Effects of soil properties on the apparent water - vapor isotope equilibrium fractionation: Implications for the headspace equilibration method

Barbara Herbstritt[1], Mathes Limprecht[1], Benjamin Gralher[2], Markus Weiler[1]

HYDROLOGY

Introduction

- Stable isotopes have proven to be a powerful tool in hydrology
- There are still significant restrictions in investigations of the unsaturated zone, especially concerning soil water extraction
- Laser-based analyzers are capable of measuring stable water isotopes in the vapor phase directly and continuously
- A method for rapid determination of soil water stable isotope signatures based on analyzing headspace vapor of samples being in isothermal equilibrium with the soil water of interest [Wassenaar, 2008] was used
- Interferences with other gaseous molecules are known [Brand et al, 2009; Hendry et al, 2011]
  ▶ Further interferences with soil characteristics are suspected

Experimental procedure

Method

- split samples from 3 technical and 5 natural substrates, dried at 105°C
- rewetted to different water contents: 1%, 5%, 10%, 20%
- with different waters:

	$\delta^{18}O$	δ^2H
FSM	-16,6 ‰	-124,88 ‰
LW	-9,34 ‰	-63,79 ‰
NoS	-0,33 ‰	-1,99 ‰

- filled in diffusion-tight bags according to pre-test (fig.1)
- filled with 2 different headspace atmospheres: dry air and N_2
- 48 h isothermal equilibration (21°C)
- headspace sampling with Picarro L2120-i
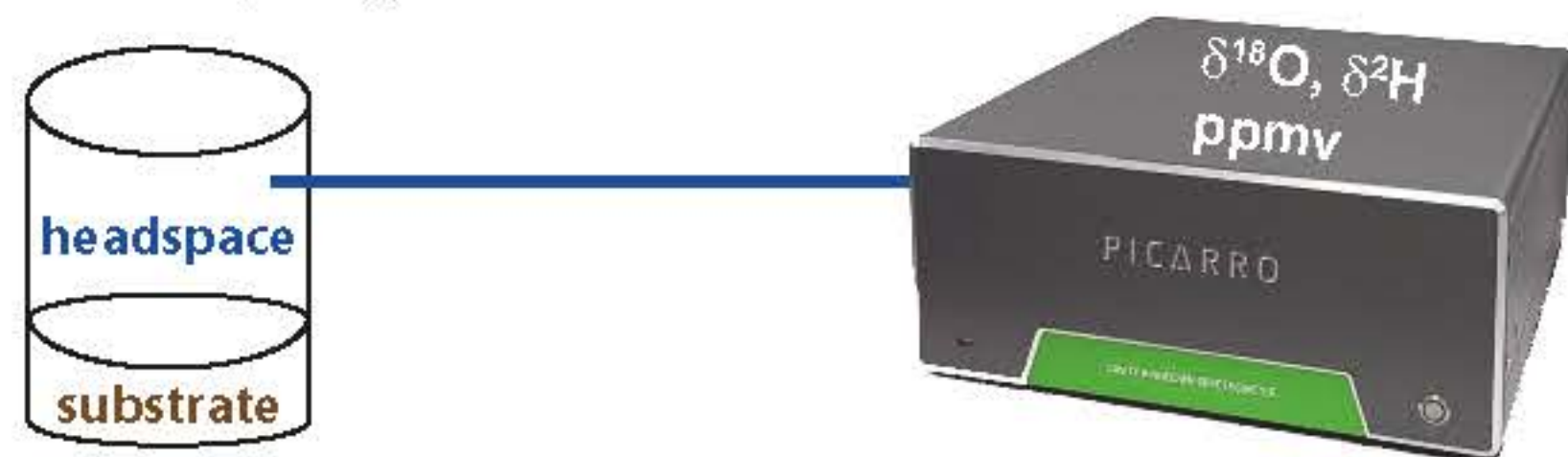
Pre-test of sampling bags

