that the diffusion characteristics of foil layered materials are directly influence by the temperature in outdoor conditions (Pons *et al.*, 2014).

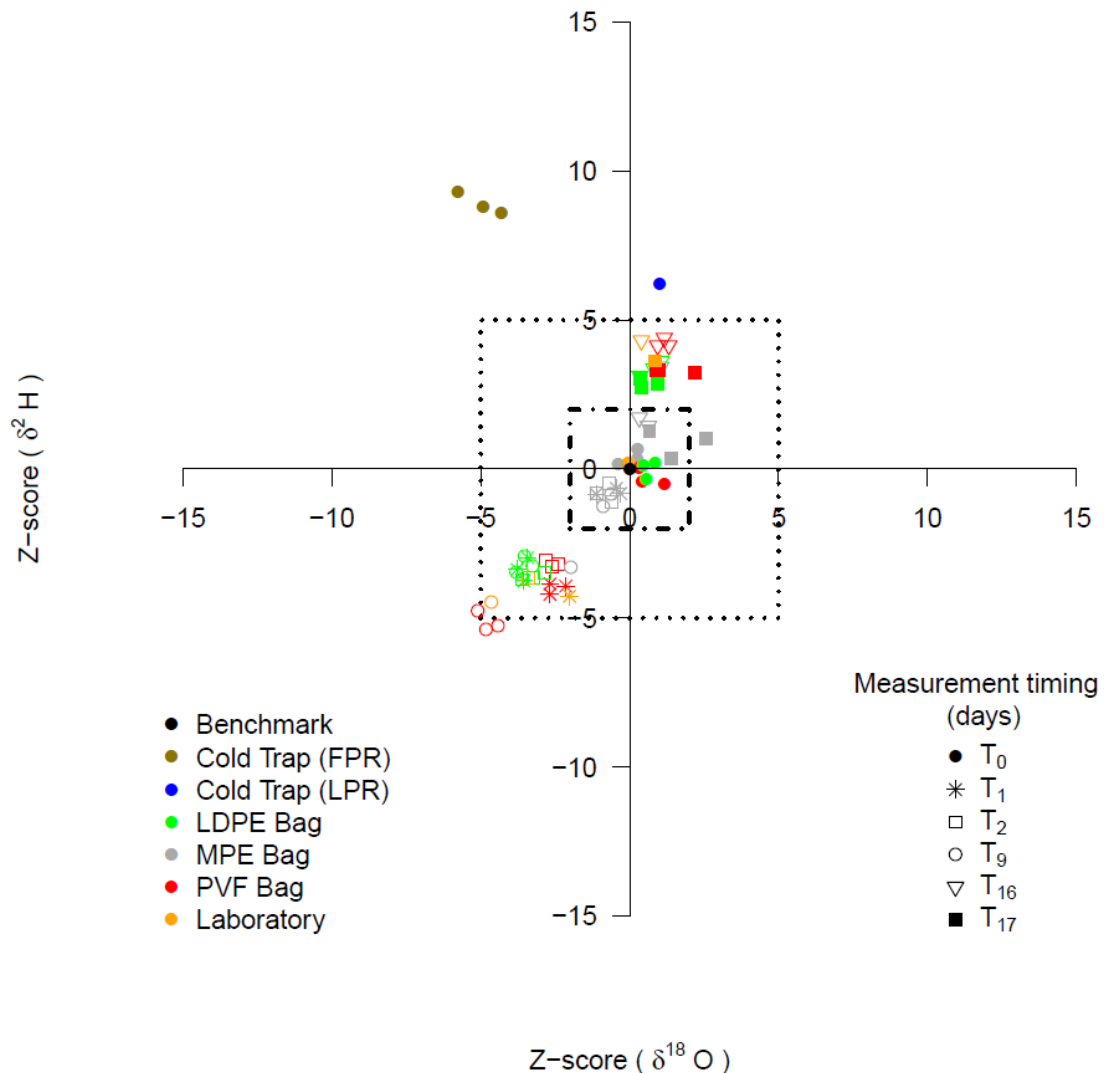


Figure 2. Dual plot for the Z-score values of $\delta^2\text{H}$ and $\delta^{18}\text{O}$ of the samples under analysis.

3. Conclusions

Water vapor sampling techniques differ in their capacity to keep reliable measurements after the sampling. The MPE bags shows the more accurate measurement of stable isotopes two weeks after its sampling. LDPE and PVF sampling bags can be used for sampling water vapor if the measurements are performed on the same day of sampling. After 24 hours, the WVTR of both materials (LDPE and PVF) allows the air sample to be in equilibrium with the surrounding air affecting the measurement accuracy. Both cold trap systems differ strongly from the benchmark in this experiment. Apparently, even the 3 hours sampling was not sufficient for a full condensation. This long sampling time, limits its use for studying evaporation process that change in short periods of time (< 30min). Thus, underline the need to determine with further research if cryogenic samples

can be used as references or benchmarks when those are compared against direct measurements performed with laser spectrometers as the WVIA.

References

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