



The stability and calibration of water vapor isotope ratio measurements

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The stability and calibration of water vapor isotope ratio measurements during long-term deployments

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Abstract

With the recent advent of commercial laser absorption spectrometers, field studies measuring stable isotope ratios of hydrogen and oxygen in water vapor have proliferated. These pioneering analyses have provided invaluable feedback about best strategies for optimizing instrumental accuracy, yet questions still remain about instrument performance and calibration approaches for multi-year field deployments. With clear scientific potential for using these instruments to carry out long-term monitoring of the hydrological cycle, this study examines the long-term stability of the isotopic biases associated with three cavity-enhanced laser absorption spectrometers – calibrated with different systems and approaches – at two remote field sites: Mauna Loa Observatory, Hawaii, USA, and Greenland Environmental Observatory, Summit, Greenland. The analysis pays particular attention to the stability of measurement dependencies on water vapor concentration and also evaluates whether these so-called concentration-dependences are sensitive to statistical curve-fitting choices or measurement hysteresis. The results suggest evidence of monthly-to-seasonal concentration-dependence variability – which likely stems from low signal-to-noise at the humidity-range extremes – but no long-term directional drift. At Mauna Loa, where the isotopic analyzer is calibrated by injection of liquid water standards into a vaporizer, the largest source of inaccuracy in characterizing the concentration-dependence stems from an insufficient density of calibration points at low humidity. In comparison, at Greenland, the largest source of inaccuracy is measurement hysteresis associated with interactions between the reference vapor, generated by a custom dew point generator (DPG), and the sample tubing. Nevertheless, prediction errors associated with correcting the concentration-dependence are small compared to total measurement uncertainty. At both sites, a dominant source of uncertainty is instrumental precision at low humidity, which cannot be reduced by improving calibration strategies. Challenges in monitoring long-term isotopic drift are also discussed in light of the different calibration systems evaluated.

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1 Introduction

The isotope ratios of hydrogen and oxygen (D/H, ¹⁸O/¹⁶O) are powerful tracers of water cycle processes. Due to their lower saturation vapor pressure, the heavier isotopes (D and ¹⁸O) preferentially condense, while the lighter isotopes preferentially evaporate (Bigeleisen, 1961; Dansgaard, 1964). Paired with humidity information, isotope ratios thus provide clues about sources of moisture to the atmosphere and about the integrated condensation history of air masses (Gat, 1996).

With the recent advent of commercial vapor isotopic analyzers, measurements of isotope ratios in water vapor have become increasingly widespread. As a result, field experiments once limited to a small number of flask samples (e.g. Ehhalt, 1974; Galewsky et al., 2007) – whose vapor content must be captured through a cryogenic trap for later liquid analysis in the lab – have been replaced by field experiments in which in situ observations can be made at a temporal resolution better than 0.1 Hz. Researchers using these new commercial technologies are resolving water cycle processes on a range of local-to-regional scales, investigating, for example, water recycling within the forest canopy (Berkelhammer et al., 2013), evapotranspiration (Wang et al., 2010) and its contribution to atmospheric moisture (Noone et al., 2013; Aemiseggar et al., 2014), mixing and convective processes in the atmosphere (Noone et al., 2011; Tremoy et al., 2012; Bailey et al., 2013), evaporation processes in the marine boundary layer (Steen-Larsen et al., 2014b), and large-scale condensation and advection dynamics (Galewsky et al., 2011; Hurley et al., 2012; Steen-Larsen et al., 2013).

Lessons learned from these early field programs are informing designs for longer-term observational campaigns, including the National Ecological Observatory Network’s (NEON) plans to measure vapor isotope ratios for three decades at sites across the United States (Luo et al., 2013). Yet questions still remain about the long-term stability of isotopic measurements made by commercial spectroscopy and the best approaches for calibrating in the field to ensure high-quality long time series. The goal of this paper is to provide guidance for field deployments by evaluating the stability of

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the isotopic biases identified in three spectroscopic isotopic analyzers, made by Picarro, Inc., for periods of up to three years. Moreover, the sensitivity of the calibration data to various statistical treatments and quality-control procedures is assessed and discussed in the context of the different calibration strategies employed.

While previous studies suggest isotopic biases are specific to each individual commercial analyzer (e.g. Tremoy et al., 2011; Aemisegger et al., 2012; Wen et al., 2012), there are nevertheless shared characteristics upon which “best practices” for instrument operation and calibration can be based. Most prominent is the shared tendency for the isotope ratio measured to change as a function of the water vapor volume mixing ratio, creating a so-called “concentration-dependence,” which numerous studies describe (e.g. Lis et al., 2008; Sturm and Knohl, 2010; Johnson et al., 2011; Noone et al., 2011; Rambo et al., 2011; Tremoy et al., 2011; Aemisegger et al., 2012; Wen et al., 2012; Bailey et al., 2013; Noone et al., 2013; Steen-Larsen et al., 2013, 2014b; Bastrikov et al., 2014; Bonne et al., 2014; Samuels-Crow et al., 2014). While a few have found the dependence of isotope ratio on water vapor concentration to be near linear (cf. Lis et al., 2008; Wen et al., 2012), most have found it to be non-linear and specific to both the instrument used and the isotope ratio measured (i.e. δD or $\delta^{18}O$, where $\delta = (R_{\text{observed}}/R_{\text{standard}} - 1) \times 1000$ and $R = D/H$ or $^{18}O/^{16}O$). Moreover, biases in the individual isotope ratios can be quite significant: Sturm and Knohl (2010) showed that failing to account for the concentration-dependence of their analyzer resulted in a bias in the second-order deuterium excess parameter ($d = \delta D - 8 \times \delta^{18}O$) of upwards of 25‰.

Characterization of the concentration-dependence can be achieved by measuring a standard of known isotope ratio across a range of vapor volume mixing ratios. However, in practice, producing a vapor source whose isotope ratio is sufficiently stable and whose humidity can be manipulated across a wide range is non-trivial. Previous studies have experimented with a variety of calibration systems for this purpose, including custom dew point generators (Wen et al., 2012; Samuels-Crow et al., 2014; Steen-Larsen et al., 2014b), systems that pump, drip, or nebulize liquid water continuously

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into an evaporation chamber (Rambo et al., 2011; Tremoy et al., 2011; Aemisegger et al., 2012; Wen et al., 2012; Steen-Larsen et al., 2013; Bastrikov et al., 2014; Bonne et al., 2014), and systems that flash-evaporate discrete liquid samples (Lis et al., 2008; Noone et al., 2013). (See Wen et al. (2012) for a more in depth discussion.) A common complication with any of these systems is hysteresis, caused by water sticking to either the instrument cavities or inlet materials. Calibration tests using flash-evaporated, liquid isotopic standards, for example, have demonstrated that “memory effects” frequently affect the first injections following a change in standard water (Lis et al., 2008; Gröning, 2011; van Gelden and Barth, 2012). Other studies have shown that tubing material connecting the calibration system to the analyzer can slow the analyzer’s response time, with Synflex particularly problematic for δD (Tremoy et al., 2011). Both Lee et al. (2005) and Sturm and Knohl (2010) speculated that failing to account for such measurement inaccuracies might result in a poor characterization of the concentration-dependence and, ultimately, influence interpretation of scientific results.