~ 250-300 g soil of medium soil moisture was filled in bags, stored at room temperature and weighed daily
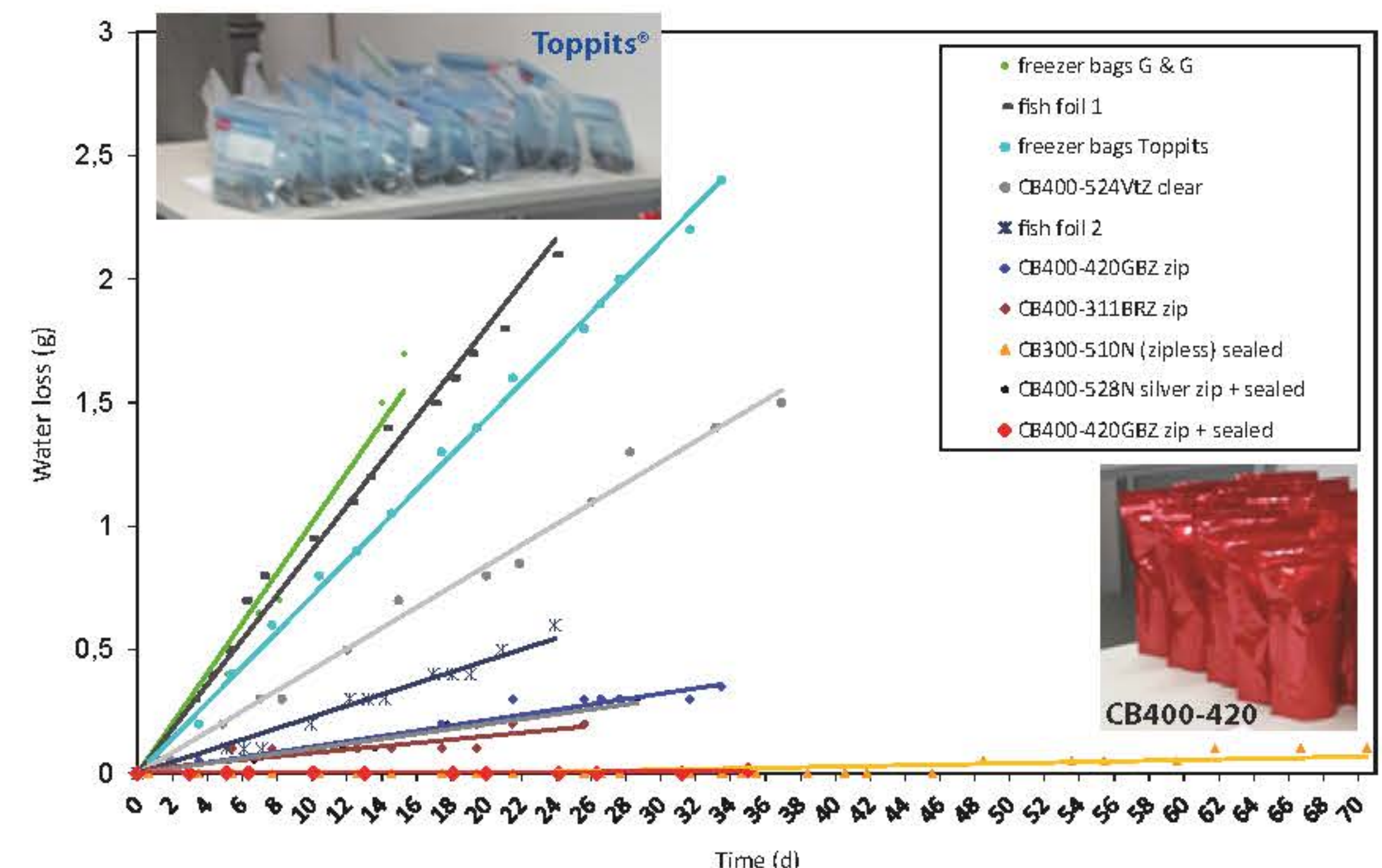

