A discussion on the paper "Identification and correction of spectral contamination in 2H/1H and 18O/16O measured in leaf, stem, and soil water"

Natalie M.Schultz et al.,RCMS,2011

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Background

Stable Isotope

Isotope Ratio $R=C_H/C_L$

$\delta=(R_{Sample}-R_{Standard})/R_{Standard}\cdot 1000‰$

International Standard :
Vienna Standard Mean Ocean Water

Why do we analyse stable isotope of plant and soil water

Water use patterns in terrestrial ecosystems

Partition of the components of evapotranspiration

Controls on surface H_2O and CO_2 fluxes

……

How to analyse it

Isotope ratio mass spectrum(IRMS)

Isotope ratio infrared spectroscopy(IRIS)

Objectives

Quantify the measurement errors

Compare the contamination effects

Correction

Test the accuracy of the corrections

Sample collection

From:

Rosemount Research and Outreach Center,USA

The Marcell Experimental Forest,USA

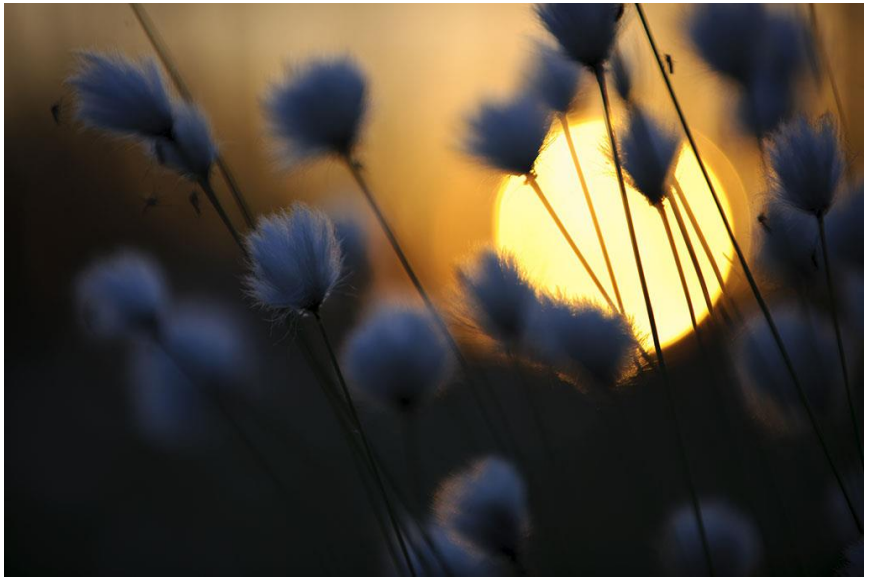
The Borden Forest Research Station,Canada

Table 1. The different plant species examined in this study. Corn, soybean, big bluestem, purple clover, and creeping spearwort samples were collected from the RROC, cotton grass and leather leaf samples were collected from the MEF, and white ash, large-tooth aspen, and red maple samples were collected from the BFRS

Common name	Species	Sample type
Corn	*Zea mays*	leaf, stem, soil
Soybean	*Glycine max*	leaf, stem, soil
Big bluestem	*Andropogon gerardii*	leaf, stem, soil
Purple clover	*Trifolium pretense*	leaf, stem
Creeping spearwort	*Ranunculus flammula*	leaf, stem
Snap peas	*Pisum sativum*	leaf, soil
Cotton grass	*Eriophorum chamissonis*	leaf, stem
Leather leaf	*Chamaedaphne calcyculata*	leaf, stem
White ash	*Fraxinus americana*	leaf
Large-tooth aspen	*Populus grandidentata*	leaf
Red maple	*Acer rubrum*	leaf


View of Commonalty


View of Commonalty



Cryogenic vacuum distillation

To extract water

Organic compounds may co-distill

Avoid isotope fractionation

Isotope analysis

a DLT-100 liquid water isotope analyzer
a HT-300A autosampler

Off-Axis Integrated Cavity Output Spectroscopy (OA-ICOS)