Additional isotopic biases indicate deviations from the VSMOW (Vienna Standard Mean Ocean Water)–SLAP (Standard Light Antarctic Precipitation) scale (cf. Gröning, 2011), and these are typically characterized by fitting a linear regression between the known values of two (or more) standards and the isotope ratios measured by the instrument (cf. Tanweer et al., 2009). A key question is whether instrumental drift causes variations in the intercept of this linear fit and influences measurement reproducibility on hourly time scales or longer. Unlike random errors associated with instrumental precision, which influence reproducibility on much shorter time scales (e.g. s to min), isotopic drift can be corrected by measuring the same isotopic standard at a constant humidity level at regular time intervals. Using such an approach, some studies have found no significant drift over multiple hours (Koehler and Wassenaar, 2011; van Geldern and Barth, 2012), while others claim significant variability in measurement reproducibility on daily timescales (Gupta et al., 2009; Tremoy et al., 2011; Aemisegger et al., 2012). Steen-Larsen et al. (2013), for instance, reported large daily variability – as high as 4‰ in $\delta^{18}O$ and 16‰ in δD – and observed seasonal drift in one of two isotope ratios and

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one of two instruments deployed. Sturm and Knohl (2010) similarly observed consistent enrichment in one isotope ratio over the course of two weeks but no change in the other. Steen-Larsen et al. (2014b), meanwhile, observed drift in both isotope ratios but of opposite sign during a 500 day deployment in Bermuda. Possible sources of such variability may be instrument sensitivities to fluctuations in environmental factors such as ambient temperature (Sturm and Knohl, 2010; Rambo et al., 2011) or uncertainties in the characterization of the concentration-dependence with time (Sturm and Knohl, 2010).

Building on these previous analyses, this study extends the understanding of long-term stability in vapor isotopic analyzers by evaluating (1) whether there are significant changes in the concentration-dependence with time, and whether these changes are exacerbated by curve-fitting inaccuracies or measurement hysteresis; and (2) whether isotopic drift is detectable over periods of six to 36 months for two different calibration systems. In light of plans to develop baseline monitoring of isotope ratios in vapor over several decades, identifying and characterizing measurement sensitivities on these longer time scales is critical. Recommendations for calibration strategies are discussed in the conclusions of this paper.

2 Methods

The primary data for this study were collected using three Picarro, Inc. vapor isotopic analyzers, which were operated at two baseline observatories: the Mauna Loa Observatory (3400 m) on the Big Island of Hawaii and the Greenland Environmental Observatory (3200 m) at Summit, Greenland.

2.1 Instruments

Picarro's spectroscopic analyzers are one of several commercial vapor isotopic analyzers based on cavity-enhanced near-infrared laser absorption spectroscopy. Los Gatos

Research, Inc. also makes an analyzer used widely in the field (e.g. Noone et al., 2011; Rambo et al., 2011). These instruments exploit near-infrared light to measure the absorption-line features for three water isotopologues: $^1\text{H}_2^{16}\text{O}$, $^1\text{H}^2\text{H}^{16}\text{O}$ (i.e. $^1\text{HD}^{16}\text{O}$), and $^1\text{H}_2^{18}\text{O}$. Cavity-enhanced techniques help create a longer effective absorption path length, which mitigates for the very weak absorption of water vapor isotopologues in the near infrared. This approach contrasts with mid-infrared isotopic analyzers (e.g. Aerodyne Research, Inc.'s), which take advantage of water vapor's stronger absorption at longer wavelengths.

2.2 Mauna Loa, Hawaii

Beginning during the fall of 2010, water vapor isotope ratios have been measured at the Mauna Loa Observatory (MLO) with a Picarro analyzer model L1115-i. The instrument, which is housed in the Charles Keeling building at the observatory, samples ambient air through 0.25 inch stainless steel tubing at a rate of approximately 300 cc min^{-1} . The stainless steel tubing protrudes through the roof of the building, through a plastic pipe, which has a rain cap to prevent precipitation from entering. The bulk of the stainless steel inlet line is housed inside the building and thus maintained at room temperature, which far exceeds the ambient dew point.

To quality-control the vapor volume mixing ratio measurements (q), the data were compared with MLO's hourly-averaged dew point values, which are measured by hygrometer. A simple linear regression between the two data sets – after converting the MLO dew points to volume mixing ratios and averaging and interpolating the Picarro data – produced a slope of 1.00, and an offset of $0.33\text{ mmol mol}^{-1}$. This suggests a small uniform low bias in the uncalibrated q measurements. However, since the accuracy of the MLO humidity measurements is not fully known, no adjustments were made to the Picarro volume mixing ratio data.

For most of the instrument's deployment, the isotopic measurements have been calibrated weekly using a LEAP Technologies PAL (Prep and Load) autosampler. Liquid samples from secondary standards spanning approximately -45 to 0‰ in $\delta^{18}\text{O}$ and

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–355 to 0‰ in δD are injected by syringe into a vaporizer, which flash evaporates the liquid in a mixture of zero-grade dry air before delivery to the instrument. The volume of water injected controls the mixing ratio of the sample. One standard is injected 18 times at a variety of humidity levels, typically spanning 2–20 mmol mol^{–1}, and a second standard is injected 6 times at a humidity level near 10 mmol mol^{–1} or greater. Early in its deployment, however, the measurements were calibrated using only three injections of a single standard every six hours. Five distinct secondary standards have been used at Mauna Loa.

Additional calibrations were performed over a larger range of humidity values (0.2–20 mmol mol^{–1}) during a few days in February 2012. These were done with a manual syringe-pump system, which steadily pumps liquid standard into a stream of heated dry air. Unlike the PAL autosampler, the syringe pump provides a continuous flow of vapor to the instrument. Moreover, by altering the rates of both the liquid injection and the dry airflow, much lower mixing ratios can be achieved. Because the syringe pump was only used for a short time period, this study does not assess similarities or differences between this manual calibration system and the autosampler.

2.3 Summit, Greenland

Two model L2120-i Picarro analyzers (named “Spiny” and “Gulper” after two types of dogfish shark) were deployed at Summit, Greenland in summer 2011 through summer 2014. The instruments were housed in an enclosed rack in an underground laboratory. While the temperature of the laboratory was approximately 10 °C for the duration of the experiment, the temperature of the enclosed rack was maintained at 15 ± 0.2 °C.

