Correcting for spectral interferences when measuring plant water stable isotopes

HYDROLOGY # 197

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Motivation

Laser based analyzers are widely used in ecohydrology to analyze plant water isotopic compositions ($\delta^{18}O$ and $\delta^{2}H$). Different methods are established to extract plant water for water stable isotope analysis like e.g., cryogenic vacuum distillation (CVD), direct vapor equilibration-laser spectroscopy (DVE-LS), and *in-situ* methods via water isotope probes (WIP). We compared these methods to answer the following questions:

- Which method is most appropriate or reliable?
- Which method is most robust or precise?
- Are the results from the different methods intercomparable?

Comparison of Extraction/ Equilibration Methods

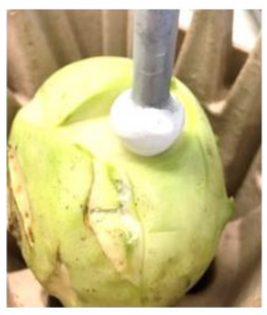
CVD

Koeniger et al., 2011

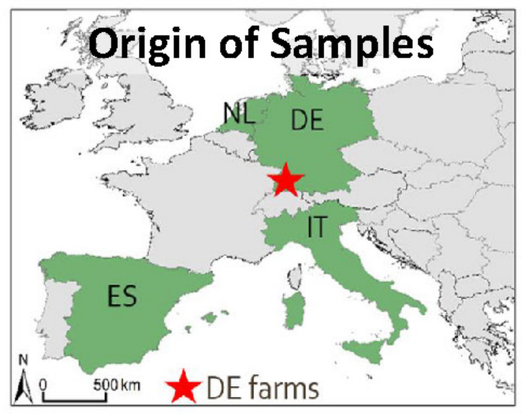
DVE-LS

Wassenaar et al., 2008

in-situ



Volkmann & Weiler, 2014

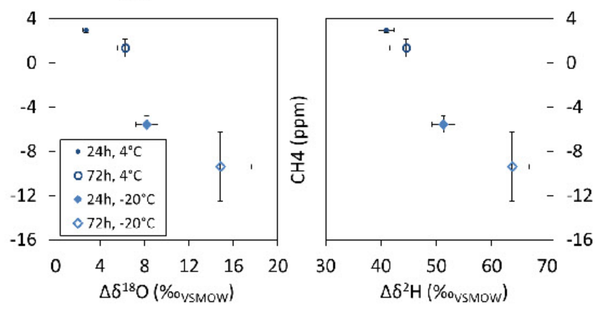


4 Regional farms close to Freiburg (DE), supermarket vegetables (NL, IT, ES).

Experimental design

- Plant material: 4 different vegetable samples (kohlrabi, cauliflower, potato, celery root - due to size).
- 5 Replicates per vegetable and farm, divided into 3 splitsamples for each of the three methods.
- 3 Extraction- and equilibration-methods (CVD, DVE-LS (bags), *in-situ*).
- Isotope analysis ($\delta^{18}O$, $\delta^{2}H$, and co-recorded spectral parameters) by CRDS (Picarro L2120-*i*, L2130-*i*, L2140-*i*).

Storage of Plant Material

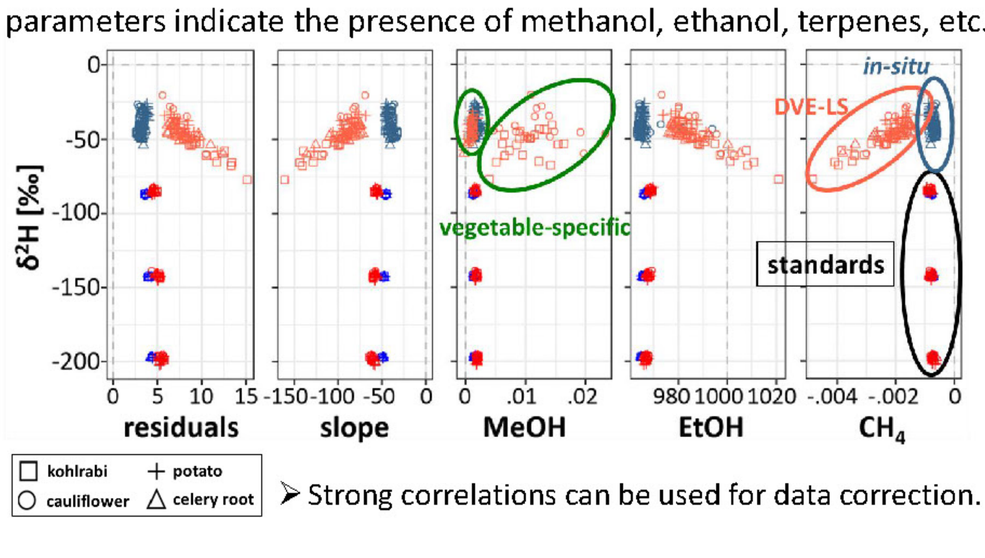


Apparent depletion in both isotopes after 1-3 days already, caused by release of organics during decomposing of cells and cell walls. Stronger effect for storage at -20°C than at 4°C.

➢ Plant tissue cannot be stored.
➢ Sampling campaigns have to be coordinated with lab capacities.

Spectral Interferences

Interferences occur at the wavelengths of water isotopologues. Spectral parameters are uncalibrated and dimensionless; selected parameters indicate the presence of methanol, ethanol, terpenes, etc.



➢ Strong correlations can be used for data correction.

Correction Equations

Linear regression approaches to correct for linear correlations.