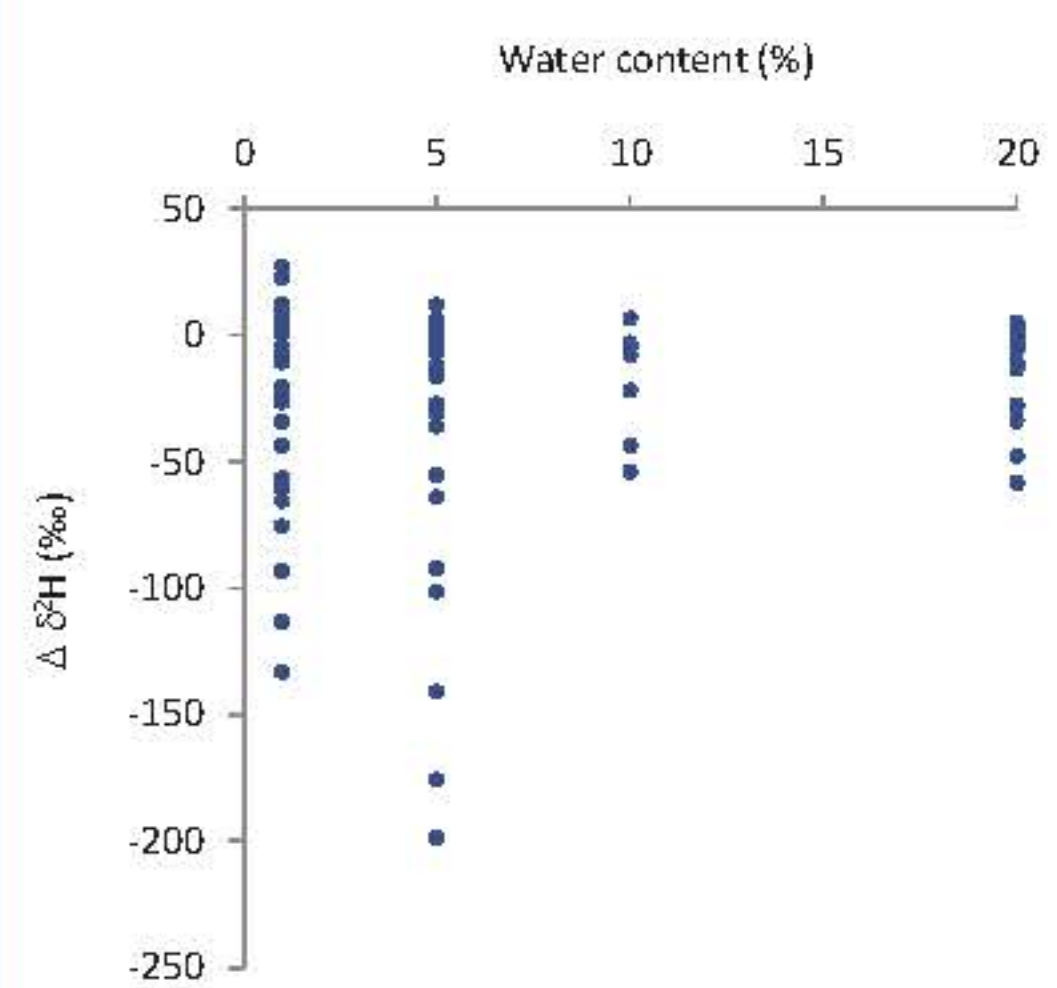Figure 1: diffusion-tightness of different bag materials

