Supplemental material

Humidity-isotope response calibration

Each individual analyzer needs to be characterized for the response of the measured isotopic value as a function of water vapor concentration [*Aemisegger et al.*, 2012; *Schmidt et al.*, 2010]. Without humidity calibration, varying humidity levels in the introduced air samples will introduce an artificial isotope signal. The humidity-isotope response calibration requires that the isotopic composition of the measured vapor remains constant despite changes in the absolute humidity. This means that complete evaporation of known liquid standards is needed during the humidity-isotope response characterization. Furthermore, the dipole moment of the water molecules creates adhesiveness between the water molecules and the inside of the tubes. These wall effects can artificially change the isotopic composition of a measured sample when the humidity is changed and should therefore be minimized. The optimal way of preventing significant wall effects during humidity-isotope response calibration is to minimize the distance between the point of dilution and the measuring cell.

Because of possible changes in the humidity-isotope response with time and during transport, calibration must be carried out in the field. The humidity-isotope response was estimated from measurements of a reference water vapour stream produced at different humidity levels by the LGR WVISS, spanning the full range of atmospheric humidity levels experienced during the campaign. The background humidity level of the dry air produced by the WVISS was ~10 ppmv. Figure S1 illustrates how the humidity-isotope response curve was measured several times to minimize uncertainty. To remove the drift of the analyzer during the humidity-isotope response curve estimation, a reference level (2500 ppmv in this case) was measured every ~1.5 hour. The resulting humidity-isotope response is shown in Figure S2 for our LGR analyzer and the two Picarro analyzers that were used. Based on the collected calibration data, idealized humidity-isotope response functions were defined. The best fit was reached with a polynomial function for the LGR analyzer, while double exponential functions were used for Picarro serial number: HBDS-12 (δD and $\delta^{18}O$) and HBDS-48 ($\delta^{18}O$). A linear function was used for HBDS-48 (δD). Note that humidity response effects are not the same for δD and $\delta^{18}O$, and can reach several ‰ in $\delta^{18}O$ for humidity levels between 1000 and 2000 ppmv.

Next, isotopic measurements of both air samples and reference water vapor were corrected for humidity effects using:

$$\delta_{\mathit{Humidity\ correction\ vs.\ reference\ level}} = \delta_{\mathit{Humidity\text{-}isotope\ response}}\,(c(H_2{}^{16}O_{ppmv}))$$

$$\delta_{\mathit{Measured\ humidity\text{-}correction\ to\ reference\ level}} = \delta_{\mathit{Measured}} - \delta_{\mathit{Humidity\ correction\ vs.\ reference\ level}}\ . \quad \text{(S1)}$$

In the above formula, $\delta_{\mathrm{Measured}}$ represents the raw measurement and $\delta_{\mathrm{Humidity\text{-}isotope\ response}}$ is the humidity-isotope response function defining the difference between the measured and true isotopic composition of a reference vapor introduced at different humidity levels as described above and shown in Figure S1.

Known-standard calibration

For calibration, we used the LGR WVISS to create a water vapor stream of known isotopic composition by inserting the liquid water uptake tube into a container with a known liquid standard. The two standards (named S1 and S2) had respective isotopic compositions determined by IRMS (S1: δ^{18}O, δD; -21.89 ± 0.05 $‰_{\text{V-SMOW}}$, -168.7 ± 0.3 $‰_{\text{V-SMOW}}$) and (S2: δ^{18}O, δD; -39.78 ± 0.05$‰_{\text{V-SMOW}}$, -309.8 ±0.3 $‰_{\text{V-SMOW}}$). Liquid standards were measured at different humidity levels (the levels used here were ~2000 ppmv, ~3500 ppmv, and 5500 ppmv) for a minimum of 15 minutes each. The raw measurements were humidity-isotope response corrected to a humidity reference level. It was assumed that the measurement period of both standards was smaller than the characteristic time for the drift of the instrument. We performed measurements of both standards at different humidity levels and used the combined results for the estimation of the V-SMOW calibration. Any error in the humidity-isotope response calibration is thereby propagated into the accuracy estimation of the V-SMOW calibration. The V-SMOW calibration was determined throughout the campaign to check for stability, but no significant variations were observed. Standards were measured on the LGR analyzer on day 144, 160, 171, and 178. Standards were measured on Picarro HBDS-48 on day 144 and on Picarro HBDS-12 on day 160, 171, and 178 (see Table 1). No significant trend in the $‰_{\text{measured}}$-$‰_{\text{V-SMOW}}$ slope was observed through the season. Table S1 summarizes the results of the calibration. The humidity-reference level corrected measurements are calibrated against V-SMOW using the following equation