Due to the need for the calibration system in Greenland to run without maintenance for 11 month periods, a custom dew point generator (DPG) was developed to produce water vapor and calibrate both Summit instruments approximately every six hours. A system with similar design elements was used by Ellehoj et al. (2013). Commercially available calibration systems were found unsuitable for this purpose. In the custom system, dry air from an industrial regenerative drier (with a dew point temperature of

–100 °C) was supplied to a 10 L Schott laboratory bottle containing water of known isotope ratio. Dry airflow bubbled through the liquid, producing vapor whose isotope ratio ($R_v = R_l/\alpha$) could be calculated as a function of the temperature-dependent fractionation factor α and the isotope ratio of the liquid (R_l). The temperature of the bottle at Summit was maintained near 20 °C by applying heat to a copper sleeve enveloping the glass. The water vapor mixing ratio of the air stream delivered to the instruments was altered through dry air dilution; and a second-stage dilution immediately upstream of the analyzer was used to achieve the lowest mixing ratios.

Since vapor and liquid within the DPG bottle were always maintained at equilibrium, one would expect the removal of water with time to have caused the isotopic composition of the remaining liquid in the reservoir to follow a predictable distillation described by Wang et al. (2009):

$$R_v(t) = \frac{R_{l0}}{\alpha} \cdot \left(1 - \frac{t}{\tau}\right)^{\frac{1}{\alpha}-1}. \quad (1)$$

Here, R_{l0} is the initial isotope ratio of the liquid water, τ is the time necessary to evaporate all liquid from the bottle, and t is the time elapsed. The analysis considers whether any or all long-term drift in the Summit calibration data can be explained by this distillation.

Beginning in the summer of 2012, isotopic drift calibrations were performed every six hours at a single isotope ratio and humidity level; and the concentration-dependences of Spiny and Gulper were spot-checked by slowly altering dry air dilution of the calibration system vapor stream to produce a large range of mixing ratios (~ 0.1 – 8 mmol mol^{-1}) over several hours. These extended concentration-calibration periods were performed both by increasing and by decreasing the vapor mixing ratio progressively. Beginning in summer 2013, the six-hourly protocol was modified so that calibrations were performed at three different humidity levels spanning 0.1 – 4 mmol mol^{-1} and the analyzers' concentration-dependences could be monitored more frequently. For all of the six-hourly calibrations, the first 9 (19) of 20 (40) minutes spent sampling

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at a given humidity level are excluded from later analyses in order to eliminate memory effects. (Longer sampling was prescribed at the lowest humidity.) The isotopic deviation from the VSMOW–SLAP scale was also checked using three standard waters and the same syringe-pump system used at Mauna Loa (see Sect. 2.2).

2.4 Statistical methods for characterizing isotopic biases

To isolate the concentration-dependences of the three analyzers from other isotopic biases, including biases arising from instrumental drift, the isotope ratios of the calibration data are first normalized. At Mauna Loa, where five distinct standards were used, isotope ratios are normalized by standard to the isotopic mean measured in the 9–11 mmol mol⁻¹ range. This normalization is performed once for the syringe-pump data and every three months for the autosampler data. At Summit, where a single isotopic standard was used to monitor both concentration-dependence and drift, one-minute averages of calibration points are normalized to the weekly mean isotope ratio measured in the 2.5–3.5 mmol mol⁻¹ humidity range. (Shrinking this range or shifting it to higher mixing ratios does not change the qualitative features of the results presented.)

The concentration-dependent isotopic biases are then characterized as a function of the natural log of the vapor volume mixing ratio. Best-fit quadratic polynomial, cubic polynomial, and non-parametric functions are selected by least squares estimation. To account for the smaller number of low-humidity calibration points at the Hawaii site, all functions associated with the Mauna Loa analyzer weight the predictor values by $1/q^2$, where q is the water vapor volume mixing ratio in mmol mol⁻¹. No such weighting is performed for Spiny or Gulper since the Summit calibration data are more evenly distributed across the humidity range of interest for Greenland.

At both sites, non-parametric characterizations are derived by fitting a locally-weighted polynomial regression using R's LOCFIT package (Loader, 1999). The degree of the polynomial and the smoothing parameter (i.e. the fraction of nearest neighbors allowed to influence a single prediction value) are selected by minimizing the generalized cross validation score. One- and two-degree polynomials and smoothing

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parameters ranging from 0.50 to 1.00, every 0.05, are evaluated. A bisquare kernel is chosen to give greatest consideration to the closest neighbors within the smoothing window, and all predictor values are scaled before fitting. In the analysis, prediction intervals are used to identify statistically significant variations in the concentration-dependence characterizations with isotope ratio and time.

Due to the fact that calibrations are performed at different humidity levels at both sites, concentration-dependent biases are removed from the calibration data before isotopic drift is evaluated. At Mauna Loa, a locally-weighted polynomial regression in two dimensions (i.e. a surface) is fit to the total absolute isotopic bias, using both the natural log of the vapor volume mixing ratio and the isotope ratio measured as predictors. This calibration approach is advantageous for Hawaii since it does not require isotopic data to be normalized to a single humidity level and because it estimates prediction errors associated with concentration-dependent biases and deviations from the VSMOW–SLAP scale jointly (cf. Bailey et al., 2013). Different estimates of calibration uncertainty emerge when errors are estimated jointly, and double-counting of correlated systematic error is avoided, or summed in quadrature – an approach that assumes all errors are uncorrelated. As before, the non-parametric regression is weighted by $1/q^2$ to give larger consideration to the more infrequent lower humidity measurements. The local regression predictions are then subtracted from the autosampler calibration points and the residuals used to examine longer-term measurement reproducibility. In comparison, the concentration-dependent biases of the Summit analyzers are characterized for the entire calibration period using a one-dimensional locally-weighted polynomial regression, with only the natural log of the vapor volume mixing ratio as a predictor. The local regression predictions are then subtracted from the six-hourly calibration points and the residuals used to evaluate long-term drift.

3 Concentration-dependence

Characterizing the concentration-dependence is a key step in calibrating the isotopic measurements made by commercial laser analyzer, particularly for older instruments, like the one in use at Mauna Loa, for which concentration-dependence is the dominant isotopic bias. This section considers the importance of statistical curve-fitting procedures and sampling hysteresis in modifying the accuracy of the concentration-dependence characterization. Assumptions about the stability of the concentration-dependence with isotope ratio and with time are also tested.