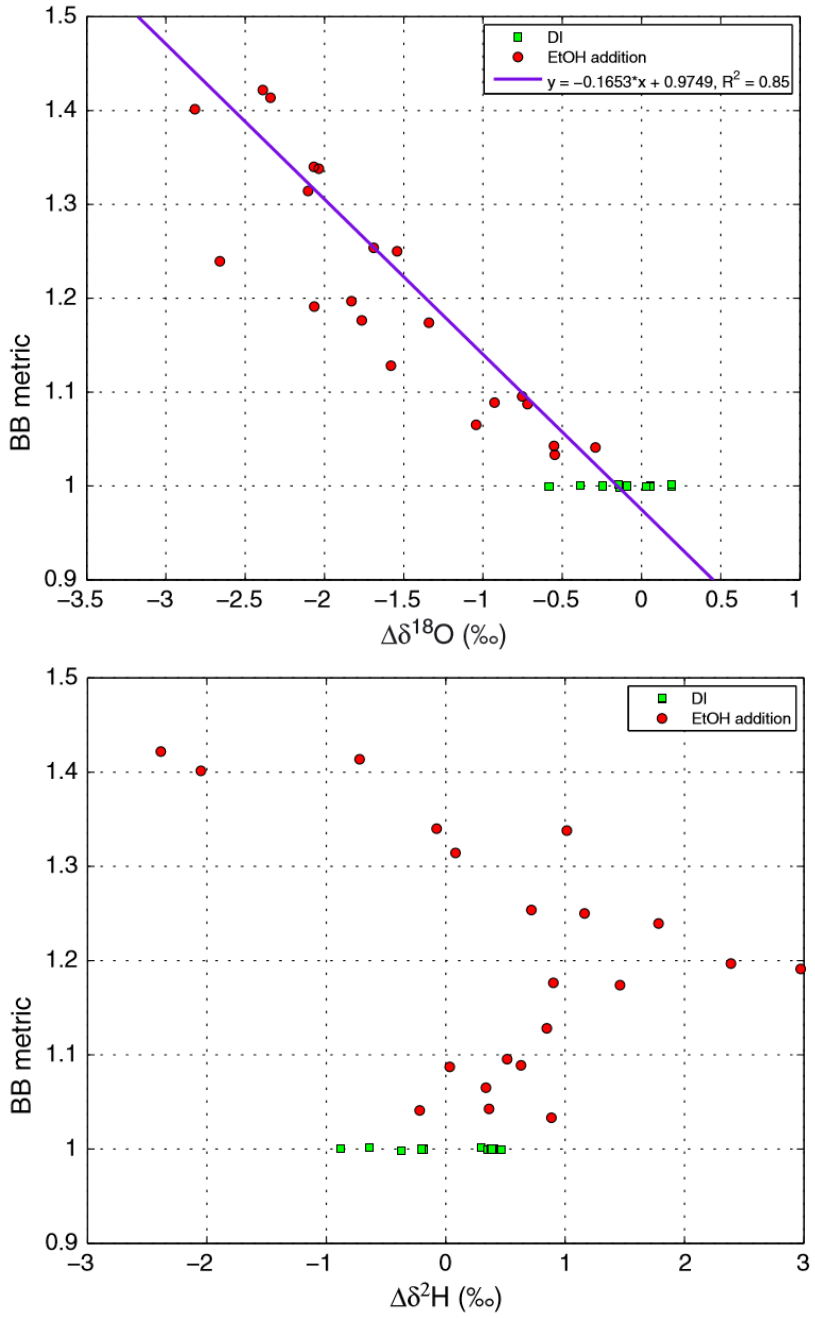
Magical Software

The LWIA Spectral Contamination Identifier (LWIA-SCI) software

Identify features in the LWIA spectra that are
consistent with water contamination