$$\delta_{Measured\ V\text{-}SMOW} = (\delta_{True\ V\text{-}SMOW\ S1} - \delta_{True\ V\text{-}SMOW\ S2})/(\delta_{Humidity\text{-}corrected\ measured\ S1} - \delta_{Humidity\text{-}corrected\ measured\ S2}) \times (\delta_{Measured\ humidity\text{-}correction\ to\ reference\ level} - \delta_{Humidity\text{-}corrected\ measured\ S2}) + \delta_{True\ V\text{-}SMOW\ S2}\,. \quad \text{(S2)}$$

$\delta_{\text{True V-SMOW S1/S2}}$ is the true value of standard S1 and S2. $\delta_{\text{Humidity-corrected measured S1/S2}}$ is the measured value of standard S1 and S2, which has been humidity corrected to a reference level following formula (S1).

	S1					S2				
Instrument	**Mean**	**True value**	**STD**	$N_{samples}$	**STD**$_{mean}$	**Mean**	**True value**	**STD**	$N_{samples}$	**STD**$_{mean}$
Picarro HBDS-12	-22.43	-21.89	0.41	61	0.05	-39.26	-39.78	0.28	48	0.04
	-191.5	-168.7	2.7	61	0.3	-324.4	-309.8	3.7	48	0.5
Picarro HBDS-48	-22.12	-21.89	0.78	182	0.06	-39.58	-39.78	0.74	140	0.06
	-182.8	-168.7	8.0	182	0.6	-323.8	-309.8	7.9	140	0.7
LGR	-20.38	-21.89	0.52	318	0.03	-38.47	-39.78	0.60	232	0.04
	-167.9	-168.7	4.3	318	0.2	-307.0	-309.8	1.5	232	0.1

Table S1: The results of the measurements of known standards S1 and S2 used to establish calibrations against V-SMOW. Table 1 informs about the timing of the calibrations. "Mean" refers to the mean value of the humidity corrected measurements carried out at the different humidity levels (~2000 ppmv, ~3500 ppmv, and 5500 ppmv). "True value" refers to the IRMS determined value of the standard used relative to the V-SMOW scale.

Drift correction

All analyzers are affected by internal drift over time that needs to be removed by a drift-correction procedure. The dual-inlet mode allows to alternate measurements of air samples and reference waters and to correct the raw measurement assuming linear drifts between measurements of reference waters. Based on pre-deployment tests, we decided to measure a vapor standard every ~1.5 hour for the LGR analyzer and every ~12 hours for the Picarro analyzer in order to drift correct the measurements. Post-campaign data analysis indicates that the Picarro analyzer should have been drift corrected more often due to strong diurnal-temperature induced drifts. Figure S3 shows the humidity- and V-SMOW-corrected measurements of the vapor standard used for drift correcting the LGR and Picarro analyzers. In the Figure S3 both the short- (intra and inter day variability) and long- (through the season) term drifts of the Picarro and LGR analyzers are shown. We see clear diurnal cycles in the drift of the LGR analyzer for $\delta^{18}O$ and δD, while the Picarro analyzer shows more random noise for δD and small indication of diurnal variability in $\delta^{18}O$. The LGR shows on short time scales (day to day) a peak-to-peak variability range of ~1 ‰ in $\delta^{18}O$ and ~5 ‰ in δD. The Picarro (HBDS 48) shows a peak-to-peak variability span of ~0.5 ‰ in $\delta^{18}O$ and ~16 ‰ in δD. A few days after performing the short-term drift analysis, we had to change from Picarro analyzer HBDS-48 to Picarro analyzer HBDS-12. The long-term drift is therefore only depicted in Figure S3 for this Picarro analyzer (HBDS-12). We did not observe any significant long-term drift in either δD or $\delta^{18}O$ for the LGR analyzer between day 145 and 205. However the peak-to-peak variability span was ~3 ‰ for $\delta^{18}O$ and ~7‰ for δD. For the Picarro analyzer (HBDS-12) we observe no long-term drift in $\delta^{18}O$ but ~4‰ in δD. The peak-to-peak variability span range ~4 ‰ in $\delta^{18}O$ and ~10 ‰ in δD. Notice that the atypical fluctuations in the drift around days 169 and 198 have been disregarded and removed from the dataset since no plausible explanation could be obtained. It is outside the scope of this paper to investigate the cause of instrumental drifts; we speculate that the diurnal drifts are caused by temperature variations in the ambient air surrounding the analyzers. Fluctuations on time steps smaller than the time between vapor standard measurements are not corrected for.