3.1 Curve-fitting and hysteresis

To evaluate uncertainties in the concentration-dependence characterization introduced by curve-fitting and sampling hysteresis, two subsets of the Mauna Loa calibration data are considered. The first subset includes *filtered* autosampler injection points, where filtering is performed by eliminating the first two injections of each standard during every calibration period. (Eliminating the first three injections would have been preferable (cf. Lis et al., 2008) but for the fact that during the first 500 days of the observational experiment each calibration period consisted of only three injections.) The second or *unfiltered* subset includes all autosampler injections and hence all possible memory effects for this calibration system. Figure 1 shows the difference in the isotope ratio adjustment that would result if fitting the filtered data (solid lines) or the unfiltered data (dashed lines) with a quadratic polynomial (black) (cf. Rambo et al., 2011), a cubic polynomial (blue) (cf. Aemisegger et al., 2012; Noone et al., 2013), or a locally-weighted polynomial regression (red). Clearly, the choice of characterization function is much more important in determining the isotopic calibration for the Mauna Loa instrument than any filtering of the autosampler data. While the typical difference between the filtered and unfiltered data is less than a few tenths of a permil, the average difference between the cubic polynomial and the non-parametric local regression is greater than 1 ‰. Root mean square errors (RMSEs) suggest the parametric functions are

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insufficient for properly capturing the true curvature of the concentration-dependence (RMSE: quadratic = 7.75 ‰, cubic = 2.36 ‰, local regression = 0.35 ‰).

In contrast, at Summit, where the Spiny and Gulper analyzers are calibrated with the DPG, memory effects are much more critical in influencing the isotopic calibration. Figure 2, like Fig. 1, shows differences in the isotopic adjustment that result from applying three functions: a global quadratic polynomial, a global cubic polynomial, and a locally-weighted polynomial regression. Hysteresis in the Summit system is evaluated by considering the different characterizations that result when isolating the extended concentration calibration periods (see Sect. 2.3) in which the vapor volume mixing ratio progressively increases (solid lines, Fig. 2) or decreases (dashed lines, Fig. 2). These are compared with the characterization obtained with a local regression when all Summit concentration calibration data are used, including the six-hourly calibrations performed at three humidity levels. Recall that unlike data from the extended concentration calibration periods, data from the six-hourly calibrations are already filtered in order to minimize memory effects.

Despite being very different in magnitude, the concentration-dependences of Spiny and Gulper are both sensitive to whether the humidity is progressively increased or decreased. Differences in the concentration-dependence characterization resulting from curve-fitting are, in contrast, negligible. This may be due to the fact that each curve in Fig. 2 is comprised of at least 68 one-minute averages, and these data points are well distributed across the humidity range of interest. Differences between the solid and dashed lines, in comparison, suggest memory effects can be quite substantial for the DPG system. Indeed, the tubing connecting the DPG to the instrument amplifies the surface area that the reference vapor contacts. As a result, equilibration may be slow and longer sampling at each humidity level required. Differences in calibration system and approach clearly affect the relative contributions of curve-fitting and hysteresis to uncertainties associated with the concentration-dependence characterization.

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3.2 Sensitivity to isotope ratio

To test whether the concentration-dependence changes with isotope ratio, normalized data from the Mauna Loa syringe-pump calibrations, which were performed over the course of two days using three standard waters, are considered. Figure 3 shows the difference in characterization that would be obtained from a single isotopic standard vs. the characterization obtained from all the syringe-pump data. All curves are fit using a locally-weighted polynomial regression. While there are clear differences between curves, there is no evidence of a monotonic shift in concentration-dependence with isotope ratio. This is statistically supported by the fact that for any given vapor volume mixing ratio, at least two curves overlap within the prediction error envelopes shown. Moreover, between 0.3 and 8 mmol mol⁻¹, the largest absolute difference between any individual curve and the curve obtained when using all the syringe-pump data is approximately 0.6 ‰. In comparison, the average difference between the local and cubic fits shown in Fig. 1 is larger. This finding again highlights the fact that great care is needed when fitting the concentration-dependence in situations where calibration data at the low end of the humidity range are infrequent. In such cases, variability in the concentration-dependence characterization is more likely to be caused by limitations in statistical fitting than by isotopic differences in the standard.

3.3 Long-term stability

To identify possible drift in the concentration-dependence with time, the concentration-dependence at Mauna Loa is characterized every three months between October 2010 and September 2013. The normalized, but unfiltered autosampler calibrations are used for this purpose in order to increase the sample size within each period. All curves are fit with a locally-weighted polynomial regression and are displayed as a difference from the characterization obtained when all three years of data are considered (Fig. 4). Although differences between characterizations are apparent, there is no evidence of a long-term directional trend. Instead, there is variability on the order of ±0.5 ‰ for q

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values less than 10 mmol mol^{-1} – similar to reports by Steen-Larsen et al. (2014b) of variability in the concentration-dependence on the order of several tenths of a permil between 10 and 30 mmol mol^{-1} . The prediction error envelopes suggest this variability is only statistically significant between approximately 4 and 6 mmol mol^{-1} . Meanwhile, sparse data coverage accounts for periods in which the absolute $\delta^{18}\text{O}$ difference exceeds 1.0‰ and for large prediction errors near the humidity-range extremes. When all three years of calibrations are considered, increasing the sample size, the prediction error drops below 0.20‰ for the entire humidity range.

The six-hourly calibration data at Summit, which span much lower volume mixing ratios, also show no trend in the concentration-dependence over a six-month period. Because of the design of the Summit calibration protocol (e.g. a large number of data at a small number of humidity levels), the data in a given month do not span a sufficient humidity range to characterize the concentration-dependence meaningfully. To address this challenge, Fig. 5 considers instead how well a single characterization – derived from all six months of one-minute-averaged data (where $q > 0.15 \text{ mmol mol}^{-1}$) – fits monthly mean calibration values. This “all data” characterization – fit with a locally-weighted polynomial regression – is shown as a gray line for both Spiny and Gulper. The colored crosses depict calibration data that are clustered by vapor volume mixing ratio and averaged in 30 day segments, approximately corresponding to the months shown in the legend. The width and height of the crosses show the one-sigma deviations of the vapor volume mixing ratios and isotope ratios, respectively. While there is clear variability within monthly means, the “all data” curves pass within one SD of nearly every cluster. Importantly, there are no instances in which more than one cluster per month lies farther than one SD away from the gray line. Thus, despite the fact that the Summit instruments exhibit substantially different biases, there is no statistical evidence for long-term drift in the concentration-dependences of either Spiny or Gulper. These results suggest that calibrations need not be performed frequently to resolve long-term directional drift in the concentration-dependence, at least in relatively clean environments like Mauna Loa and Summit; however, they may nevertheless be useful

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for characterizing the concentration-dependence precisely, particularly at low humidity where the signal-to-noise ratio is very small.