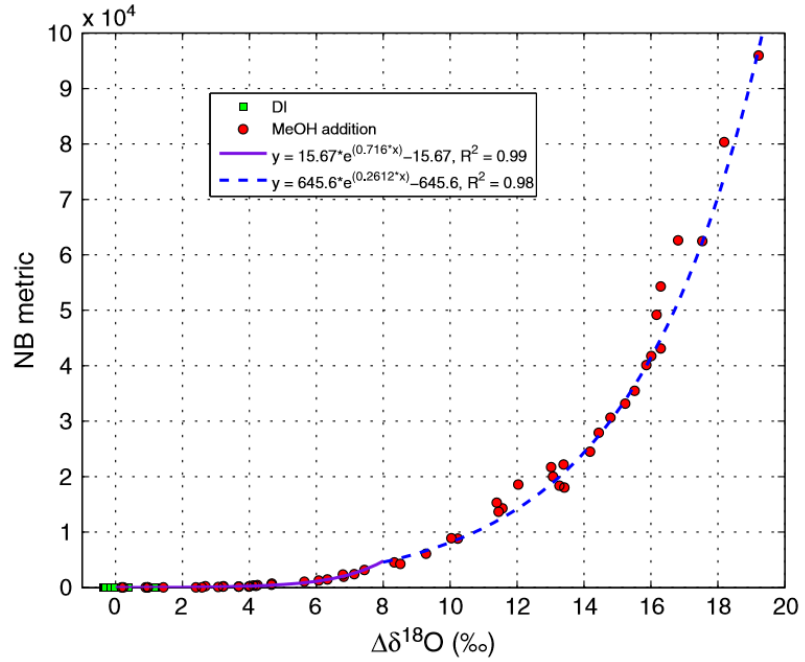
Create correction curves

Spike deionized water with varying amounts of EtOH and MeOH
EtOH: 0.5%-5.0%
MeOH:45 ppmv -0.2%



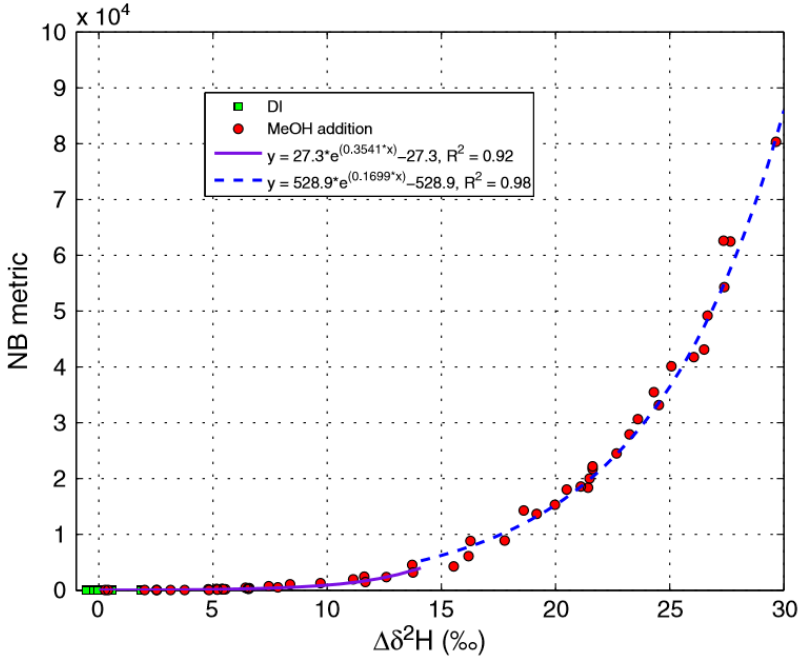
$$BB = -0.1653 \times \Delta\delta^{18}O - 0.9749 \quad (1)$$

Figure 1. Ethanol correction curves for $\delta^{18}O$ (top) and $\delta^{2}H$ (bottom). Ethanol was added to deionized water, resulting in a linear relationship between the broad-band (BB) contamination metric from the LWIA-SCI software and the offset in $\delta^{18}O$ ($\Delta\delta^{18}O$) (BB = $-0.1653 \times \Delta\delta^{18}O + 0.9749$). There was no clear relationship between the BB contamination metric and the offset in $\delta^{2}H$ ($\Delta\delta^{2}H$).



