Coping with spectral interferences when measuring vegetable water (vapor) isotopic composition

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1. Introduction

- Accurate measurements of ^{18}O and ^{2}H ratios are inevitable for tracing water movement through the critical zone
- Many studies apply different water extraction/water vapor equilibration techniques to obtain ^{18}O and ^{2}H ratios from soils and plants
- Volatile organic compounds (VOCs) can be co-extracted/equilibrated with the water/vapor and lead to erroneous isotope results in isotope ratio infrared spectroscopy analysis (IRIS) [1]

Aims:

- Compare different water stable isotope extraction/equilibration techniques for measurements of different types of vegetables
- Examine how co-extracted/ equilibrated VOCs (i.e., MeOH and EtOH) affect the isotopic ratios of the measured vegetables

2. Materials & Methods

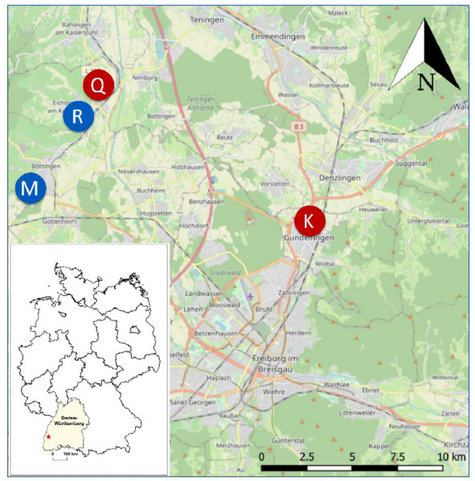

Fig. 1. Vegtable sampling sites at four farms (two organic in red and two conventional in blue) in the state of Baden-Wuerttemberg, DE.

5 replicates from:

- 4 farms (Fig. 1):
  - –2 organic (K, Q)
  - –2 conventional (M, R)
  - – plus supermarket (S)
- Of 4 vegetables:
  - – Cauliflower (CAU)
  - – Celery root (CEL)
  - – Kohlrabi (KOH)
  - – Potato (POT)

- 3 Water extraction/vapor equilibration methods:
  1. In situ water vapor sampling probes (in situ) (L2120-i)
  2. H_2O(liquid)-H_2O(vapor) equilibration (DVE-LS) (L2120-i)
  3. Cryogenic vacuum extraction (CVD) (L2130/40-i)
- Isotope analysis via cavity ring-down spectroscopes (CRDS, L2120–40-i, Picarro Inc., Santa Clara, CA, US)
- Precision: ±0.6 ‰ for δ^2H and ±0.16 ‰ for $\delta^{18}O$ (liquid); ±1.0 ‰ for δ^2H and ±0.15 ‰ for $\delta^{18}O$ (vapor)

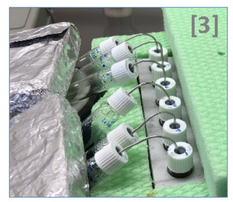

Fig 2. Applied water extraction/vapor equilibration techniques for obtaining vegtable water isotopic composition (left to right: in situ water vapor sampling, $H_2O_{(liquid)}$-$H_2O_{(vapor)}$ equilibration, and cryogenic vacuum extraction.

3. Results & Discussion

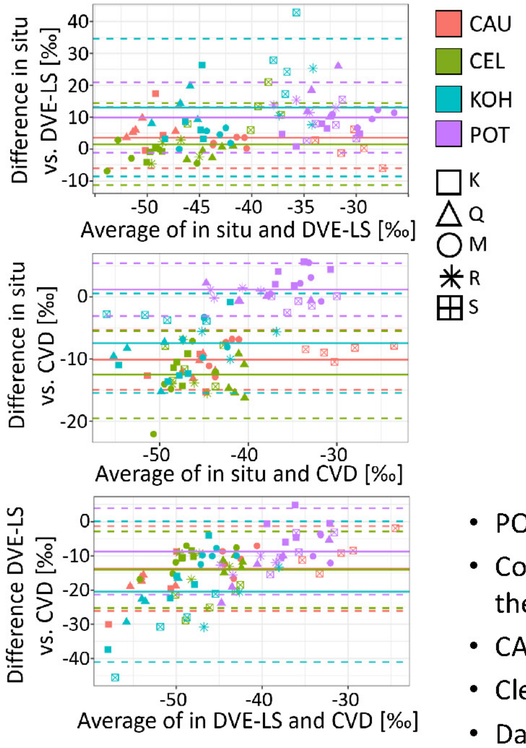

Fig. 3 Bland-Altman plots for all vegetable measurements (different colours) from all farms (different symbols). Lines indicate bias, same coloured dashed lines indicate the upper and lower 95% limits of agreement. Data is corrected for VOCs as recommended by Picarro.

