Low-cost mobile water vapour sampling for in-situ measurements of water stable isotopes



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In-situ sampling probes for water vapour stable isotopes (δ^{18} O, δ^{2} H) can provide valuable information to elucidate eco-hydrological processes. They are non-destructive and field-deployable and were already sucessfully used for monitoring soils^[1] and trees^[2]. To operate laser-based isotope analysers in the field, heavy and expensive equipment has to be brought to the field with the risk of damages and the disadvantage of relative immobility. Rough and/or spacious terrains are virtually excluded with this approach.

To overcome these limitations, the aim of this study is to

- develop a method to collect vapour samples in the field
- sample via these probes the isotopic signature in xylem sap and analyze the collected samples later in the lab.

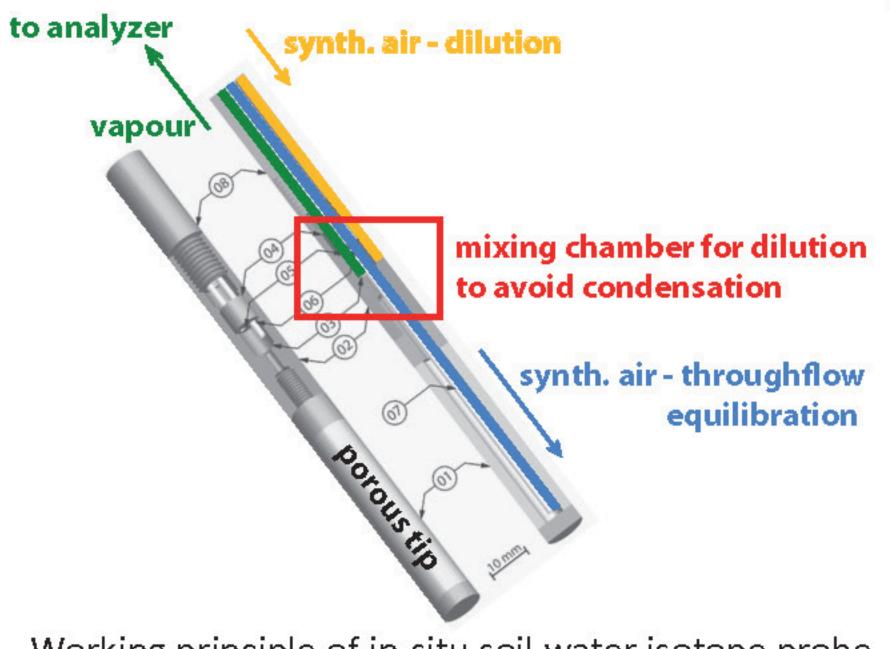
pressure

replace analyzer by gas-sampli.

isotope

www.hydro.uni-freiburg.de

Setup for direct in-situ monitoring of xylem water stable isotope composition Volkmann et al., 2016, PCE





Contamination

Application tests

> through valves

- Sampling 'conventionally' directly through the probe compared to sampling of vapour via probe into bags

diffusive mixing with ambient air over time

Required properties for containers

inexpensive or reusable

quick and easy to handle

conservative:

> diffusion-tight

Reliability tests

Filling with pure N₃ to identify

contamination by bag material

> through wall of container

> inert

sufficient volume (500-1000 mL)

rugged and inflatable to avoid

underpressure during measurement

> suitable for long-term storage

- Increased flowrate (150 mL/min) compared to Picarro method (35 mL/min) - for reasonable filling times in the field of ~ 5 min/bag
- Isotopically different sources (moist sand)

Gasbag types

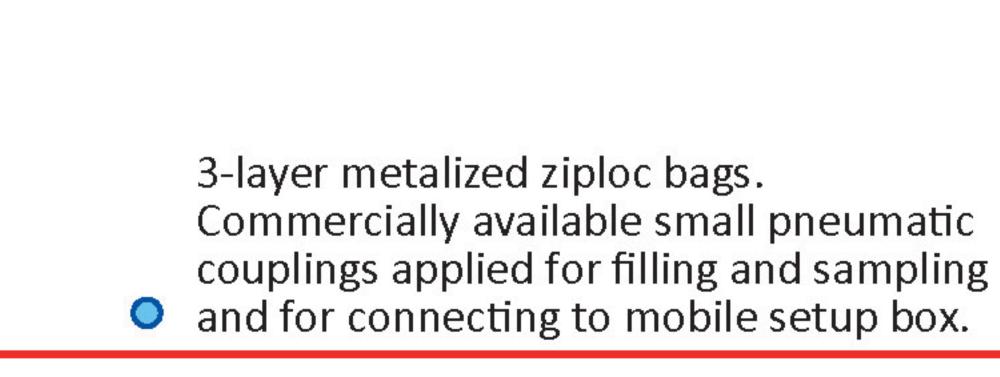
PE-spoutbags and Al-spoutbags. Caps were replaced by caps with septa Filling and sampling through septum □ via needle and 1/8" tubing.



