S1 IRMS methodology

The δ^2H and δ^{18}O measurements were done on a Delta$^+$XL isotope ratio mass spectrometer coupled to a high-temperature conversion reactor (HTC) via a ConFloIII. The analysis method is described in Gehre et al. (2004). A daily sequence consisted of the DI1 or DI2 water samples, an in-house reference standard www-j1 (Willi Working Water-Jena1; δ^2H: -66.45 ± 1.0 ‰, δ^{18}O: -9.78 ± 0.10 ‰), an in-house scaling standard BGP-j1 (Brand Greenland Precipitation-Jena1; δ^2H: -187.94 ± 1.0 ‰, δ^{18}O: -24.46 ± 0.10 ‰), and an in-house quality control RWB-j1 (ReinstWasser Brand-Jena1; δ^2H: -1 ± 1.0 ‰, δ^{18}O: 7.8 ± 0.10 ‰). The daily average standard deviation of www-j1 was better than 0.16 ‰ (n = 44) for δ^{18}O, and better than 0.7 ‰ (n = 41) for δ^2H measurements. All in-house standards are regularly calibrated and checked against the international IAEA standards VSMOW2 and SLAP2. Thus the DI1 and DI2 isotope values are given on the VSMOW/SLAP scale.
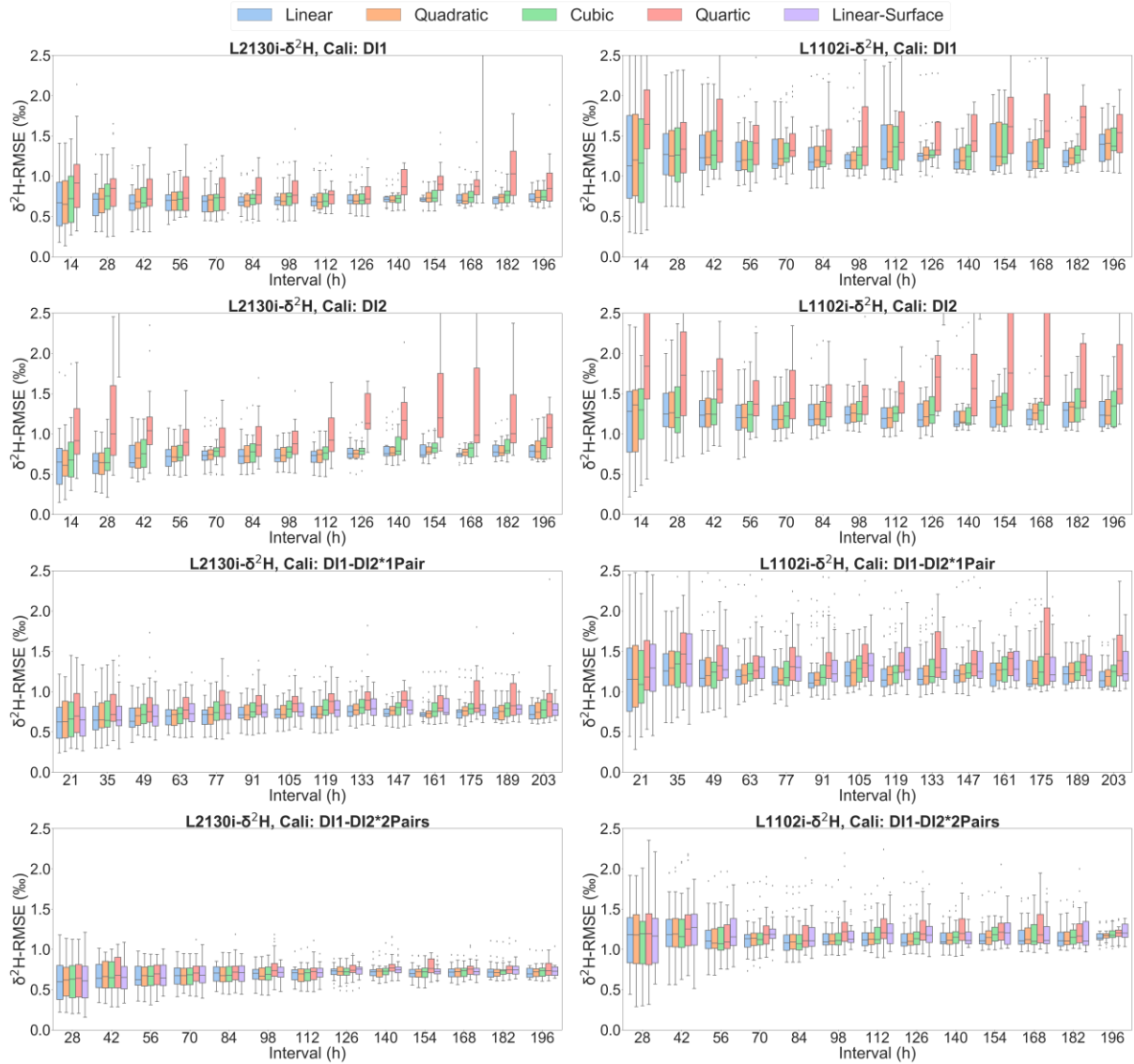
Figure S1 Boxplots of root mean square error (RMSE) of $\delta^{18}O$, derived from calibrating [H$_2$O]-dependence of δ^2H measurements by each of five fitting methods (i.e., linear, quadratic, cubic, quartic, linear surface fitting methods) for each of four calibration strategies: DI1, DI2, DI1-DI2*1Pair, DI1-2*2Pairs. The left-hand figures present boxplots of RMSE of δ^2H measurements by the L2130i, depending on interval length (i.e., the time period used for calibrating [H$_2$O]-dependence). The right-hand figures display boxplots of RMSE of $\delta^{18}O$ measurements by the L1102i, depending on interval length. The procedure for assessing [H$_2$O]-dependence uncertainties (= RMSE) is described in section 2.3.

References

Gehre, M., Geilmann, H., Richter, J., Werner, R. A. and Brand, W. A.: Continuous flow ^{2}H/^{1}H and ^{18}O/^{16}O analysis of water samples with dual inlet precision, Rapid Communications in Mass Spectrometry, 18(22), 2650–2660, doi:10.1002/rcm.1672, 2004.