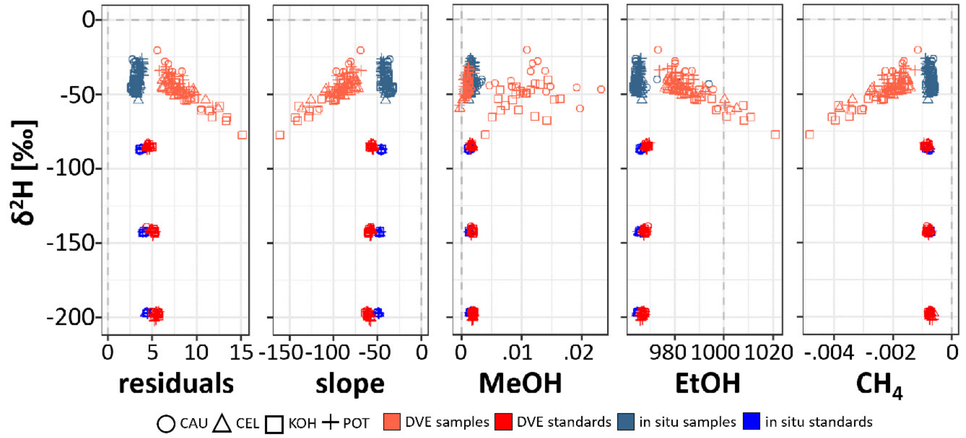

Fig. 4 Selected spectral parameters (L2120-i, Picarro) plotted against δ^2H values (light red: DVE sample values, bright red: DVE standards, blue: in situ samples, bright blue: in suit standards; different symbols represent different vegetables).

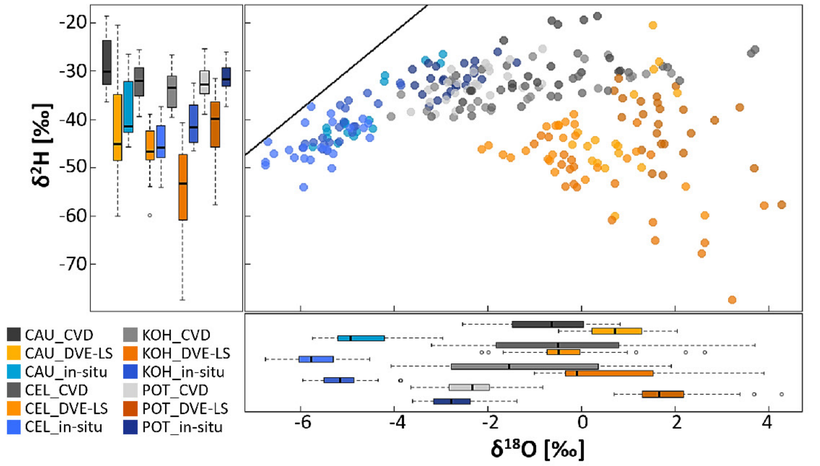

Fig. 5 Dual isotope plot of the four vegetable types (cauliflower - CAU, celery - CEL, kohlrabi - KOH and potato - POT) from all sampling sites obtained from three methods (cryogenic vacuum distillation - CVD, in situ water vapor sampling - in situ and H_2O(liquid)-H_2O(vapor) equilibration - DVE-LS). Data is corrected for VOCs as recommended by Picarro.

- POT results were the most comparable between methods (Fig. 3)
- Comparison of in situ and CVD worked best for CAU, KOH and POT and comparison of in situ and DVE-LS worked the best for CEL (Fig. 3)
- CAU and KOH produced the most VOCs (Fig. 4)
- Clear relationships between DVE-LS samples and spectral parameters indicated co-equilibrated VOCs (Fig. 4)
- Data from DVE-LS method varied the most (Fig. 5)
- In situ method showed the smallest data spread across measurements, farms and vegetables and was comparable to CVD for some type of vegetables (Fig. 5)

4. Conclusions & Future Needs

- VOCs caused interferences during CRDS measurements
- Vegetables produced different amounts of VOCs, which affected methods differently
- Standardized correction protocols for IRIS analysis for individual VOCs and machines needed
- Correction protocols need to include other VOCs

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Reference
[1] Brand et al., 2009, Rapid Commun Mass Spectrom doi: 10.1002/rcm.4083