3-layer metalized ziploc bags. Silicone blot serves as septum Filling and sampling through septum via needle and 1/8" tubing.



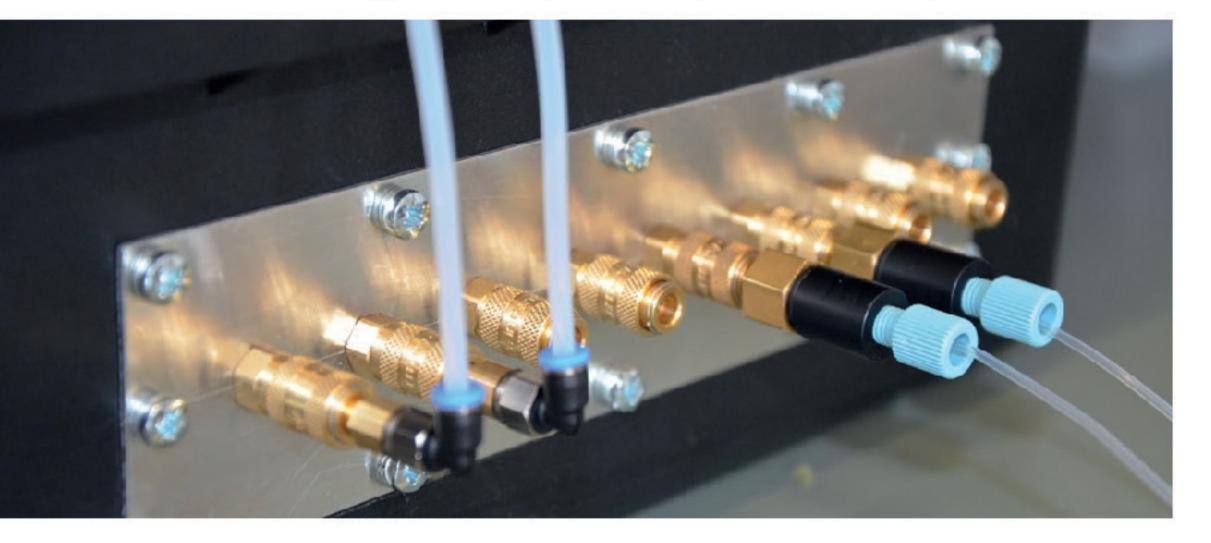
3-layer metalized ziploc bags. Commercially available gasvalves applied for filling and sampling via tubing.

