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Technical note: Conservative storage of water vapour – practical in situ sampling of stable isotopes in tree stems

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1 VSVS diffusive exchange during storage trial

The protocol below describes the analysis of the vials filled with dry air and stored for 14 days to check for diffusive exchange with the atmosphere. The outcome is the water vapor concentration in the vial at the start of the measurement.

1. The time it takes for most of the sample to reach the cavity was estimated at 50 seconds from the insertion of the needle marking the beginning of the 5 min measuring interval. Therefore, we set aside the first 50 s after needle insertion from the analysis.
2. The assumed flow rate of the CRDS was 30 ml/min and with the vial volume (50 ml) that would lead to a turnover rate in the vial of 1% sec^{-1}. We modelled the expected decline in concentration using these values.
3. The mean vapor concentration measured at the last 20 seconds of the five-minute interval was assumed to be the vapor concentration coming from the desiccant tower on the measurement day (C_{in}).
4. We used this incoming dry air concentration from each measurement cycle (n=3) to model from there to the beginning of the sequence therewith deriving the initial vapor concentration of the vial:

$$C_n = C_{n+1} - 0.01C_{in} + 0.01C_{out}$$

Where C_n is the initial concentration of the sample vial, C_{n+1} and C_{out} are the concentrations flowing out at the timestep n+1 (in seconds). At each step C_n was set to C_{n-1} and the process repeated.

5. We ran the model backward until we reached the last of the 50 s that were initially set aside, which was then the vapor concentration of the initial sample after 14 days of storage.

Table S 1 Calculated water vapor concentration of samples filled initially with dry air, measured after 14 days of storage.

Sample filled with dry air	Calculated initial H_2O concentration after 14 d storage (ppmV)	H_2O concentration dry air from dessicant tower on measurement day (ppmV)
1	1792.369	535
2	1056.724	500
3	1297.58	474

Table S 2 Changes in the isotopic composition in reference to the "0-day" samples by Source ID and Storage time. Columns 3 through 8 depict minimum, mean, median and maximum change for $\delta^{2}H$, while columns 9 through 14 show analogous data for $\delta^{18}O$. Significance levels for the pairwise Wilcox test base on the comparison of each storage groups mean with the "0-day" isotopic composition mean of the respective source and are defined as follows: p-value >= 0.05 "ns"; p<0.05 ""; p<0.01 "**"; p<0.001 "***"; p<0.0001 "****"; p<0.00001 "*****"*

ID	stored	min change $\delta^{2}H$	mean change $\delta^{2}H$	median change $\delta^{2}H$	max change $\delta^{2}H$	sig. level ($\delta^{2}H$) Wilcox	min change $\delta^{18}O$	mean change $\delta^{18}O$	median change $\delta^{18}O$	max change $\delta^{18}O$	sig. level ($\delta^{18}O$) Wilcox
light	**1**	-1.11	6.29	5.24	14.61	**	-0.43	0.49	0.45	1.20	*
light	**3**	-8.26	-0.55	-0.36	4.31	ns	-0.36	0.69	0.54	2.20	**
light	**4**	0.34	2.11	2.26	3.79	ns	0.85	1.62	1.64	2.49	****
light	**7**	-7.04	4.37	2.84	18.27	ns	-1.15	1.07	1.43	3.47	*
light	**14**	-2.60	2.34	2.44	7.46	ns	1.15	2.32	1.83	4.18	****
medium	**1**	-1.83	1.19	2.46	3.61	ns	-0.57	0.00	0.03	0.71	ns
medium	**3**	-3.92	1.77	1.30	8.66	ns	-0.21	0.95	1.04	2.23	*
medium	**4**	-5.18	-0.40	-0.21	4.40	ns	-0.25	0.56	0.53	1.52	ns
medium	**7**	4.82	6.11	6.32	7.19	**	0.42	0.71	0.78	0.98	ns
medium	**14**	1.72	3.48	3.55	5.85	ns	1.66	1.89	1.92	2.20	***
heavy	**1**	-2.18	0.41	-0.12	3.24	ns	-0.22	0.13	0.20	0.47	ns
heavy	**3**	-2.93	-0.89	-0.76	0.73	ns	-0.20	-0.06	-0.10	0.10	ns
heavy	**4**	-4.61	-3.84	-4.18	-2.70	**	0.32	0.74	0.53	1.75	**
heavy	**7**	0.33	1.22	1.29	1.99	ns	0.31	0.68	0.57	1.03	**
heavy	**14**	-2.79	-0.06	0.50	3.26	ns	1.28	1.56	1.54	1.95	**
very heavy	**1**	-15.76	-9.35	-10.22	-2.25	*	-0.93	-0.37	-0.42	0.40	ns
very heavy	**3**	-80.60	-27.68	-11.93	-0.19	*	-0.06	0.46	0.33	1.36	ns
very heavy	**4**	-32.93	-24.63	-21.03	-18.57	**	-0.17	0.12	-0.02	0.43	ns
very heavy	**7**	-69.31	-43.70	-38.26	-12.32	**	0.39	1.26	1.34	2.00	*
very heavy	**14**	-57.60	-21.27	-19.76	-2.74	*	1.16	1.81	1.94	2.20	**
crazy heavy	**1**	-60.21	14.36	17.78	72.43	ns	-1.43	0.06	0.03	1.28	ns
crazy heavy	**3**	-66.67	11.62	15.46	64.29	ns	-0.03	0.48	0.24	1.54	*
crazy heavy	**4**	-121.21	-20.94	-13.71	36.12	ns	-1.43	0.30	0.31	1.68	ns
crazy heavy	**7**	-183.16	-33.46	-12.96	35.98	ns	-0.14	0.83	0.83	2.12	***
crazy heavy	**14**	-133.79	-52.66	-36.72	39.54	*	1.28	2.00	2.00	2.70	****

Table S 3 Mean isotopic composition and standard deviation of ^{2}H and ^{18}O before (columns 3 – 6) and after correction and calibration (columns 7 – 10).

