Discrete *in situ* Vapor Sampling for Measurements of Matrix-bound Water Stable Isotopes ($\delta^{18}O$, $\delta^{2}H$)

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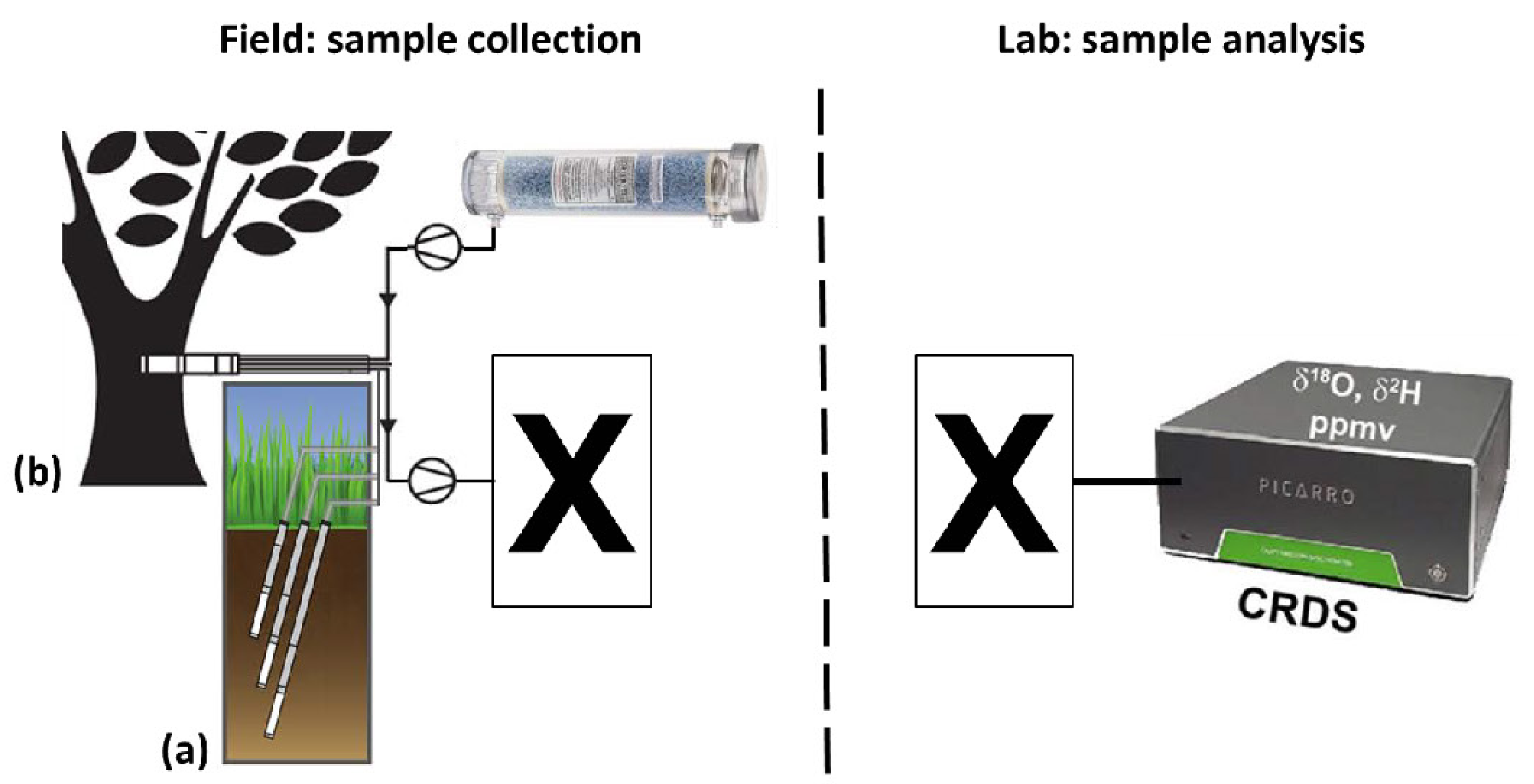
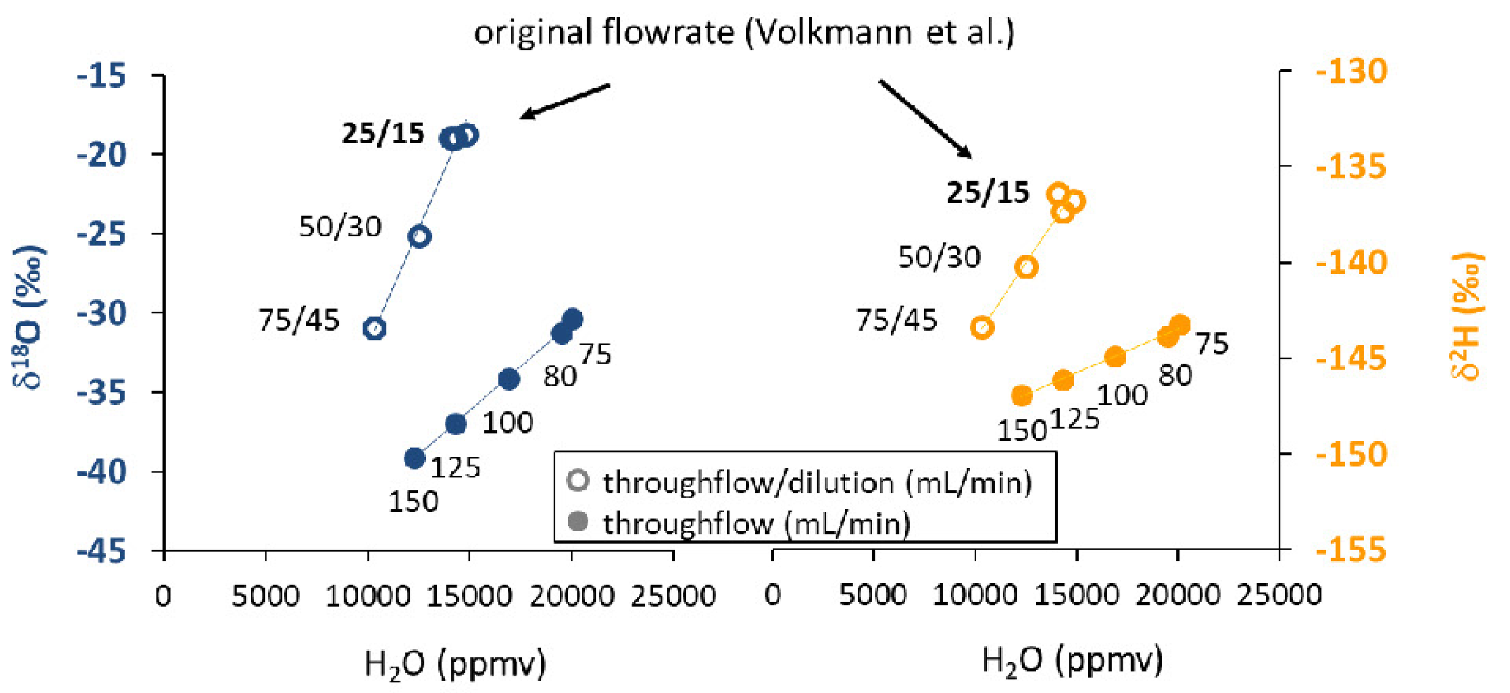
Motivation and Overview