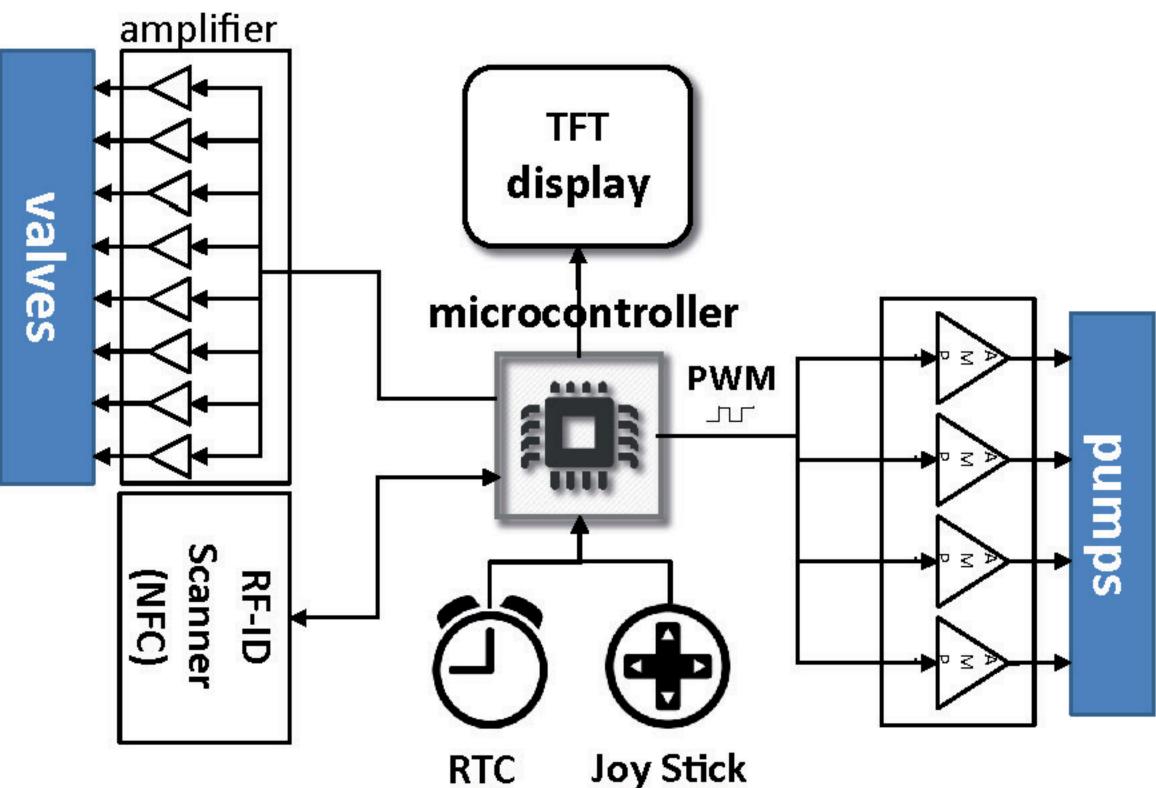


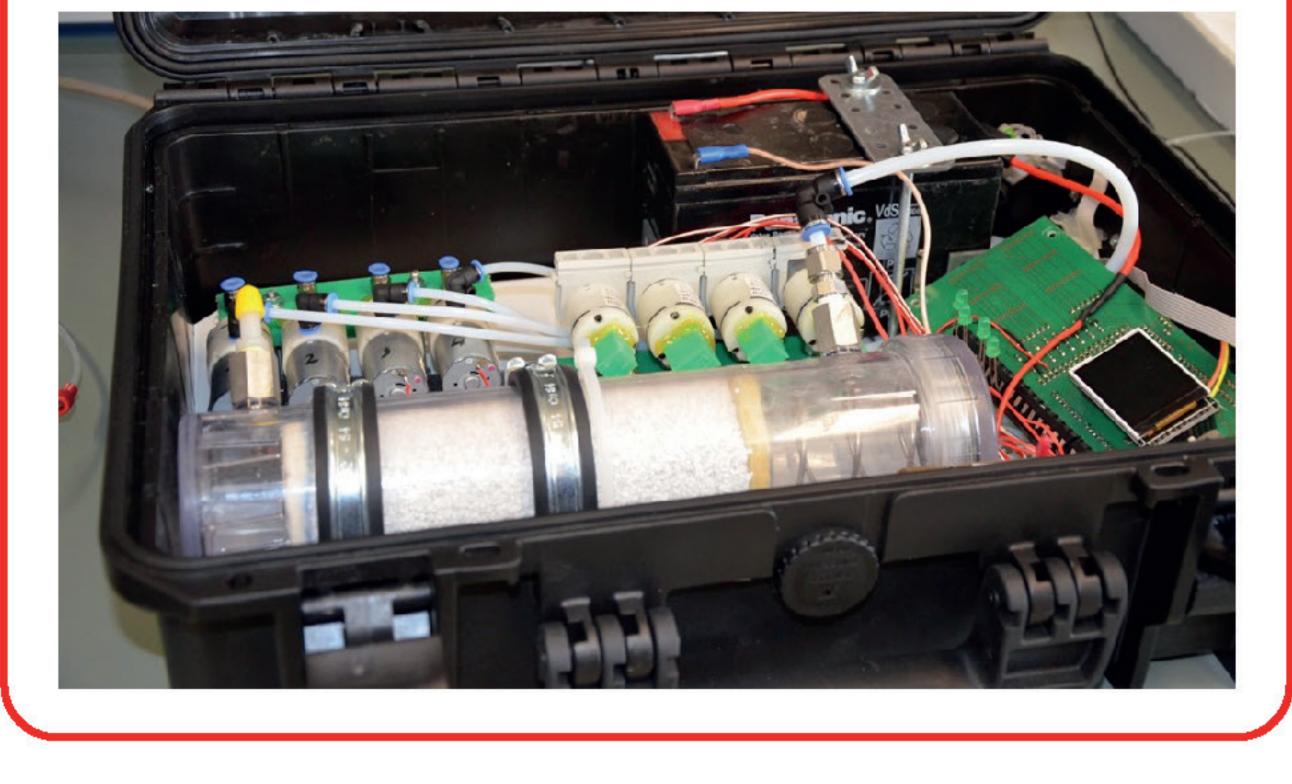
Direct vs. bags

Mobile setup box

The box couples both, probes and sampling bags. A microcontroller-based unit controls flowrates through the probes and thus filling times of the bags via small pumps and valves. Dried air ('DRIERITE') provides dry air for diffusive exchange with xylem sap inside the probes.







