Identifying and Correcting the Gas Matrix Effects on a Cavity Ring-Down Water Stable Isotope Analyzer

Benjamin Gralher[1)*)], Barbara Herbstritt[1)], Markus Weiler[1)], Leonard I. Wassenaar[2)], Christine Stumpp[3)]

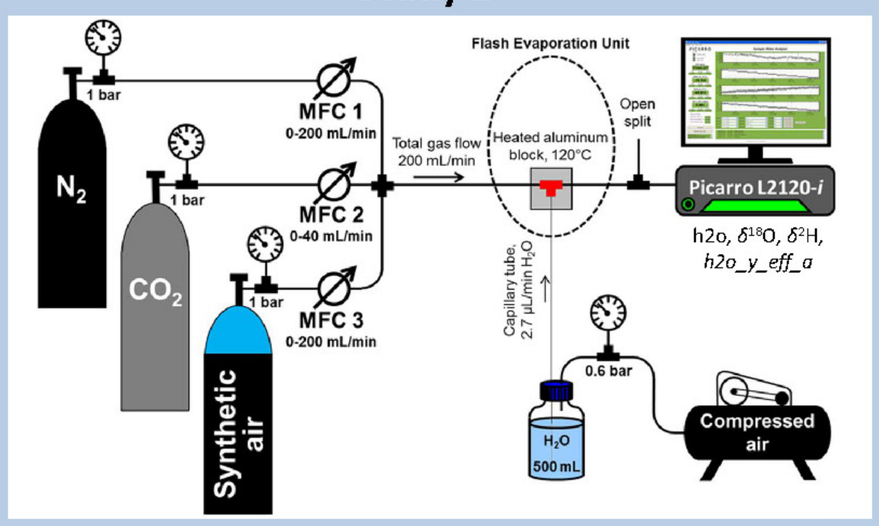
Motivation

Laser-based water stable isotope analyzers have enabled new experimental approaches, e.g. *in situ* observations in the soil-plant-atmosphere continuum.

Thereby, these analyzers will occasionally be subjected to inhomogeneous background gas matrices between different samples and/or in comparison with calibration standards, the effect of which was to be investigated.

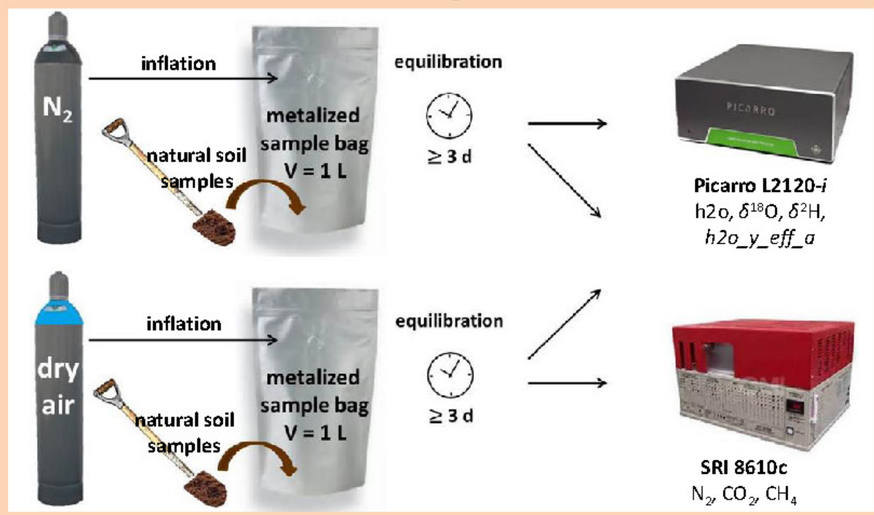
Experimental Setups

Study 1[1]



- Flash-evaporation and analysis of a continuous stream of identical water
- Stepwise change of carrier gas matrix in environmental relevant ranges

Study 2[2]



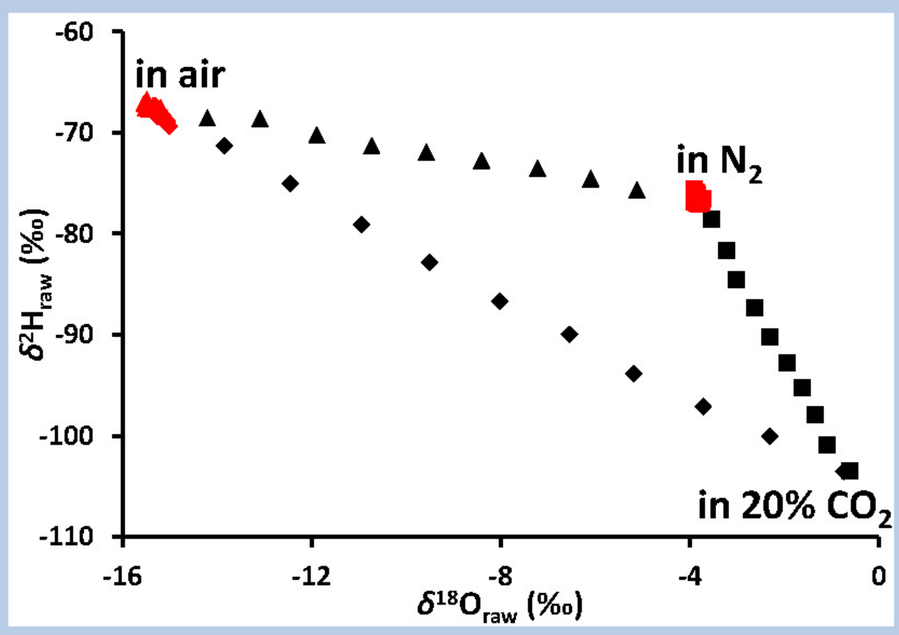
- Repeated analysis of soil sample headspace vapor over the course of 4 weeks
- Prevention of diffusional vapor loss due to metalized sampling bags