Continuously measuring laser-based analyzers (e.g. CRDS) allow for non-destructive and minimal-invasive *in situ* approaches even in remote locations in the field. However, they are expensive, heavy, and rely on access to electrical power.
To overcome these limitations, we developed a new, inexpensive technique to collect discrete vapor samples in the field via established *in situ* probes (WIPs) into diffusion-tight inflatable bags for storage and later analysis in the lab.



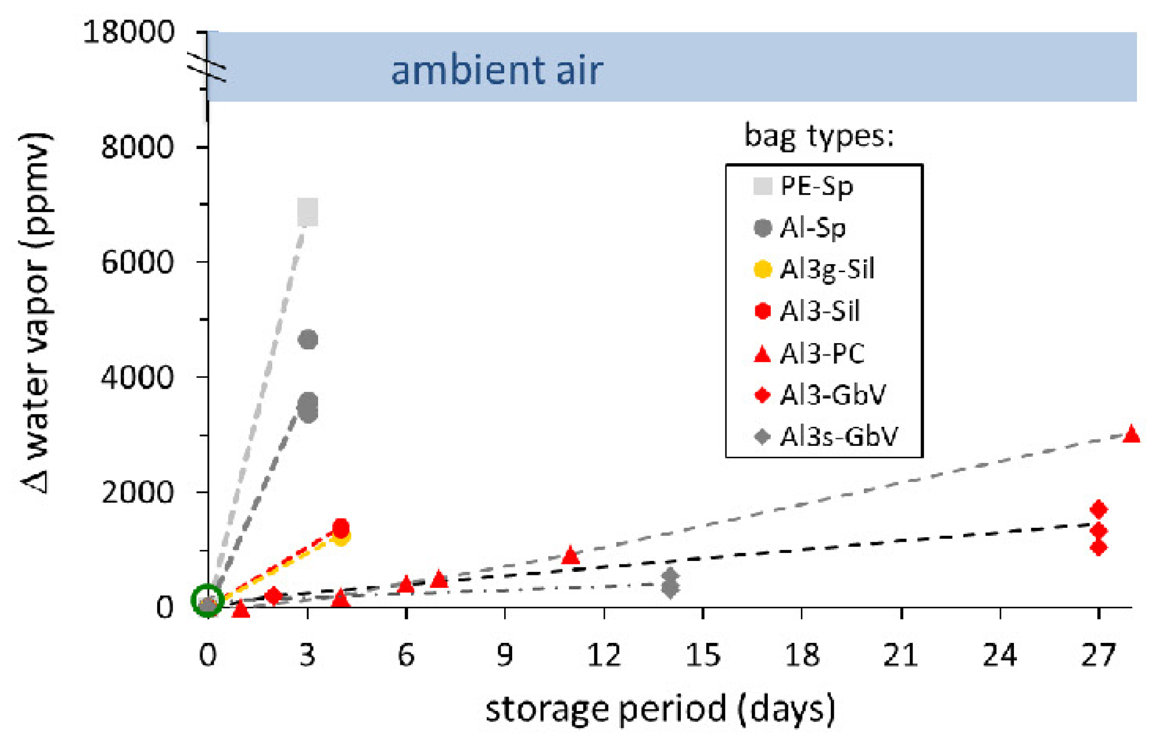
Aim of the study
Vapor sampling from matrix bound water e.g. via *in situ* (a) soil- and (b) xylem-water isotope probes (WIPs) (modified from Volkmann & Weiler, 2014 and Volkmann et al., 2016a).
The sampled vapor will first be filled into appropriate, to-be-identified containers (**X**) in the field (left) and later analyzed via CRDS in the lab (right).

Method Development



Effect of gas flowrates through *in situ* probes (increased, to reduce filling time of bags): Decrease of water vapor content and depletion in isotopes (left: $\delta^{18}O$, right: $\delta^{2}H$) is obtained by increasing gas flowrates with (open symbols) and without (closed symbols) dilution, due to incomplete equilibrium. Numbers refer to the respective gas flowrates applied: throughflow/dilution or throughflow-only.

Material selection
Various combinations of bags and seal types with different properties were tested for vapor sampling.