'Picarro'-correction (L2120-*i* and older)

$$uncal_{(org_{d18O})} = delta_{(1816_{slope})} \times (org\ 77/org\ splinemax) + delta_{(1816_{intercept})}$$

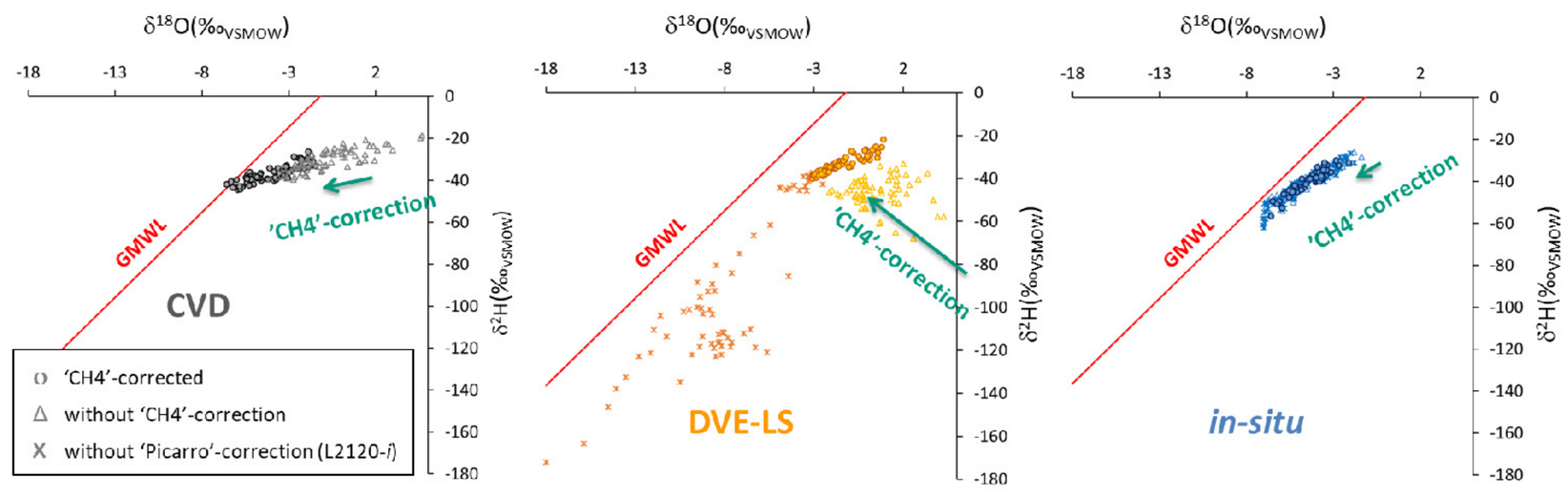
$$uncal_{(org_{d2H})} = delta_{(dh_{slope})} \times (org\ 82/org\ splinemax) + delta_{(dh_{intercept})}$$

'CH4'-correction ('organics_ch4') Herbstritt et al. (2024)

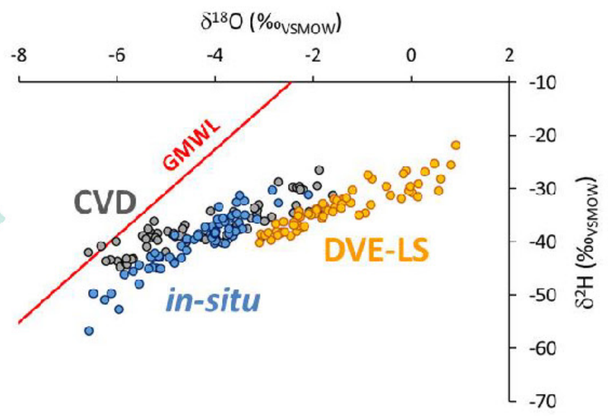
$$\delta_{i,cor} = \delta_{i,obs} - m_{l,i} \times (\text{org_CH4}_{obs} - \text{org_CH4}_{ref})$$

m: specific slopes for each of the methods
org_CH4_{obs}: measured 'CH4' values
org_CH4_{ref}: mean 'CH4' value of the co-measured water standards

Results: Effect of Method-specific Data Corrections



➢ Wide data spread before post-correction procedure. Each method is differently affected by organics.



➢ 'CH4'-corrected data for the three methods.

Boxplots of deuterium excess values for the different sites for each vegetable. Stars indicate the levels of significance from the Kruskal-Wallis tests for each method (*: p <=0.05; **: p <= 0.01).

➢ All methods are sensitive enough to resolve differences in natural abundance.

Conclusion

- Pre-tests showed: plant tissue cannot be stored, neither at 4°C nor at -20°C. => Sampling campaigns have to be coordinated with lab capacities.
- *in-situ* method is almost not affected by organics => best for plant samples
  disadvantage: not applicable for small samples due to size of probe.
- Slopes for organics-corrections have to be determined for all types of instruments and all measurement modes individually.
- Isotope data from all three methods are comparable – after 'CH4-correction'.
- Correction approaches improve data quality without knowing the exact chemical composition of the plant sap.
- Standardized tools for contaminant removal or post-correction applications from manufacturers - in particular for vapor-mode analysis - are still needed.

References

Herbstritt, B., Wengeler, L. and Orlowski, N., 2024. Coping with spectral interferences when measuring water stable isotopes of vegetables. Rapid Communications in Mass Spectrometry, 38(22), p.e9907. doi: 10.1002/rcm.9907

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