4 Isotopic drift

While the previous section suggests the concentration-dependence may be considered stable with time for measurement calibration purposes, this section considers whether the same is true for the isotopic offset from the VSMOW–SLAP scale, particularly in light of the two different calibration systems in use at Mauna Loa and Summit. We examine, first, trends in the residuals of the Mauna Loa isotopic bias once the autosampler data are corrected for concentration-dependence and scaled to VSMOW–SLAP, as described in Sect. 2.4. While at first glance Fig. 6 suggests the remaining isotopic bias does increase with time, closer inspection suggests this apparent multi-year trend is the result of changes to the standards used to calibrate the instrument. The colored symbols in Fig. 6a represent the mean biases of individual standards calculated for 20 day periods following dates on which the standards were replaced with new water. (Note that not all standards have been used throughout the entire measurement campaign.) While variability from one standard-replacement-date to the next is discernible, there is no clear evidence of directional drift. Moreover, although there is a large jump in the bias measured with Boulder water between days 279 and 860, this jump coincides with the period in which the standard was replaced with new water that was more than 1.5‰ more depleted than the original. (For this reason, the symbols are not connected in the figure.)

To evaluate the effect of changes in the Boulder standard on the appearance of long-term isotopic drift at Mauna Loa, a simple linear regression is fit to all of the residuals and another to all residuals except those associated with the new Boulder calibration points (darker shading, Fig. 6a). The first regression suggests a linear drift of 0.162‰ year⁻¹ (not shown); however, the second suggests a drift of only 0.055‰ year⁻¹ (Fig. 6a, red line). The latter would have caused a total increase in the isotopic

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bias remaining after calibration of 0.166‰ over the course of the 3 year campaign – a change smaller than the mean uncertainty associated with the locally-weighted surface regression used to calibrate the data. While drift of this magnitude would be significant over many years, it is negligible relative to the atmospheric variability (i.e. the signal) for the 3 year measurement campaign at Mauna Loa.

Figure 6b, which shows cubic polynomials fit to the calibration data – normalized for each isotopic standard – during the four periods in which different bottles of standard water were used, provides additional evidence that changes in the calibration standards create the appearance of long-term drift at Mauna Loa. During every period, there is a consistent increase in the residual bias with time, suggesting that the standards themselves have drifted in the field. This may be due to the fact that each week the Mauna Loa instrument is calibrated by pipetting standard water from the glass bottle in which it is stored into small vials, which are loaded onto the autosampler. Over time, weekly opening and closing of the standard bottles allows isotopic exchange between the water reservoir and the ambient vapor. Though this unfortunately impedes characterization of shorter-term measurement reproducibility, it importantly showcases the susceptibility of standards to drift in the field if not stored in airtight containers. Long-term campaigns wishing to characterize weekly-to-seasonal variability in measurement reproducibility will thus need to replace standards sent to the field every few weeks or use an onsite, airtight storage system for standards such as that described by Tanweer et al. (2009).

At Summit, in comparison, the six-hourly DPG calibrations – once corrected for concentration using a locally-weighted polynomial regression – show an expected enrichment in $\delta^{18}\text{O}$ of 1.4‰ year^{-1} (Fig. 7a). As water is continuously vaporized and removed from the DPG bottle, the isotopic composition of the remaining liquid reservoir should become more enriched, following a theoretical Rayleigh distillation (Dansgaard, 1964). Moreover, as a result of fractionation differences, the $\delta^{18}\text{O}$ of the remaining liquid should increase faster than δD (Fig. 7b), resulting in a decrease in the deuterium excess ($d = \delta\text{D} - 8 \times \delta^{18}\text{O}$) (Fig. 7c) (Craig, 1961; Sharp, 2007).

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The relevance of the Rayleigh model for describing the long-term drift observed at Summit is evaluated by comparing the predicted drift in $\delta^{18}\text{O}$ and d from Eq. (1) with the Spiny observations. However, since τ , the time necessary to evaporate all liquid, is unknown for the DPG, a range of possible values is considered for the period following July 2013 – when the DPG bottle was last refilled – (i.e. the last 150 days of the experiment). These estimates are then compared with the slopes of isotopic change observed, which – for such a short period – are well described by linear models. τ 's spanning 1500–1800 days (or approximately 4–5 years) produce the smallest differences in slope between model and observations (e.g. $< 0.04\text{‰ year}^{-1}$ in $\delta^{18}\text{O}$). This range of τ 's is then used to extrapolate the distillation that would have occurred after 421–727 days of continuous operation of the DPG, which corresponds to the first year of calibration points plotted. Normalizing and plotting these extrapolated curves suggests the 1800 day distillation model best reproduces the observations and explains the directional drift in both isotope ratios and in deuterium excess (Fig. 7a–c).

Assuming the linear enrichment in $\delta^{18}\text{O}$ in Spiny and Gulper is entirely explained by distillation of the calibration system, uncertainty due to shorter-term variability (i.e. measurement reproducibility errors) can be estimated once the linear trend is removed. For the period following July 2013 the residual standard error is 0.21‰ . For the period before July 2013 the residual standard error is 0.72‰ . Importantly, the fact that both analyzers record much of the same short-term variability suggests the latter is either inherent to the DPG system or caused by fluctuations in environmental variables such as temperature.

Indeed, more than one previous study has speculated that ambient temperature fluctuations cause instrumental accuracy to change with time (cf. Sturm and Knohl, 2010; Rambo et al., 2011); however, the data presented here do not support this claim. During the summer of 2013 (represented by dark gray shading in Fig. 7), the temperatures of the Summit analyzers plummeted following a change in the temperature of the underground chamber in which they were housed (Fig. 7d). No concurrent change in either isotope ratio occurred.

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In comparison, changes in the temperature of the DPG do appear to influence the isotopic calibrations. During the fall of 2013 (the period represented by light gray shading in Fig. 7), the DPG bottle temperature increased from 20 to 24 °C (Fig. 7e). A change of this magnitude should have altered the rates at which heavy and normal water isotopes change phase relative to one another, resulting in an increase in $\delta^{18}\text{O}$ of about a 0.25 ‰. Such enrichment is evident in the temperature-uncorrected Spiny drift curve of Fig. 7a (dotted line). Yet this factor alone cannot explain all of the isotopic variations around the long-term drift estimate, once again pointing to the possibility that such variability is inherent to the DPG. Clearly, long-term deployments choosing a dew point generator for a calibration system should monitor both the system's temperature and distillation over the course of the campaign. And, the calibration approach needs to be sufficiently flexible to allow for inaccuracies in continuous vapor generation that will influence the total error associated with calibrated ambient measurements.

5 Error estimation

Having examined two of the key factors contributing to uncertainties in the calibration of laser isotopic analyzers, we now consider how these uncertainties affect total error and discuss how the latter may be effectively reduced for the calibration strategies herein described. Known error at both Mauna Loa and Summit primarily stems from three sources: (1) prediction errors associated with characterizing the isotopic biases of the field data, (2) variability in measurement reproducibility that is not captured by linear drift estimates, and (3) instrumental precision, which is here estimated from the SDs associated with the calibration data. Recall that at Summit, calibration data represent one-minute averages, while at Mauna Loa the autosampler values are estimated from approximately two minutes of vapor flow through the instrument's optical cavity. Error estimates are compared with ambient data in order to evaluate the relevance of the calibration strategy in influencing the signal-to-noise ratio at each site.