Results

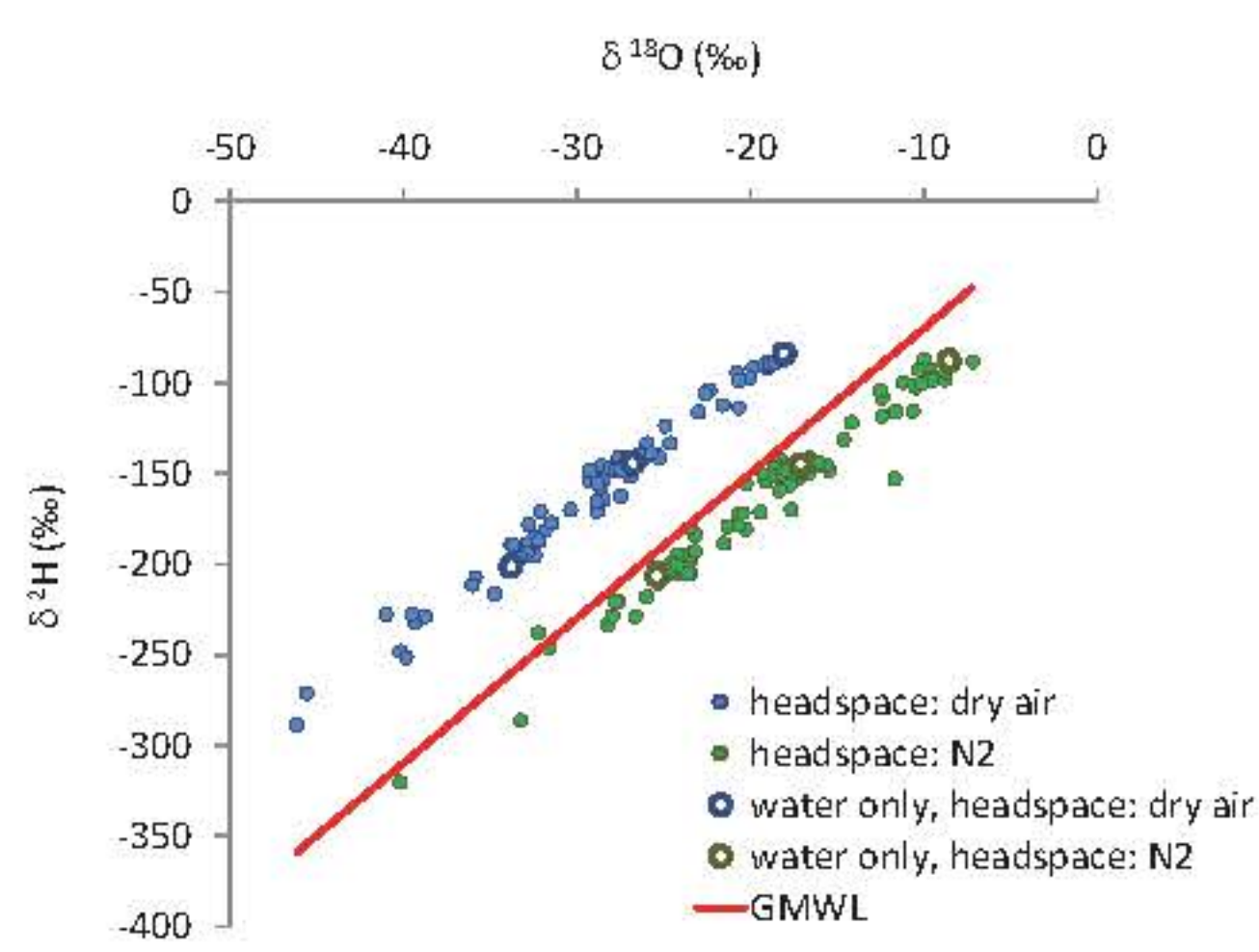Figure 2: moisture dependency of isotopic signature