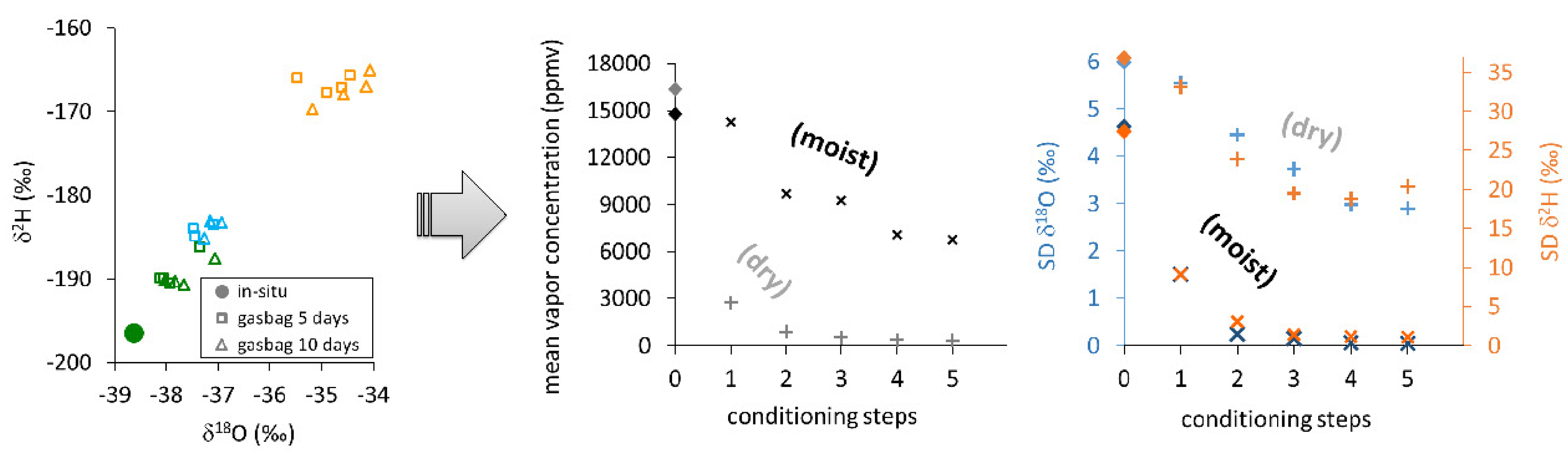


Diffusivity test
Change in water vapor content over time inside different bag types, initially filled with pure N_2 (green circle)

Reusability of bags

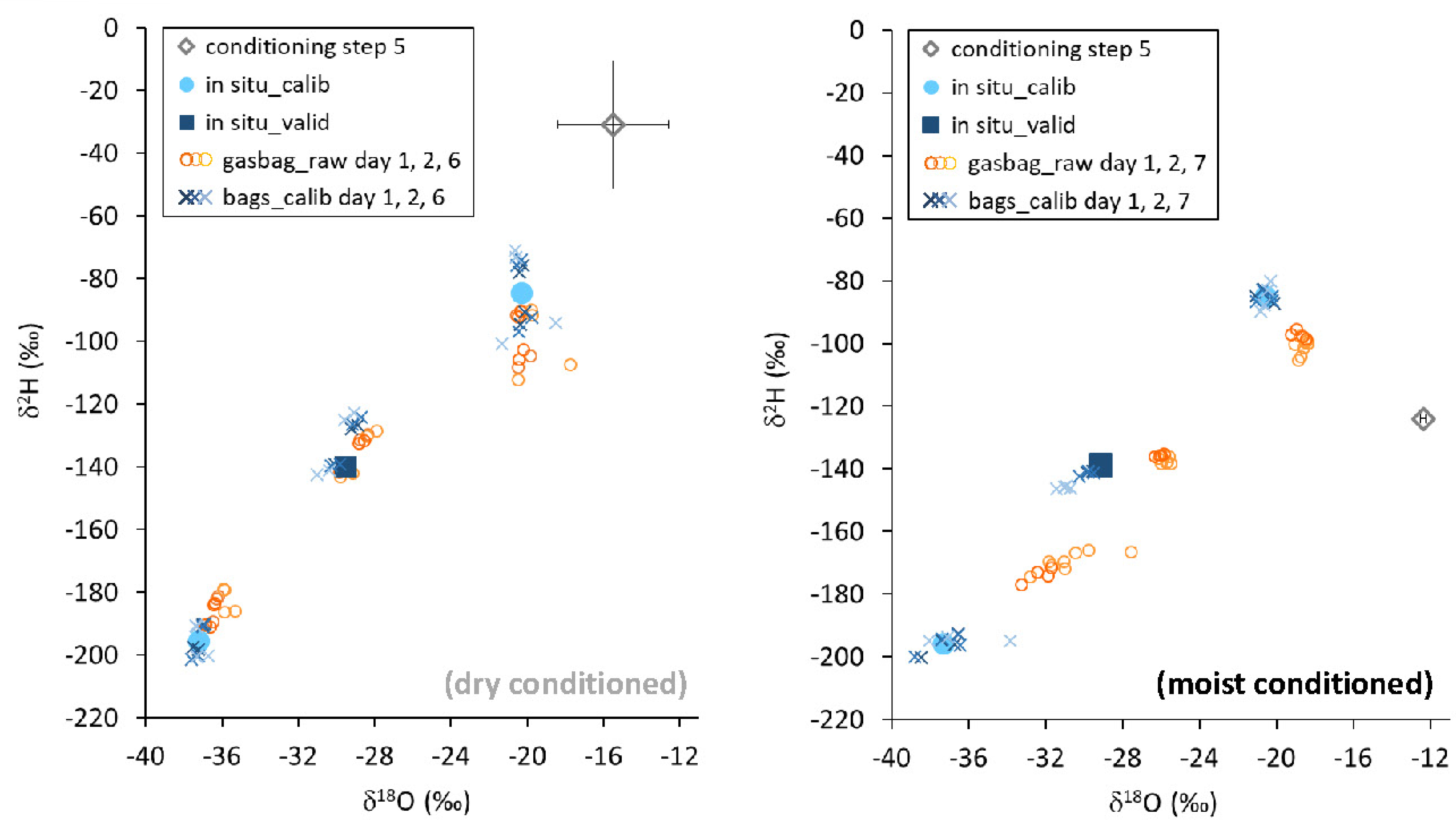
Gasbag measurements of reused bags, filled via an *in situ* probe (filled dot) from **one single isotopic reservoir** were rather inconsistent. Different colors indicate different isotopic levels of the previous samples, stored in the respective bags, although evacuated and flushed with dry gas.