5.1 Mauna Loa, Hawaii

Since there is no constant reference humidity at Mauna Loa and multiple isotopic standards are used for calibrations, the total isotopic bias is jointly characterized as a function of both the isotope ratio and humidity of the autosampler injections using the locally-weighted surface regression described in Sect. 2.4. Only filtered calibration data are used for this purpose (see Sect. 3.1). Bias is then predicted for every pair of $\delta^{18}\text{O}$ and q measurements and subtracted from the ambient isotope ratio data. No long-term drift correction is made. Mass-weighted averages of the calibrated field data are shown as a function of humidity for the period October 2010–September 2013 in Fig. 8a. Even for q values exceeding 2 mmol mol^{-1} , the mean isotope ratios range from -31.75 to -15.33 ‰ , a 16 ‰ span, which is frequently observed at Mauna Loa Observatory during the diurnal growth and collapse of the convective boundary layer. SDs are greater than 6 ‰ at the lower end of this range and near 2 ‰ at the high end.

Known measurement uncertainties at Mauna Loa are shown beside the ambient data in Fig. 8b. Because prediction errors associated with the non-parametric calibration approach are not a monotonic function of humidity, the 99th percentile of prediction error (0.58 ‰) is used as a conservative estimate of inaccuracy associated with the isotopic bias characterization (black line, Fig. 8b). Meanwhile, uncertainty related to measurement reproducibility (gray line, Fig. 8b) is estimated from the root mean square error associated with the linear regression shown in red in Fig. 6a: 0.51 ‰ . This estimate would increase by only 0.04 ‰ were the second set of Boulder calibration points (darker shading, Fig. 6a) also included in the drift analysis. While these two sources of inaccuracy dominate the total error at vapor volume mixing ratios greater than 2.2 mmol mol^{-1} , the precision of the autosampler and isotopic analyzer assembly clearly regulates total error at lower humidity (blue line, Fig. 8b). The one-sigma uncertainties shown are similar to those reported by Galewsky et al. (2011) for the same model Picarro analyzer. Though sizeable, errors of this magnitude are smaller than the range of $\delta^{18}\text{O}$ observed at Mauna Loa Observatory; and they are also smaller than the

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variations in isotope ratio observed at a particular humidity level (Fig. 8a). Since the humidity range at Mauna Loa is largely a function of whether the observatory is exposed to boundary layer or free tropospheric air, these findings suggest diurnal variations in isotope ratio would be clearly discernible, as would variations associated with synoptic meteorology.

5.2 Summit, Greenland

With most calibrations made with a single isotopic standard, the Greenland data are calibrated sequentially, first by characterizing the global concentration-dependence, using a locally-weighted polynomial regression, and second by linearly scaling the concentration-corrected data to the VSMOW–SLAP scale. The calibrated Gulper field data are shown in Fig. 9 as monthly averages (for months with at least 10 days of data) spanning mid-2012 to mid-2014. While there is some variability from year to year, particularly near the shoulder seasons, there is a clear annual cycle in both $\delta^{18}\text{O}$ and δD , with ranges of about 14 and 111‰, respectively. The SD shading gives an indication of the synoptic variability within each month and ranges from 1.8 to 9.4‰ in $\delta^{18}\text{O}$ and 15.8 to 54.7‰ in δD , with means of 4.8 and 33.2‰, respectively. Isotope ratios from surface snow samples collected in 2013, which were analyzed at the University of Colorado (A. Kaushik, personal communication, 2014) and are plotted in black for comparison, suggest a similar annual signal and monthly variability.

Uncertainties associated with the Gulper measurements are shown in Fig. 10, with d uncertainties estimated by summing δD and $8 \times \delta^{18}\text{O}$ errors in quadrature. Prediction errors associated with the local regression used to characterize the concentration-dependence (black dots, Fig. 10) contribute the least to the total uncertainty, since the characterization is strongly constrained by the large number of calibration points at low humidity. Uncertainties associated with measurement reproducibility (gray dots, Fig. 10) are estimated from the root mean square errors produced by fitting linear distillation trends to the six-hourly drift calibrations. (Recall that the DPG bottle was refilled in summer 2013; therefore the distillation curve is estimated independently for

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periods before and after). Here we consider only the larger RMSE for each isotope ratio: 0.43‰ in $\delta^{18}\text{O}$ and 0.88‰ in δD . While these two inaccuracy terms are significant, they are smaller than the instrumental precision (blue dots, Fig. 10) for δD and d in all months, and for $\delta^{18}\text{O}$ in winter, when humidity is lowest. Although annual and synoptic variability in $\delta^{18}\text{O}$ and δD are clearly large enough to be distinguished despite these errors, d variability is not, at least for short averaging times. The results presented here suggest the signal-to-noise ratio would be most effectively increased by improving instrumental precision at low humidity and by accounting for short-term isotopic variability (i.e. reproducibility errors) associated with the instrument and calibration system assembly.

6 Implications for long-term deployments

There are a number of different factors that need to be considered in calibrating isotope ratio data, and, as described in the introduction of this paper, many of these factors have been documented previously (e.g. Sturm and Knohl, 2010; Johnson et al., 2011; Tremoy et al., 2011; Aemisegger et al., 2012; Gröning, 2011; Noone et al., 2013; Steen-Larsen et al., 2013). However, only recently are data sets sufficiently long to evaluate the long-term stability of laser isotopic analyzers in the field. This analysis has evaluated the stability of the isotopic biases – beginning with the concentration-dependence, or the change in isotope ratio with vapor volume mixing ratio – in three field-operational vapor isotopic analyzers. The instruments, which were deployed at the Mauna Loa Observatory on Hawaii and at Summit, Greenland, include both the early Picarro model L1115-i and the later L2120-i models, which have been used in previous studies to study atmospheric hydrological phenomena (e.g. Galewsky et al., 2011; Noone et al., 2011; Hurley et al., 2012; Bailey et al., 2013) and water exchange between the land surface and atmosphere (e.g. Berkelhammer et al., 2013; Noone et al., 2013; Aemisegger et al., 2014; Steen-Larsen et al., 2014a). Factory pre-calibration has helped reduce concentration-dependence biases in the later 2000 series (cf. Aemisegger et al., 2012).

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all ambient data. Remaining isotopic biases represent deviations from the VSMOW–SLAP scale, and these may be corrected either simultaneously with the concentration-dependence or sequentially by fitting a simple linear regression between the known values of three or more standards and the (concentration-corrected) isotope ratios observed. Unfortunately, neither experiment presented here could determine conclusively whether this deviation changes with time. At Mauna Loa, while calibration data appeared to drift between the dates on which the standard waters were replaced – suggesting the standards themselves drifted – there was no evidence of a linear instrumental drift from one replacement-date to the next. In comparison, at Summit, though the possibility of instrumental drift could not be ruled out, changes in the individual isotope ratios and deuterium excess of the calibration points were consistent with distillation of water in the DPG with time.