$$NB_{\leq 4000} = 27.3e^{(0.3541 \times \Delta\delta^2H)} - 27.3 \quad (2a)$$

$$NB_{>4000} = 528.9e^{(0.1699 \times \Delta\delta^2H)} - 528.9 \quad (2b)$$



$$NB_{\leq 4000} = 15.67e^{(0.716 \times \Delta\delta^{18}O)} - 15.67 \quad (3a)$$

$$NB_{>4000} = 645.6e^{(0.2612 \times \Delta\delta^{18}O)} - 645.6 \quad (3b)$$

Figure 2. Methanol correction curves for $\delta^{18}O$ (top) and δ^2H (bottom). Methanol was added to deionized water to create relationships between the narrow-band (NB) contamination and the offsets in $\delta^{18}O$ and δ^2H. To best describe the offset in δ^2H and $\delta^{18}O$ over the full range of contamination, two separate equations were used for $\delta^{18}O$ and δD. For $\delta^{18}O, NB_{\leq 4000} = 15.67e^{(0.716 \times \Delta\delta^{18}O)} - 15.67$, and $NB_{>4000} = 645.6e^{(0.2612 \times \Delta\delta^{18}O)} - 645.6$. For $\delta D, NB_{\leq 4000} = 27.3e^{(0.3541 \times \Delta\delta^2H)} - 27.3$, and $NB_{>4000} = 528.9e^{(0.1699 \times \Delta\delta^2H)} - 528.9$.

IRMS analysis and comparison

78 leaf samples from the BEF

A blind comparison between IRIS and IRMS

Determine the $\delta^{18}O$ values

CO2 equilibration method

$C^{16}O^{16}O(gas)+H_2{}^{18}O(liquid) \rightleftharpoons C^{16}O^{18}O(gas)+H_2{}^{16}O(liquid)$

a DeltaPlus XP mass spectrometer with a Gas Bench interface

Determine the $\delta^{2}H$ values

a chromium reaction

$2Cr+3H_2O \rightarrow Cr_2O_3+3H_2$

a ThemoFinnigan MAT 253 mass spectrometer with an H-device

Statistical analysis one-way analysis of variance (ANOVA)

Table 2. Contamination effects by species/sample type. The second column (n) refers to the total number of samples. The third column (# cont.) refers to the number of contaminated samples. All values are reported in per mil (‰). The p-values shown in bold are significant at the 95% confidence level

			Before correction		$\Delta\delta^2H$			$\Delta\delta^{18}O$			After correction		p-values	
Sample Name	n	# cont.	mean δ^2H	mean $\delta^{18}O$	mean	max	sdev	mean	max	sdev	mean δ^2H	mean $\delta^{18}O$	δ^2H	$\delta^{18}O$
corn leaf	26	22	−28.41	5.87	3.68	11.97	3.61	1.98	5.79	1.80	−32.09	3.88	0.3025	0.0568
soybean leaf	25	23	−20.48	7.19	6.03	34.76	8.61	3.45	20.94	5.01	−26.50	3.73	0.2096	**0.0285**
big bluestem leaf	7	4	−43.95	−1.94	0.35	0.83	0.32	0.28	0.65	0.25	−44.24	−2.22	0.9811	0.9076
clover leaf	7	7	−11.14	10.61	11.76	27.27	11.87	6.59	15.65	6.71	−22.89	4.02	0.2422	**0.0389**
spearwort leaf	5	5	−11.54	11.18	15.73	24.47	11.51	9.27	18.08	6.93	−27.26	1.91	0.2608	**0.0166**
snap pea leaf	3	3	−37.02	7.47	13.84	25.54	11.26	7.85	14.32	6.14	−50.86	−0.38	0.3073	0.0515
cotton grass leaf	14	5	−51.57	−1.35	2.48	6.41	3.18	1.13	2.67	1.35	−54.05	−2.49	0.8861	0.7014
leather leaf leaf	14	3	−49.77	1.61	2.65	7.65	4.33	1.43	4.04	2.26	−52.42	0.18	0.9360	0.7864
white ash leaf	26	26	−23.07	13.71	14.81	23.46	4.62	8.84	14.18	2.42	−37.88	4.90	**0.0036**	**<.0001**
lg. tooth aspen leaf	26	26	−35.90	5.37	0.90	3.47	0.94	0.56	1.91	0.54	−36.80	4.81	0.8464	0.6809
red maple leaf	25	25	−32.79	8.99	0.44	4.66	0.43	0.26	0.94	0.25	−33.23	8.73	0.9198	0.8614
corn stem	7	7	−51.04	−6.27	1.77	4.94	1.54	0.47	3.11	1.69	−52.81	−6.73	0.5577	0.1836
soybean stem	10	9	−47.90	−2.27	7.07	28.11	8.70	4.27	17.24	5.29	−54.97	−6.54	0.0850	**0.0081**
big bluestem stem	8	3	−56.46	−4.49	6.62	10.17	5.52	3.81	5.79	3.12	−63.08	−8.30	0.8724	0.3485
clover stem	9	9	−40.27	1.33	13.70	34.63	12.87	7.97	20.83	7.54	−53.97	−6.64	**0.0134**	**0.0014**
spearwort stem	7	7	−48.16	−1.72	7.82	20.91	7.74	4.22	11.93	4.26	−55.44	−5.94	0.6343	0.2419
cotton grass stem	15	14	−64.97	−5.70	6.36	18.84	6.40	3.45	10.66	3.52	−71.34	−9.15	0.0680	**0.0020**
leather leaf stem	14	2	−60.23	−6.20	1.17	2.13	1.37	0.55	1.10	0.77	−61.40	−6.75	0.9691	0.9270
soil	45	0	−51.50	−5.70	x	x	x	x	x	x	−51.50	−5.70	x	x