Figure 3: apparent isotopic signature of different waters derived from different headspace atmospheres and soil compositions
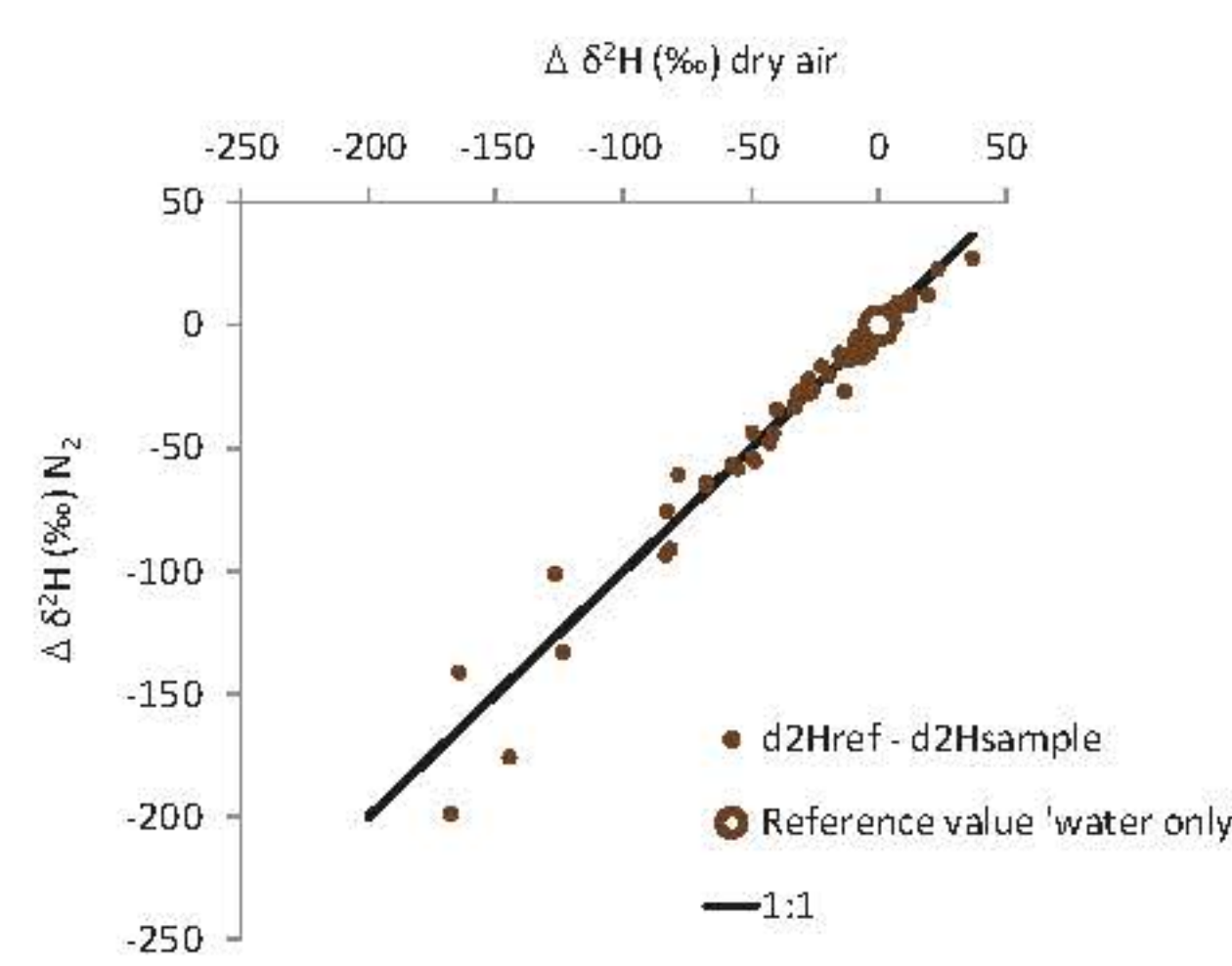