Correction Procedure

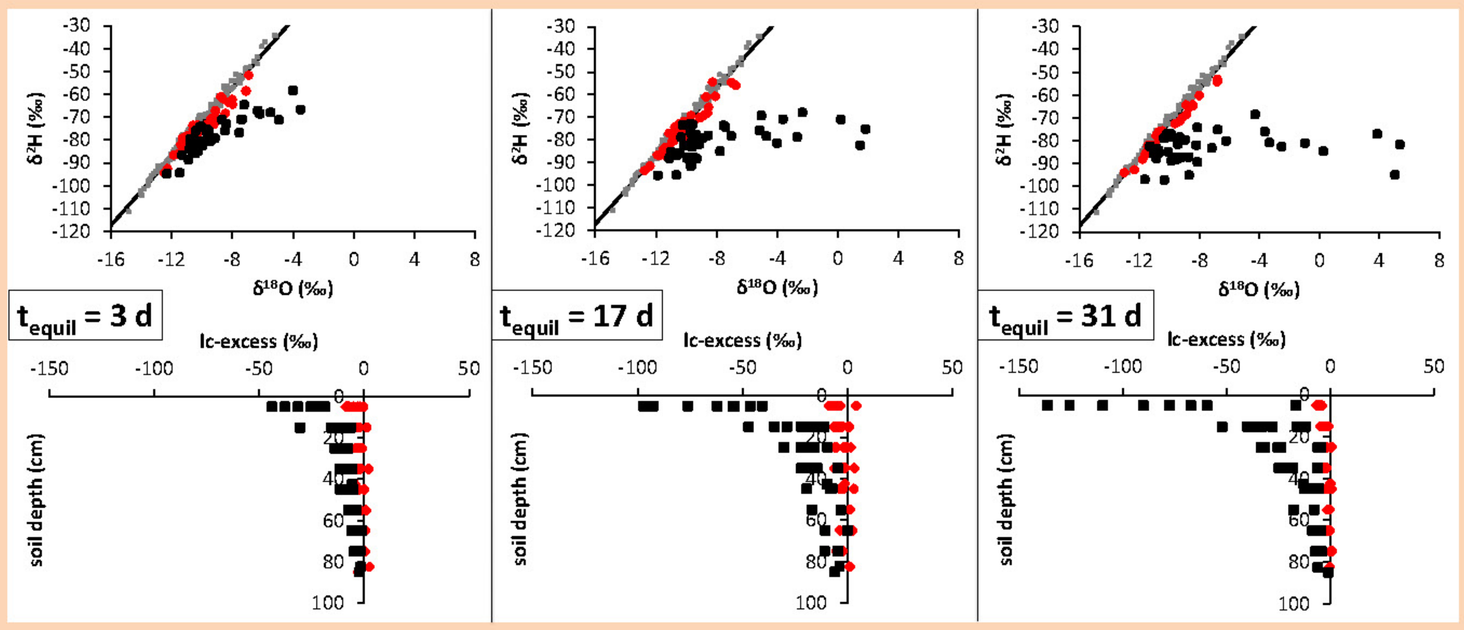
We used the strong linear correlations between carrier gas changes, isotope readings, and the co-recorded line width-related variable *h2o_y_eff_a* (all $R^2 > 0.99$[1]; R^2 up to 0.98, only for air inflation[2]). Raw isotope readings were corrected using the following equation where **m** = $\Delta\delta_i/\Delta h2o\_y\_eff\_a$ and the control variable ***i*** refers to the different isotope ratios:

$$\delta_{i,corrected} = \delta_{i,observed} - m_i \times \left(h2o\_y\_eff\_a_{observed} - h2o\_y\_eff\_a_{reference}\right)$$

Isotope data flawed without correction



- Pre-correction bias: up to **+14.57‰** for $\delta^{18}O$, up to **-35.9‰** for δ^2H
- Post-correction uncertainties: **< 0.11‰** for $\delta^{18}O$, **< 0.7‰** for δ^2H



- Pre-correction data **falsely suggest** colder season origin and evaporative enrichment of heavy isotopes especially for topsoil samples
- Post-correction **data plausibility confirmed** by similarity with local meteoric water line (solid line) and suction cup data (grey dots)

Discussion and Conclusions

Changes of carrier gas composition in environmentally relevant ranges cause **changes** of isotope readings **exceeding accepted measurement uncertainties** by **two orders of magnitude**

Air carrier is recommended for direct vapor equilibrium method as N_2 filling is prone to CH_4 formation

Proposed post-correction

- **restores measurement precision and accuracy** necessary for observations of natural variations
- **prevents misinterpretations** of natural soil water isotope data
- is **possible for pre-existing datasets** and **different equilibration times**
- is **possible without additional analytical capabilities** and resources (e.g. GC, specialty gases)
- is even **possible without exact knowledge** of carrier gas composition
- is **indispensable when inconsistent background gas matrices** between samples or a mismatch in this regard between samples and calibration standards **cannot be excluded**

References

[1] Gralher et al 2016, EST doi:10.1021/acs.est.6b01124

[2] Gralher et al 2018, VZJ doi:10.2136/vzj2017.08.0157

Correspondence to:

benjamin.gralher@cep.uni-freiburg.de

Author affiliations: [1)] Hydrology, U. of Freiburg, Germany; [*)] now at: Ecosystem Physiology, U. of Freiburg; [2)] Isotope Hydrology Section, IAEA, Vienna, Austria; [3)] Institute for Soil Physics and Rural Water Management, BOKU, Vienna, Austria