Table 3. The effects of activated charcoal on the degree of contamination observed – all samples treated with activated charcoal (AC) are shown in parentheses. All values are reported in per mil (‰)

	Before correction				After correction		p-values	
Sample type (AC)	mean δ^2H	mean $\delta^{18}O$	$\Delta\delta^2H$	$\Delta\delta^{18}O$	mean δ^2H	mean $\delta^{18}O$	δ^2H	$\delta^{18}O$
corn leaf	−29.19 (−28.09)	6.35 (6.44)	4.96 (4.58)	2.59 (2.44)	−33.15 (32.67)	3.76 (4.00)	0.9104	0.8874
corn stem	−51.43 (−51.04)	−6.07 (−6.14)	2.19 (1.95)	1.00 (0.91)	−53.62 (−53.00)	−7.07 (−7.05)	0.9260	0.9856
big blue stem	−51.02 (−60.26)	−2.75 (−7.66)	9.43 (0)	5.42 (0)	−60.45 (−60.26)	−8.17 (−7.66)	x	x
clover stem	−36.67 (−36.88)	2.91 (2.62)	16.41 (15.88)	9.41 (9.14)	−53.08 (−52.76)	−6.47 (−6.51)	0.9384	0.9868
soybean leaf	−6.80 (−6.81)	14.28 (13.11)	15.80 (15.24)	9.41 (9.13)	−22.59 (−22.06)	4.86 (3.98)	0.9712	0.7012
soybean stem	−47.90 (−48.25)	−0.98 (−2.09)	9.23 (8.74)	5.66 (5.39)	−57.13 (−56.99)	−6.64 (−7.49)	0.9833	0.4070

