High frequency, realtime measurements of stable isotopes in liquid water

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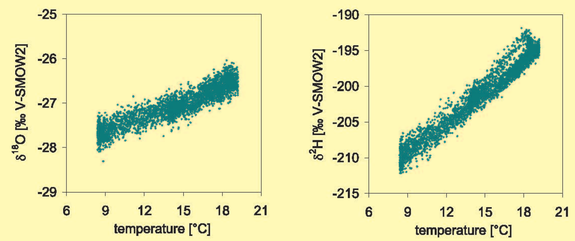
HYDROLOGY

Pre-application steps

Determination of membrane-specific fractionation factors

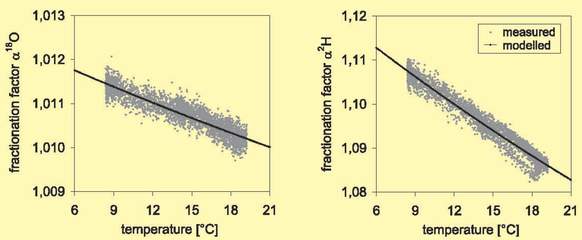
1. Measuring of thermal dependancy of water vapor isotopes and calibration



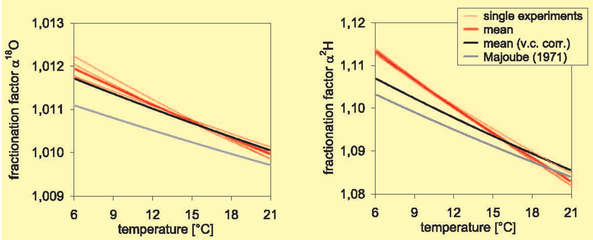
2. Calculation and modelling of fractionation factors α

$$\alpha = \exp\left(\left(a\left(10^6/T_K^2\right)+b\left(10^3/T_K\right)+c\right)/1000\right)$$

a, b, c - empirical parameters
T_K - temperature in K



3. Repetition and comparison with free water surface



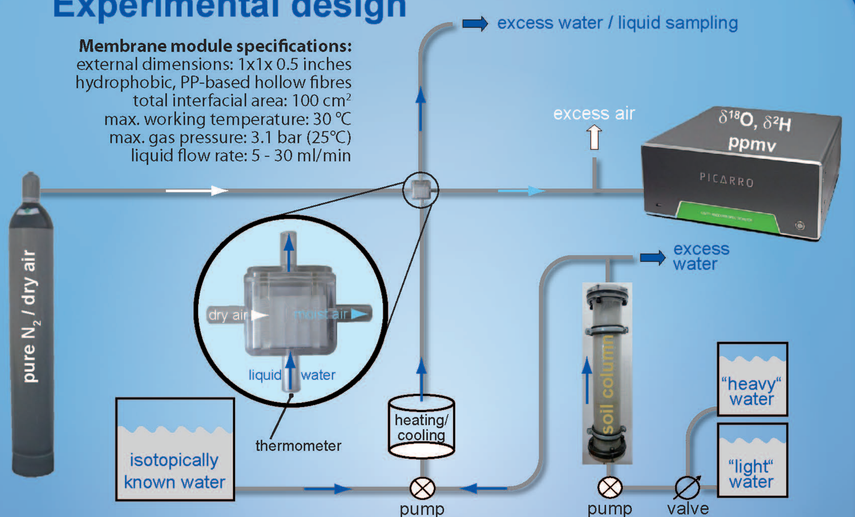
Introduction

- Isotope studies are still a trade-off between limited spatio-temporal resolution and extensive lab work
- In conventional isotope analytics a significant time lag exists between sampling and data acquisition (unlike EC or T measurements)
- Laser-based analyzers are now available and capable of measuring stable water isotopes in the vapor phase directly and continuously

Challenge:
Convert liquid water to water vapor and continuously provide it to analyzer

Experimental design

Membrane module specifications:
external dimensions: 1x1x 0.5 inches
hydrophobic, PP-based hollow fibres
total interfacial area: 100 cm²
max. working temperature: 30 °C
max. gas pressure: 3.1 bar (25°C)
liquid flow rate: 5 - 30 ml/min

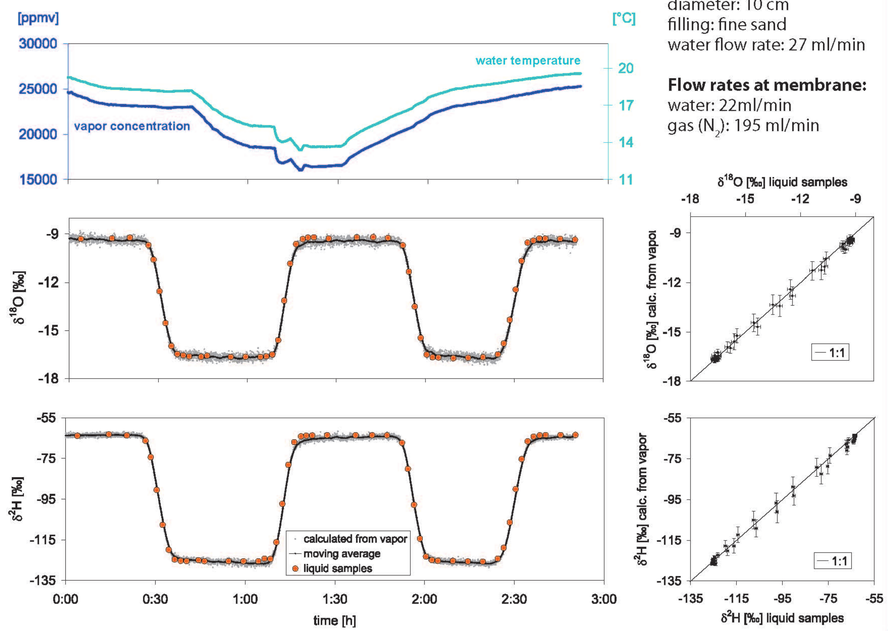


Conclusion

- Hydrophobic membranes may have specific isotopic fractionation factors
- The proposed method provides real-time data and captures even abrupt changes
  - **Response time**: about 10s (depending on setup dimensions and flow rates)
  - **Resolution**: minutes or below
  - **Precision**: comparable to conventional analysis (0.16‰ for $\delta^{18}O$, 1.1‰ for δ^2H)
  - **Supervision**: minimum requirements
  - **Restrictions**: water temperature must not exceed ambient temperature (else: heating / dilution)

Application: soil column experiment

Testing the method under highly unstable conditions (isotopically, thermal)
Verification by conventional analysis



Soil column parameters:
length: 50 cm
diameter: 10 cm
filling: fine sand
water flow rate: 27 ml/min

Flow rates at membrane:
water: 22ml/min
gas (N_2): 195 ml/min

Possible future applications

Suitable wherever dynamic processes have to be observed in real time and with high temporal resolution

Precipitation

Soil water

Runoff

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