The drift is corrected using the following equation:

$$\delta_{\mathit{Drift\ corrected\ V\text{-}SMOW}} = \delta_{\mathit{Vapor\ std\ t1}} \times T + \delta_{\mathit{Vapor\ std\ t2}} \times (1 - T) - \delta_{\mathit{True\ vapor\ std\ V\text{-}SMOW}}$$

$$\delta_{\mathit{Measured\ V\text{-}SMOW\ drift\ corrected}} = \delta_{\mathit{Measured\ V\text{-}SMOW}} - \delta_{\mathit{Driftcorrection\ V\text{-}SMOW}}\ , \qquad \text{(S3)}$$

where T = (t-t_1)/(t_2-t_1) and t_1 and t_2 is respectively the time when $\delta_{\text{Vapor std t1}}$ and $\delta_{\text{Vapor std t2}}$ were measured for the vapor standard. $\delta_{\text{True vapor std V-SMOW}}$ is the true value of the water used to produce the vapor stream.

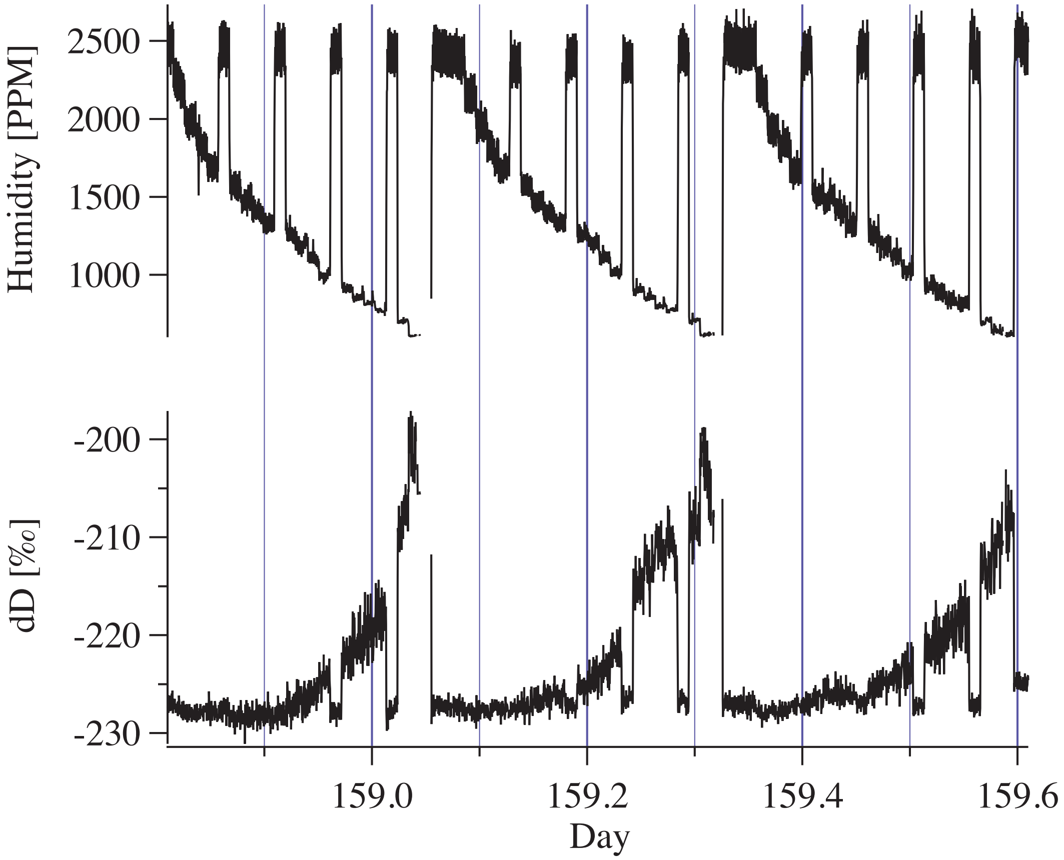

Figure S1: Procedure for performing calibrations.