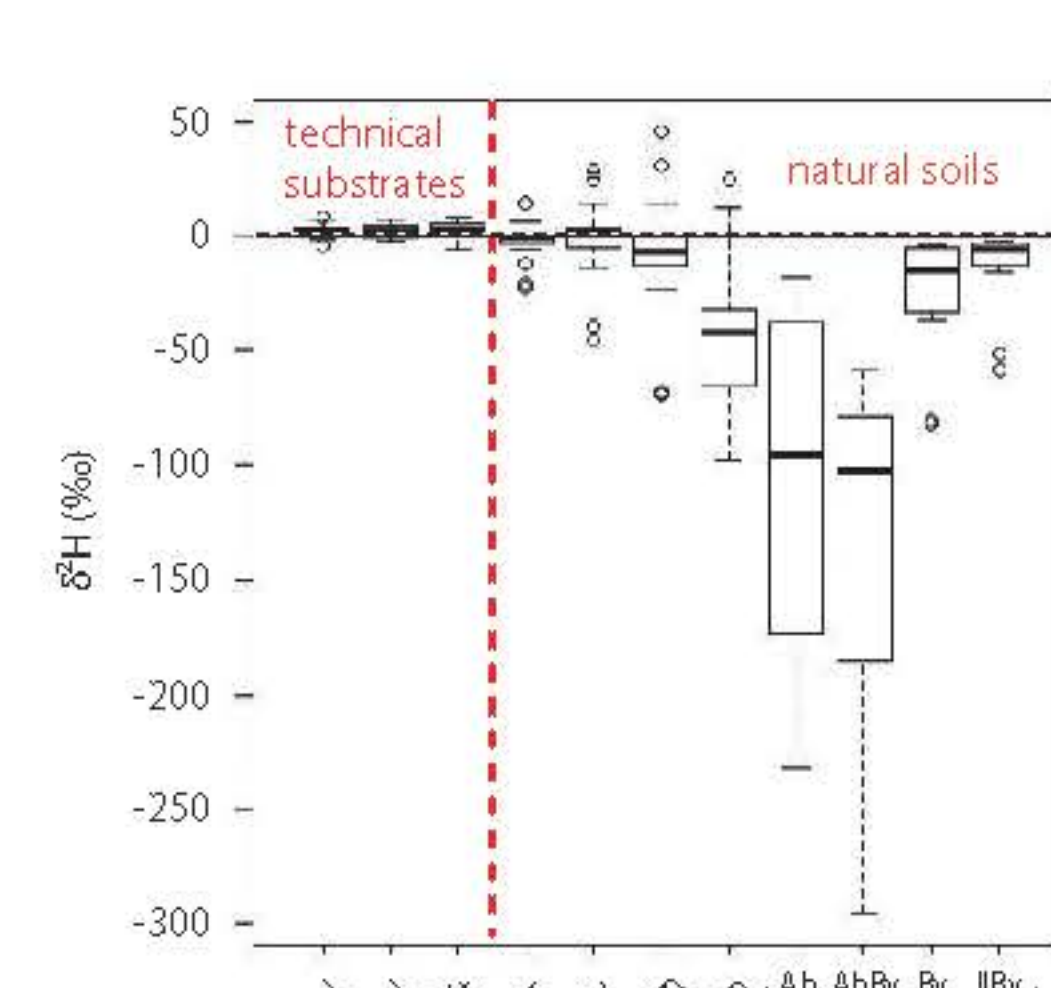Figure 4: substrate-induced deviation of δ^2H from the respective reference in the different atmospheres