For field experiments using continual vapor generation to calibrate their analyzers, eliminating or accurately modeling drift in the standards used to calibrate the instruments is paramount. Modeling distillation in a DPG, for example, requires knowing the exact time to remove all water from the liquid reservoir. This, in turn, depends on the initial volume (or mass) of water and the flow rate of dry air through the liquid reservoir. In contrast, for calibrations with an autosampler, large amounts of secondary standards should either be stored onsite in an airtight container, such as described by Tanweer et al. (2009), or shipped to the site every 3–4 weeks to avoid excessive fractionation associated with opening standard bottles in the field. Such precautions will make it possible to evaluate more accurately whether instrumental drift exists for laser-based isotopic analyzers and whether changes in deviations from the VSMOW–SLAP scale are significant with time.

Advancements in commercial technology over the last few years suggest that the accuracy and precision of laser isotopic analyzers will continue to improve. Nevertheless, the biases examined in this paper remain critical to evaluate, particularly since they are unique to each instrument. To that end, the following recommendations are offered for long-term deployments.

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The ideal *calibration system* should:

1. Enable very accurate evaluation of the concentration-dependence. This can only be achieved by producing very low and stable volume mixing ratios of water vapor for extended periods of time. This study found that a custom dew point generator could achieve volume mixing ratios $< 0.3 \text{ mmol mol}^{-1}$, but that a vapor stream of at least 30 min was necessary to obtain a stable 10 min average and minimize hysteresis. The autosampler, in contrast, was unable to produce low volume mixing ratios reliably.
2. Exhibit minimal or carefully controlled drift. While the former can be achieved by storing standards in specially designed airtight containers (Tanweer et al., 2009), the latter requires both that the liquid standard be temperature-controlled and that distillation be carefully modeled and spot-checked.
3. Allow multiple standards to be delivered to the instrument. At least three standards are recommended for sequential-calibration approaches, in which deviations from the VSMOW–SLAP scale are corrected after the concentration-dependence is accounted for. More standards will be necessary to reduce prediction errors associated with correcting the biases simultaneously, such as with a locally-weighted surface regression. While an autosampler can easily accommodate any number of standards through simple swapping of vials, a DPG would require different water reservoirs for each standard or for quantitative blending.

The ideal *calibration approach* should:

1. Characterize the concentration-dependence by sampling a single isotopic standard at a large number of humidity levels. Sampling at low humidity (e.g. $< 1 \text{ mmol mol}^{-1}$) should be conducted for sufficient periods of time in order to bolster the signal-to-noise ratio. While frequently repeated characterizations of the concentration-dependence are not necessary for verifying the stability of this bias,

field programs may nevertheless wish to recheck their characterizations every few months, particularly if operating in polluted environments.

2. Choose a statistical-fitting procedure that minimizes the magnitude of fitting biases introduced into the data.
3. Consider whether simultaneously correcting the concentration-dependence and deviation from the VSMOW–SLAP scale improves data accuracy.

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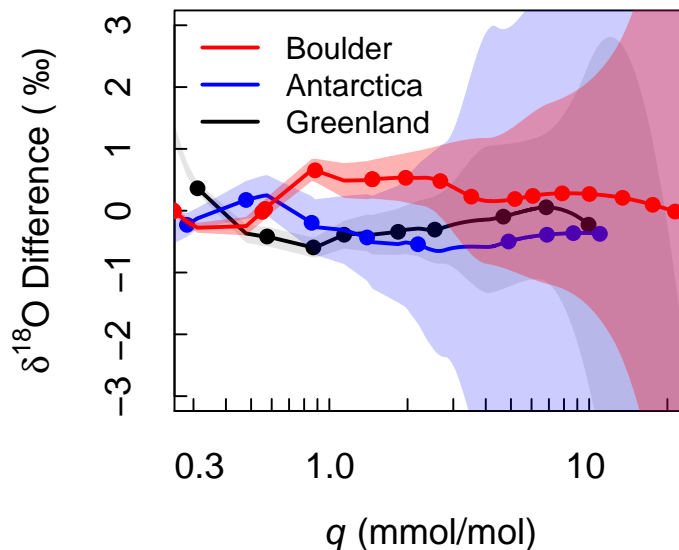


Figure 3. Mauna Loa concentration-dependence characterizations for three different isotopic standards. Curves – fit with a local regression – are shown as differences from the concentration-dependence obtained when data from all three standards are considered and are depicted as a function of q – the vapor volume mixing ratio – on a log scale. Solid circles represent the humidity values at which calibration points were measured. Prediction errors are represented by shading.

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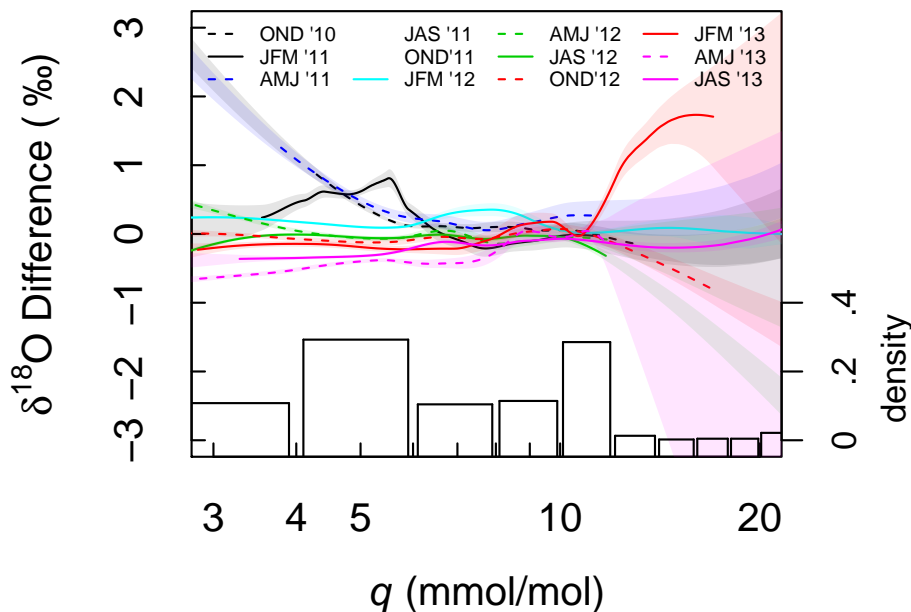


Figure 4. Mauna Loa concentration-dependence characterizations for three-month periods described in the legend. Only periods where $n \geq 30$ are shown. Curves, which are fit with a local regression, are depicted as a difference from the concentration-dependence obtained when using all three years of data and are plotted as a function of q – the vapor volume mixing ratio – on a log scale. Prediction errors are represented by shading. The calibration data density is depicted by bars (rightmost ordinate).