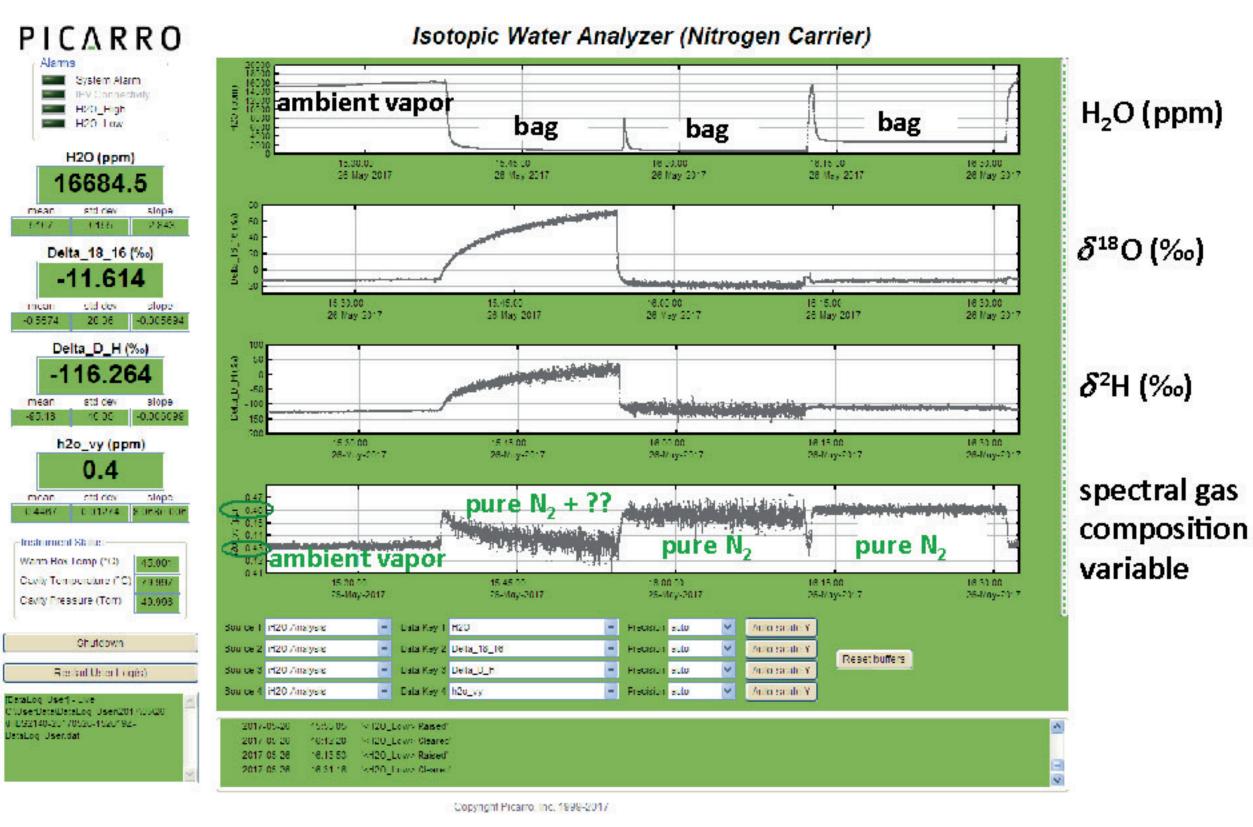
Effect of flowrates through probe on isotope readings Diffusion-tightness and long-term storage

original flowrate (Volkmann et al.) 25/15 💫 50/30 75/45 150 125 80 -35 10000 15000 20000 25000 10000 15000 20000 25000 H₂O (ppmv) H₂O (ppmv) o with dilution: throughflow/dilution (mL/min) w/o dilution: throughflow (mL/min)

gas

Original flowrates are defined by the internal pump of the isotope analyzer (35 mL/min). Flowrate of dry gas through the probe was increased stepwise up to 150 mL/min for reasonable filling times of the bags (\sim 5 min) in the field.