→ **Conditioning is needed before reuse!**



Vapor content (left) and standard deviations (SD) of vapor isotopes (right) from a batch of bags, stepwise conditioned with dry synthetic air (light plus symbols) and **moist** air (dark cross symbols). Diamond symbols on vertical axes represent respective mean values of pre-conditioning measurements

Results



Repeated bag measurements (1, 2, 7 days) from sampling of three different isotopic reservoirs. Sampling bags were conditioned with dry (left) and **moist** (right) atmosphere. *In situ* measurements (filled symbols) were more reliably calculated from moist than from dry conditioned bag measurements (crosses). Pre-sampling measurements are shown as gray open diamonds. Note that their error bars (black) are smaller than the symbol, in the case of **moist** conditioning.

Key findings

- Light-weight method for collection, storage and subsequent isotope analysis of **discrete** water vapor samples through established *in situ* probes (WIPs) has been developed successfully.
- Method uses only light, robust, off-the-shelf components, is easy to use, cost-efficient and allows for multiple measurements.
- Increase of **gas flowrates** through probes (WIPs) leads to lower vapor concentrations and **isotopic depletion** due to incomplete equilibrium.
- Thorough systematic **material testing** and **selection** guarantees air-tightness and avoids contamination by material outgassing.
- Co-measurement of **calibration standards**, undergoing identical conditioning, is indispensable to correct for the implicit shift of the obtained isotope signal, induced by the conditioning procedure.
- Achieved **precision** and **accuracy** are not only appropriate for labelling experiments, but even sufficient for resolving natural variations of isotope signatures.

References

Volkmann, T. H. M.; Weiler, M. (2014) Continual in situ monitoring of pore water stable isotopes in the subsurface, HESS, 18 (5), 1819–1833
Volkmann, T. H. M.; Kühnhammer, K.; Herbstritt, B.; Gessler, A.; Weiler, M. (2016) A method for in situ monitoring of the isotope composition of tree xylem water using laser spectroscopy, PCE, doi: 10.1111/pce.12725

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