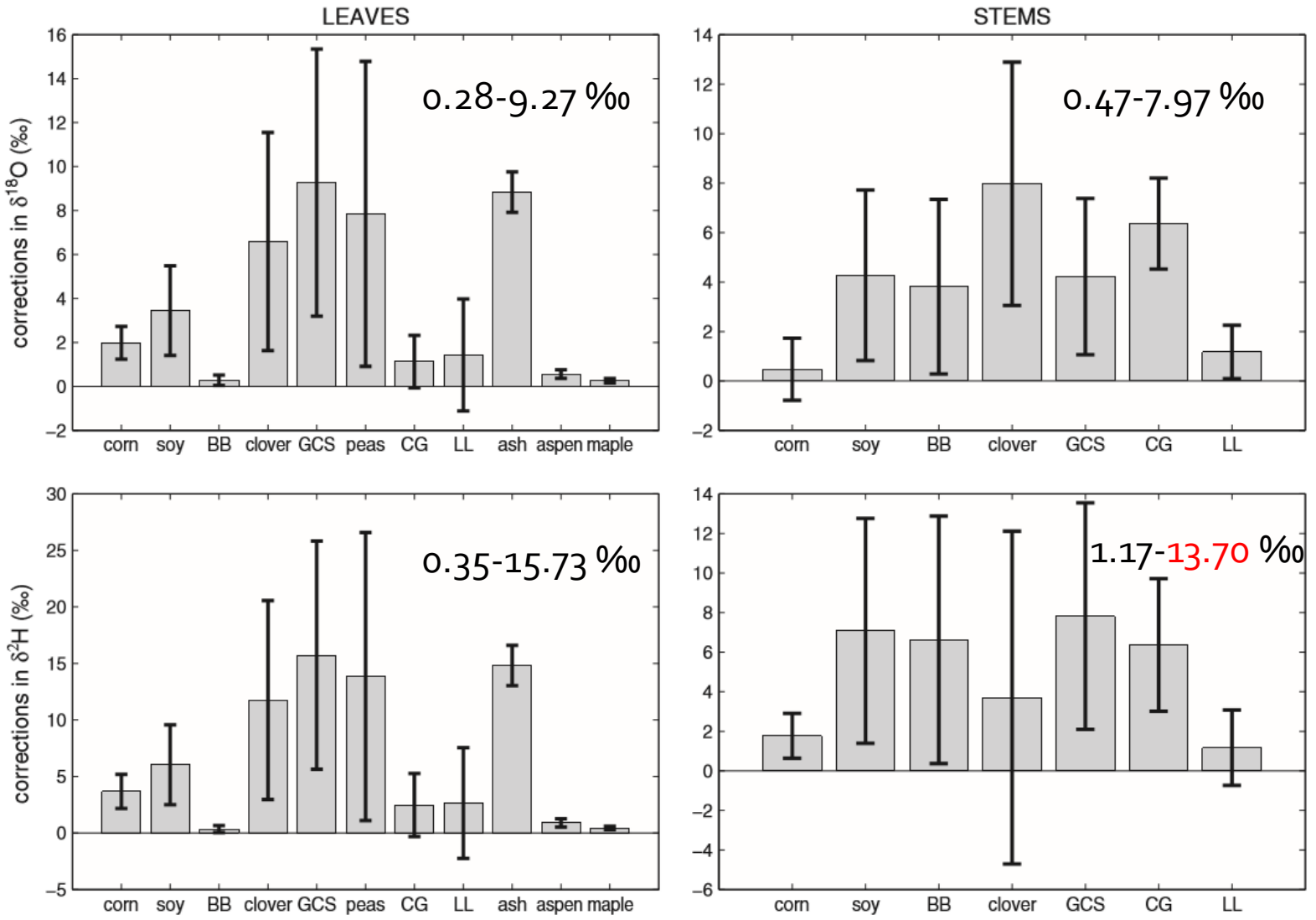


Figure 3. Average corrections for the leaf and stem samples analyzed. The error bars represent the 95% confidence interval. The average corrections in leaf samples ranged from 0.35 to 15.73‰ for δ^2H and 0.28 to 9.27‰ for $\delta^{18}O$. The average corrections in stem samples ranged from 1.17 to 13.70‰ for δ^2H and 0.47 to 7.97‰ for $\delta^{18}O$. There was no contamination observed in soil water.