Figure 5: substrate dependency of δ^2H in technical and natural substrates

→ Isotope data from soils with low water content show significantly higher variations (fig. 2).

→ The systematic shift in $\delta^{18}O$ for different atmospheres is instrument specific (fig. 3 and 4).

→ 'water only' as reference shows: isotopic signature of substrates appears to be systematicly depleted, regardless of employed water (fig. 3 and 4).

→ Isotope data derived from natural soils show very large variations compared to technical substrates (fig. 5).

Correction attempt for natural soils

- split samples of natural soil (cambisol on shist)
- oven-dried at 105°C
- rewetted to same soil moisture
- with different waters:

	$\delta^{18}O$	δ^2H
FSM	-16,56 ‰	-125,26 ‰
BL V	-12,31 ‰	-88,49 ‰
BL IV	-7,52 ‰	-51,34 ‰

- headspace-atmosphere: N_2
- 48 h isothermal equilibration (21°C)
- headspace sampling of stable isotopes with Picarro L2120-i
- C_{org} was analyzed after headspace sampling with elementar vario EL cube
- additional internal Picarro data 'CH4_mean' was correlated with C_{org} for correctional purposes
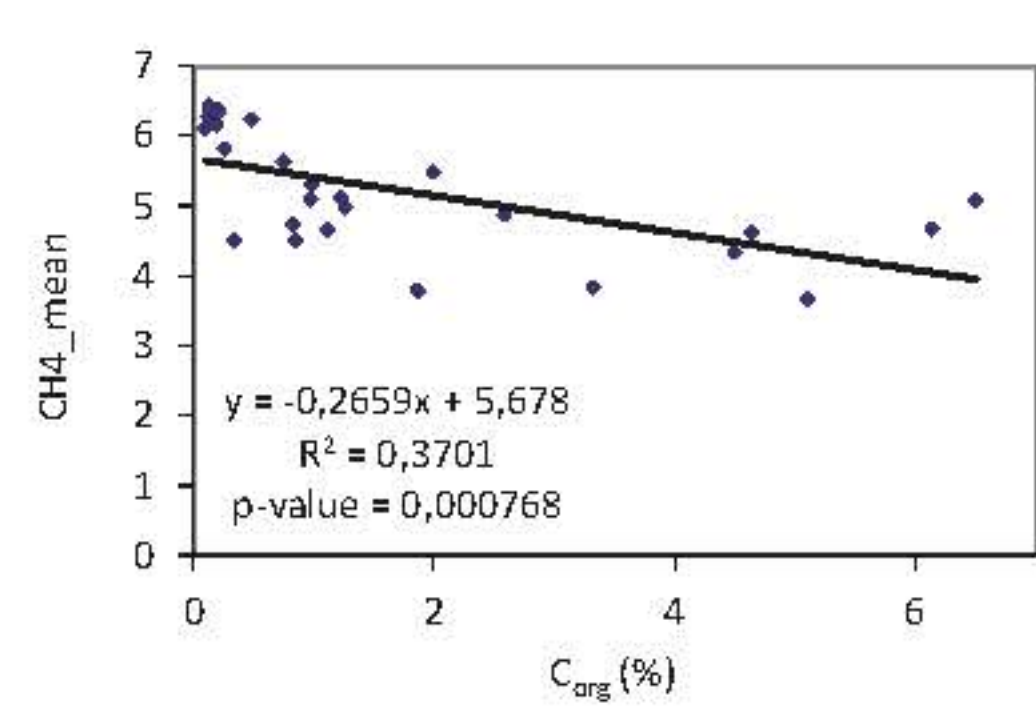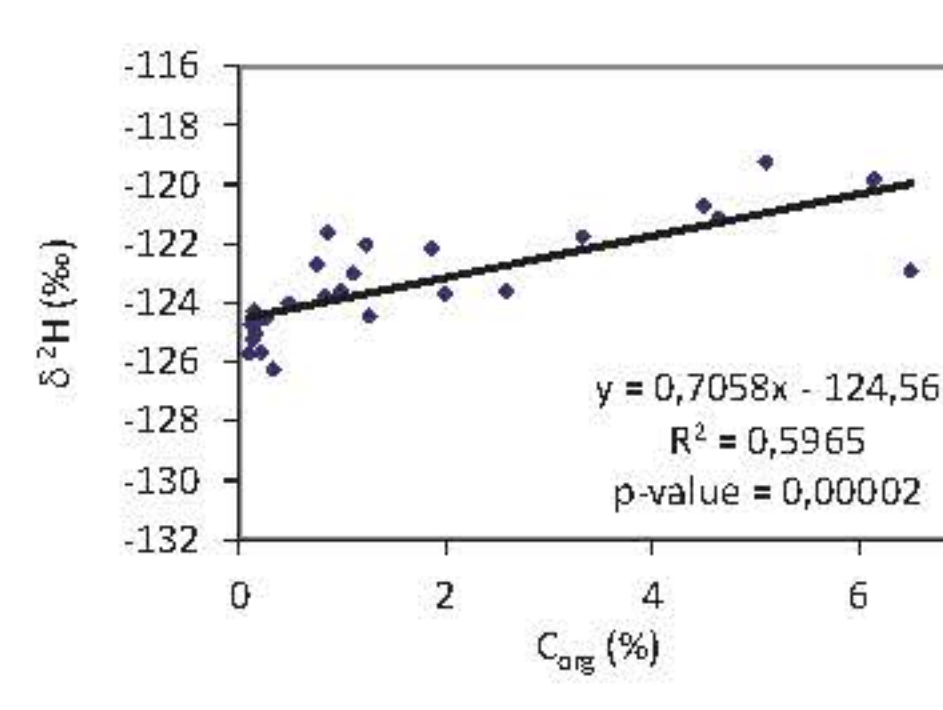