→ No establishment of equilibrium but clear kinetic fractionation effect, which is stronger for δ^{18} O than for δ^{2} H. Since fractionation is strongly temperature dependend, temperature has to be logged during sampling; calibration has to be performed under the same temperature and flow conditions.



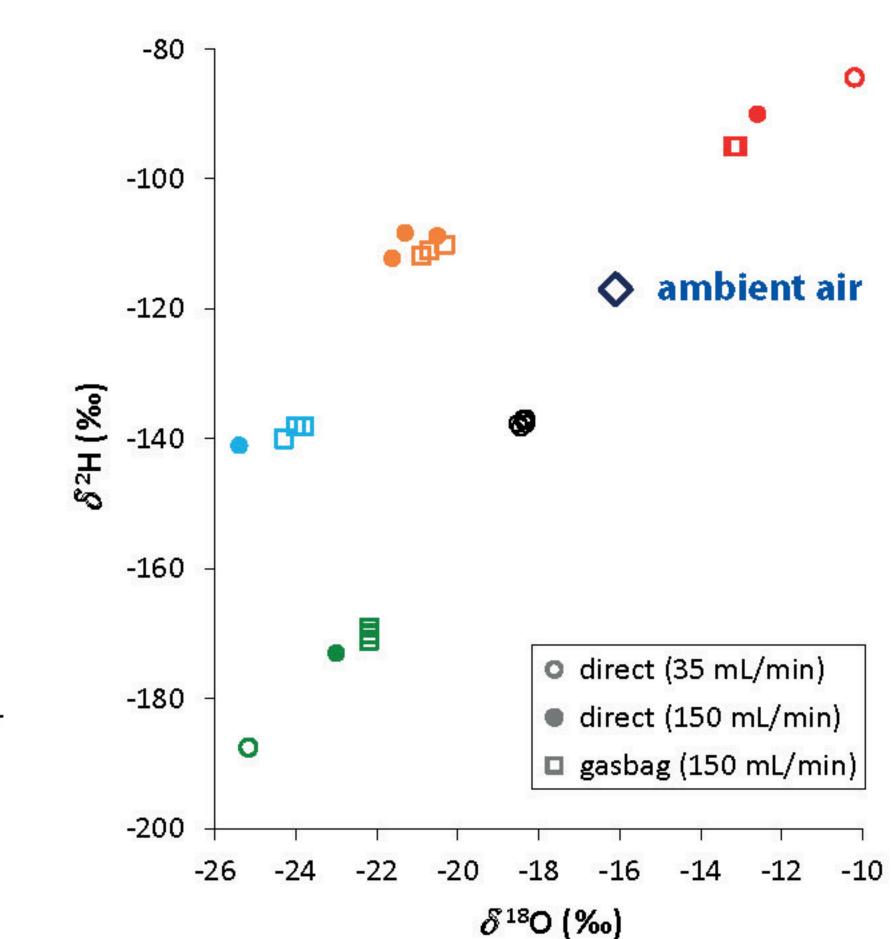
Isotope analyzer readings during measurement of ambient air and different bag types. Some substances may lead to flawed isotope data, even though vapour concentration looks inconspicious.

→ Spectral variable for gas-composition 'h2o_vy' shows clear evidence of contamination in this case.

18000 spoutbag_PE **5** 16000 □ spoutbag Al gasbag_Al-3-layer 14000 gasbag_Al-3-layer w/ valve gasbag_Al-3-layer w/ valve final flushing gasbag_Al-3-layer w/ coupling 10000 o pure N2 8000 ambient air 6000 2000 storage time (days)

Performance of different bag types, filled with pure N₂.

→ Increasing vapour concentration over time for different bag types indicates insufficient diffusion tightness of either bag material or valve type.



Sampling and analyzing vapour directly with probes (circles and dots) vs. sampling via probe into bag type with gasvalve (open squares).

Different colors represent source waters of different isotopic composition.

Conclusions

- Reliable bags were identified, suitable for vapour sampling and storage times up to 2 - 4 weeks.
- Sampling and filling of bags through probes with increased flowrates of 150 mL/min is possible, but identical calibration (flowrate, temperature) is crucial.
- Data of direct measurements agree well with bag data.
- Lab-tests look promising, field employment will be in May.

Soil water isotope probe