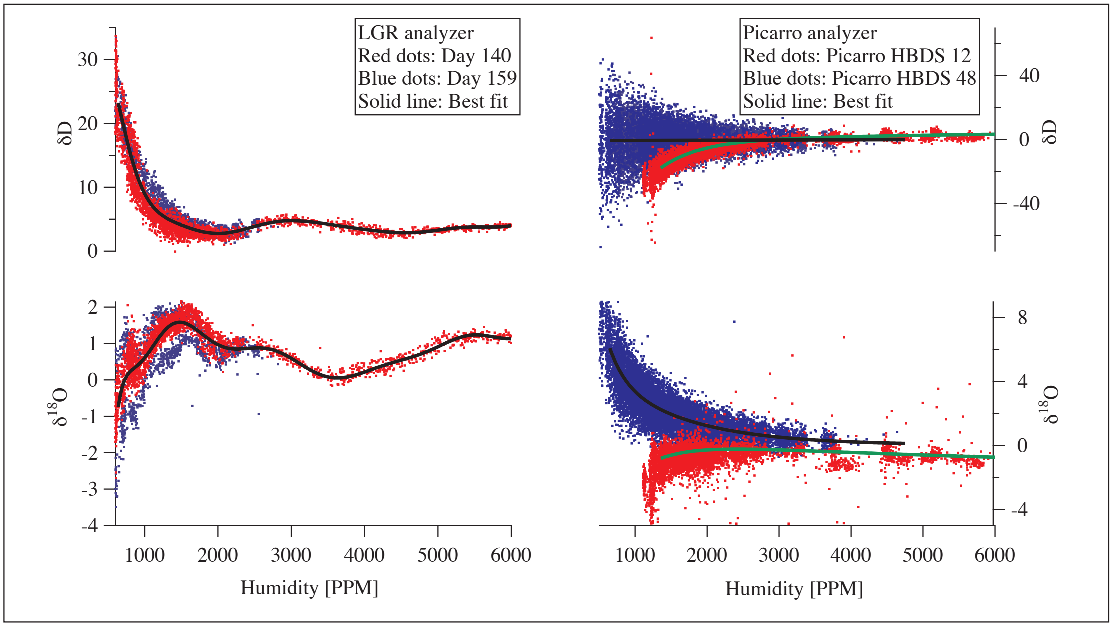

Figure S2: The humidity-isotope response for the LGR analyzer (left panel) at day 140 (red dots) and day 159(blue dots) and for the Picarro analyzers (right panel) HBDS 12 (red dots) and HBDS 48 (blue dots).

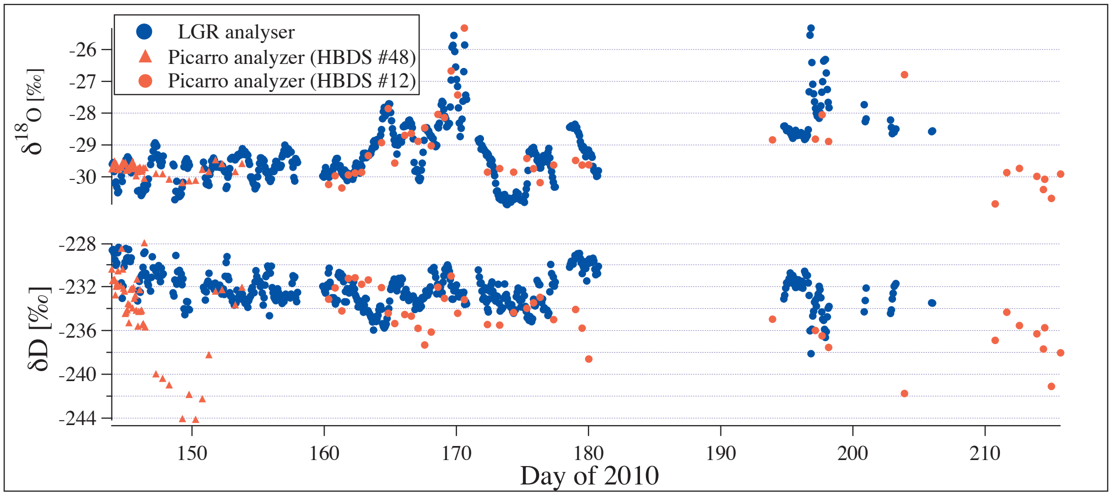

Figure S3: Short-term and long-term drift of LGR analyzer (blue dots), Picarro analyzer (HBDS # 48 – red triangles), and Picarro analyzer (HBDS #12 – red dots)