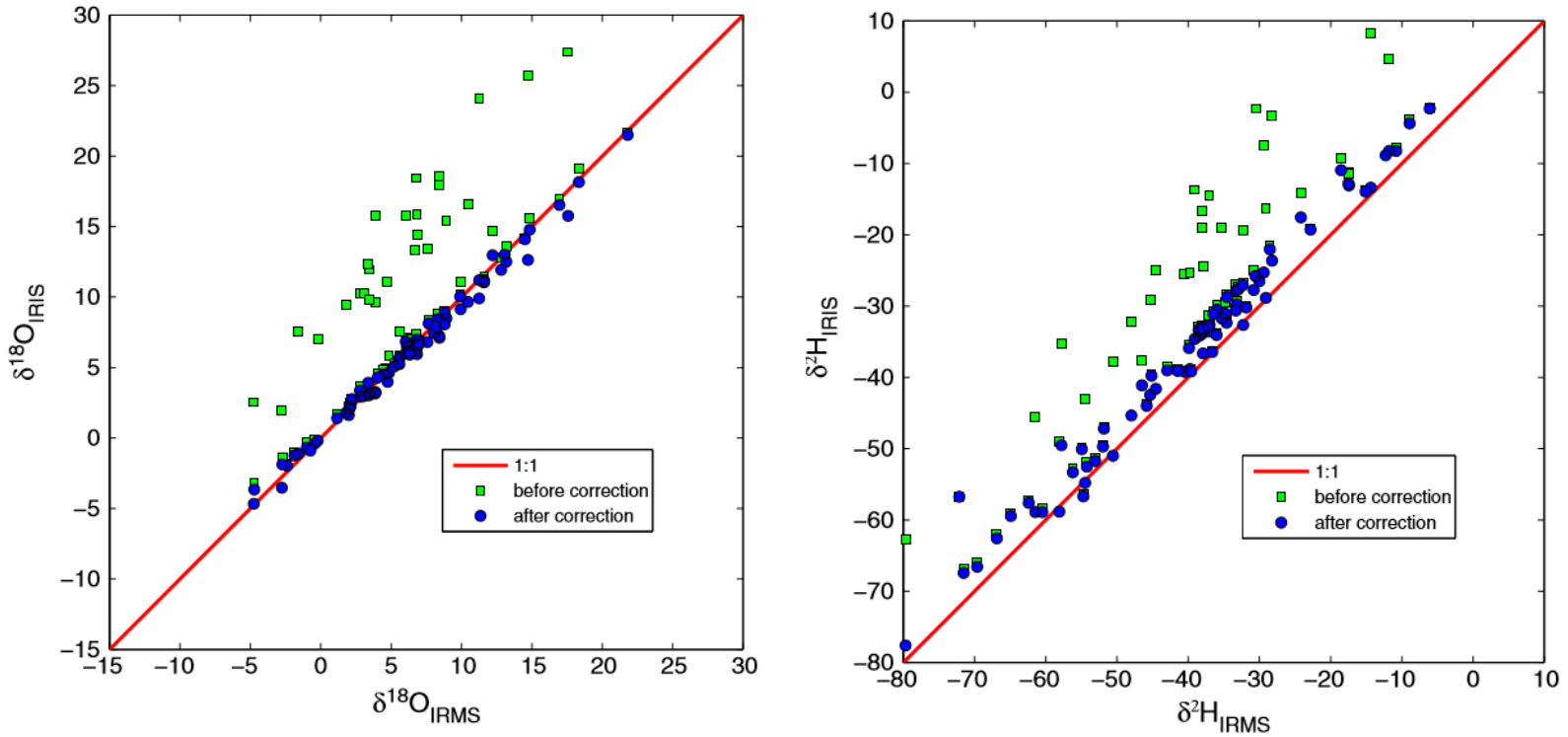


Figure 4. The corrected IRIS values of 78 leaf samples were compared with those for the same samples analyzed using IRMS in a double-blind comparison. Overall, the corrections eliminated the discrepancies between IRMS and IRIS for $\delta^{18}O$, and greatly reduced the discrepancies for $\delta^{2}H$. The mean differences in the isotope ratios between IRMS and corrected IRIS methods were 0.19‰ for $\delta^{18}O$ and −3.54‰ for $\delta^{2}H$. The inability to create an ethanol correction curve for $\delta^{2}H$ probably caused the larger differences.

Disscussion

eliminate the errors in $\delta^{18}O$ and reduce the errors in $\delta^{2}H$
confirm the primary contaminants
Each individual analyzer needs respective correction curves.

If there is a time drift ?
Do curves have the same accuracy across all species?
accuracy of curves at higher contamination levels

correcting instead of discarding
no contamination in water vapor

Conclusion

It is possible to correct the $\delta^{18}O$ values for MeOH and EtOH contamination, but it is only possible to correct the $\delta^{2}H$ values for MeOH contamination.

Contamination exists in all plant species but not in soil water.

△ $\delta^{18}O$ equals to 0.18‰ within the margin of error of the instrument
△ $\delta^{2}H$ equals to -3.39‰,
probably due to the inability to correct EtOH contamination.

IRIS methods are feasible and
IRMS methods are still needed for quality validation.

This correction method presents a viable alternative to IRMS
before the ability to remove all contaminants.