ID	stored	raw mean $\delta^{2}H$	sd $\delta^{2}H$	raw mean $\delta^{18}O$	sd $\delta^{18}O$	cor. cal. mean $\delta^{2}H$	sd cor. cal. $\delta^{2}H$	cor. cal. mean $\delta^{18}O$	sd cor. cal. $\delta^{18}O$
light	0	-87.49	3.94	-12.03	0.55	-91.19	4.16	-12.63	0.59
light	1	-81.20	4.86	-11.54	0.47	-89.27	5.46	-12.22	0.51
light	3	-88.05	3.10	-11.34	0.66	-91.75	3.27	-12.54	0.72
light	4	-85.38	1.20	-10.41	0.47	-90.82	1.37	-11.65	0.50
light	7	-83.13	10.97	-10.96	1.34	-91.09	11.54	-12.44	1.37
light	14	-85.16	3.10	-9.71	0.99	-92.11	3.37	-12.38	1.09
medium	0	-53.80	4.41	-8.02	0.79	-55.57	4.66	-8.37	0.84
medium	1	-52.61	2.25	-8.02	0.40	-57.19	2.52	-8.42	0.44
medium	3	-52.02	3.88	-7.07	0.74	-53.69	4.10	-7.88	0.81
medium	4	-54.20	2.47	-7.46	0.49	-55.40	2.80	-8.51	0.52
medium	7	-47.69	1.08	-7.32	0.23	-53.79	1.14	-8.70	0.24
medium	14	-50.32	1.65	-6.14	0.21	-54.31	1.79	-8.44	0.23
heavy	0	1.10	0.60	-5.37	0.05	-1.62	4.36	-5.54	0.05
heavy	1	1.52	2.07	-5.24	0.30	0.31	4.09	-5.40	0.33
heavy	3	0.21	1.28	-5.43	0.13	2.69	1.85	-6.08	0.14
heavy	4	-2.74	0.81	-4.63	0.55	-0.44	3.81	-5.49	0.59
heavy	7	2.32	0.61	-4.68	0.29	2.16	3.57	-5.99	0.30
heavy	14	1.04	2.31	-3.80	0.25	-3.85	6.10	-5.86	0.28
very heavy	0	729.88	4.30	-11.60	0.43	786.20	4.68	-12.17	0.45
very heavy	1	720.54	4.86	-11.97	0.51	771.46	5.23	-12.69	0.55
very heavy	3	702.21	32.03	-11.14	0.55	758.88	34.45	-12.32	0.60

very heavy	4	705.25	6.95	-11.49	0.28	773.77	7.63	-12.79	0.30
very heavy	7	686.18	23.41	-10.34	0.74	761.64	25.88	-11.81	0.76
very heavy	14	708.61	21.89	-9.80	0.43	786.70	24.62	-12.48	0.48
crazy heavy	0	1590.49	65.79	-10.31	0.31	1721.34	71.49	-10.80	0.33
crazy heavy	1	1604.85	51.63	-10.25	0.68	1723.83	55.60	-10.83	0.74
crazy heavy	3	1602.11	45.76	-9.83	0.52	1726.73	49.22	-10.89	0.57
crazy heavy	4	1569.54	52.16	-10.01	0.86	1723.19	57.30	-11.22	0.91
crazy heavy	7	1557.03	68.10	-9.48	0.64	1724.54	75.30	-10.92	0.66
crazy heavy	14	1537.83	60.57	-8.32	0.59	1719.31	68.12	-10.84	0.65

Table S 4 Comparison of model coefficients and fits between the full models presented in Fig. 5 and each single source. Data show that storage effect correction is not different for natural abundance full model and each single source. See main text for more details.

Source	Intercept 2H	slope 2H	adj. R2	intercept 18O	slope 18O	adj. R2
light	3.36	-0.08	-0.02	0.50	0.13	0.29
medium	0.62	0.26	0.08	0.13	0.12	0.43
heavy	-1.10	0.08	-0.02	-0.06	0.12	0.63
very heavy	-21.93	-0.59	-0.03	-0.28	0.16	0.63
crazy heavy	14.01	-5.21	0.14	-0.12	0.15	0.51
Full model (natural abundance)	1.46	0.06	<0.01	0.08	0.14	0.43
Full model (enriched hydrogen)	2.03	-3.67	0.11	-	-	-

Table S 5 Means and standard deviations (sd) of VSVS samples for the field trial. All samples were taken on the bottom borehole of a pine tree (ca. 40cm aboveground). Mean and sd were calculated based on five replicas. Correction for storage was done using the storage model coefficients from the lab trial, and subsequent calibration according to storage group.

ID	stored	δ^2H‰ mean (±sd)	δ^{18}O‰ mean (±sd)	cor.cal. δ^2H‰ mean (±sd)	cor.cal. δ^{18}O‰ mean (±sd)
Sample	0	3.23 (1.17)	-11.05 (0.16)	-3.76 (1.19)	-12.03 (0.21)
Sample	1	-3.25 (0.96)	-10.84 (0.16)	1.12 (1.11)	-12.26 (0.20)
Sample	3	-5.22 (1.33)	-10.63 (0.19)	-5.04 (1.36)	-11.16 (0.19)
Sample	7	-3.74 (4.37)	-9.65 (0.31)	-5.57 (4.65)	-11.31 (0.41)
Sample	14	6.92 (1.61)	-8.76 (0.31)	6.33(1.68)	-11.35 (0.41)