Figure 6: correlation of C_{org} and CH4_mean

Figure 7: correlation of C_{org} and isotopic composition

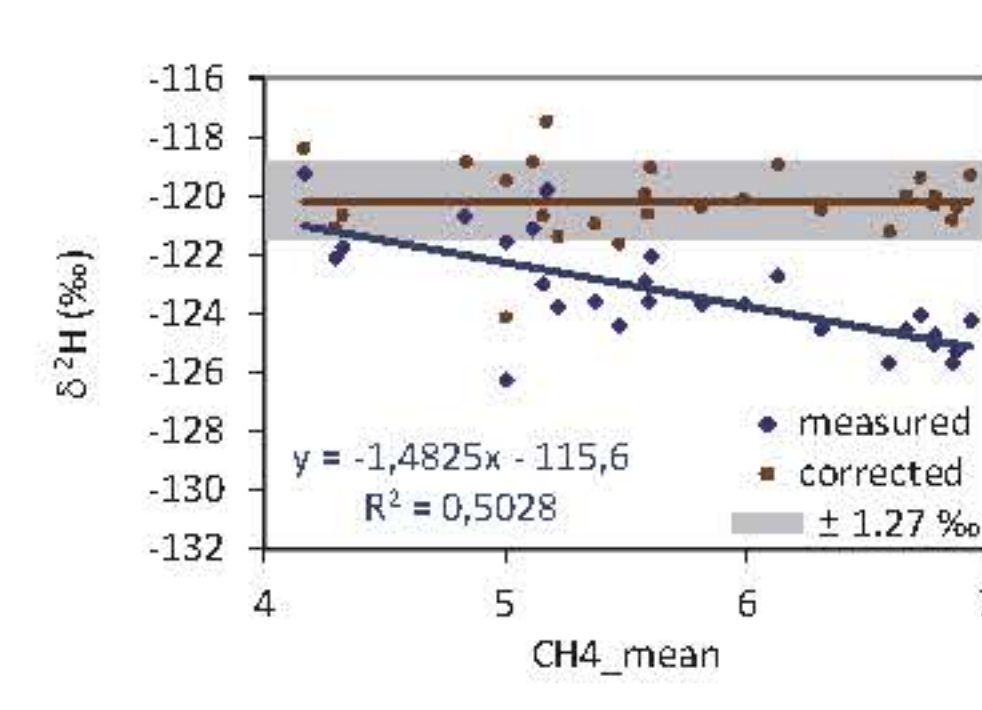Figure 8: correlation between CH4_mean and isotope values (blue), which was used for correction (brown)

→ A correlation between C_{org} and CH4_mean exists (fig. 6).

→ Correlation for C_{org} and δ^2H is slightly better than for C_{org} and $\delta^{18}O$ (fig. 7).

→ Correlation for CH4_mean and $\delta^{18}O$ is slightly better than for CH4_mean and δ^2H (fig. 8).

→ Correction procedure reduces SD from 1,8 to 1,27 and from 1,14 to 0,36 for δ^2H and $\delta^{18}O$ respectively (fig. 8).

Conclusion

Isotopic compositions from natural soils seem to be depleted compared to technical substrates.

Organic carbon contents seem to have a systematic impact on the apparent isotopic composition of soil water.

Correlations with additional internal Picarro rawdata (e.g. CH4_mean) can be used for data correction.

Not all variations can be explained with organic compounds, high contents of clay or salt may play a role, too.

Future calibration and correction procedures need to take this into account.

References

Brand, W.A., Geilmann, H., Crosson, E.R., Rella, C.W., 2009. Cavity ring-down spectroscopy versus high-temperature conversion isotope ratio mass spectrometry; a case study on δ^2H and $\delta^{18}O$ of pure water samples and alcohol/water mixtures. Rapid Communications in Mass Spectrometry, 23(12): 1879-1884

Hendry, M.J., Richman, B., Wassenaar, L., 2011. Correcting for Methane Interferences on δ^2H and $\delta^{18}O$ Measurements in Pore Water Using H2O (liquid)–H2O (vapor) Equilibration Laser Spectroscopy. Analytical chemistry, 83(14): 5789-5796

Wassenaar, L., Hendry, M., Chostner, V., Lis, G., 2008. High Resolution Pore Water δ^2H and $\delta^{18}O$ Measurements by H2O (liquid) – H2O (vapor) Equilibration Laser Spectroscopy. Environm. Science & Technology, 42(24): 9262-9267