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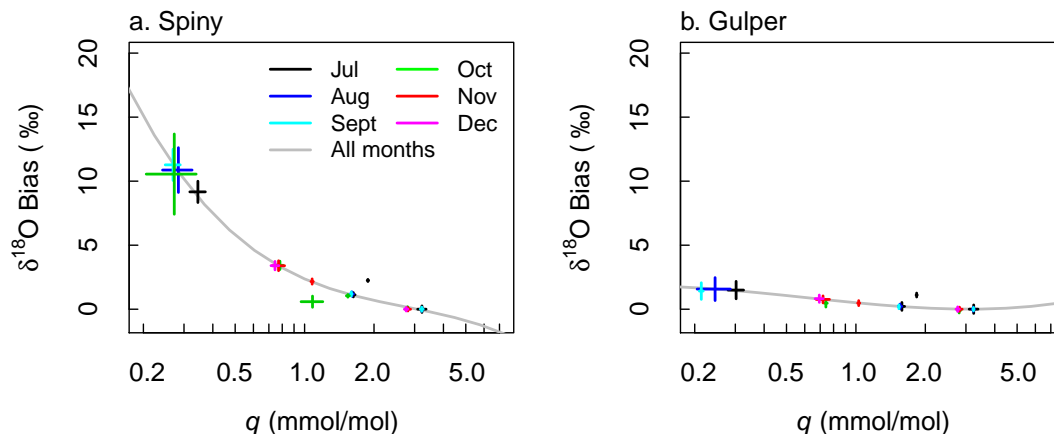


Figure 5. Monthly mean concentration-dependent biases in $\delta^{18}\text{O}$ (‰) for the Summit instruments shown as crosses whose width and height represent one-sigma SDs in $\delta^{18}\text{O}$ and q . The concentration-dependence characterizations obtained when fitting a locally-weighted polynomial regression to all six months of data are represented by gray lines.

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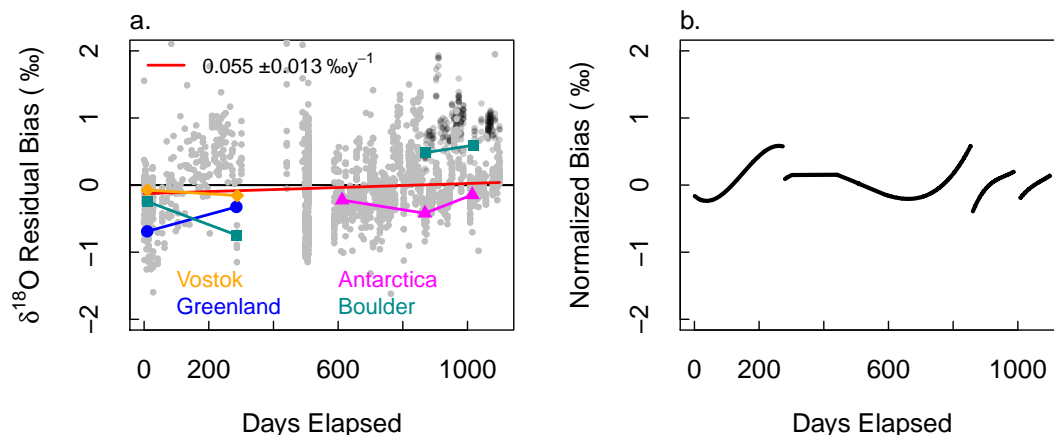
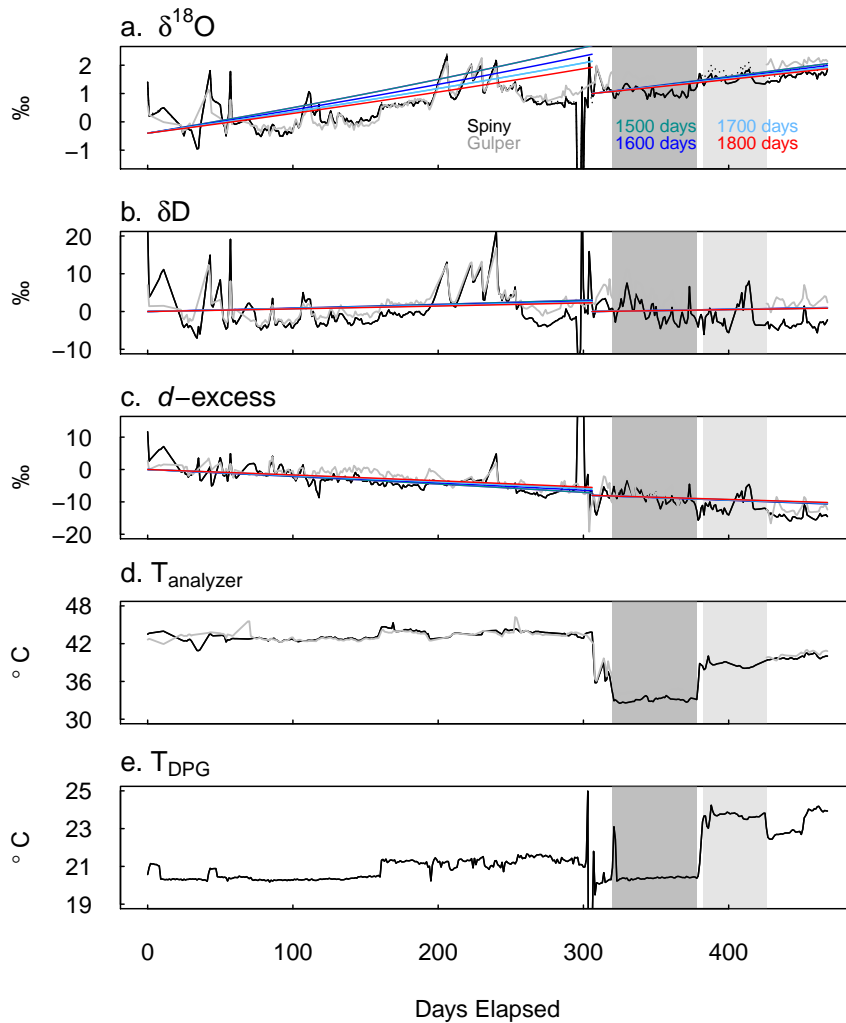


Figure 6. (a) The isotopic bias remaining at Mauna Loa – after correcting for concentration-dependence and scaling to VSMOW–SLAP – plotted as a function of time (gray points). Long-term drift is estimated by the simple linear regression (red line), which is fit to all data except those associated with the second set of Boulder standard water (points with darker shading). Mean residual biases for 20 day periods following the replacement of each standard with new water are represented by the larger symbols and are colored by standard (see legend). **(b)** Cubic polynomials fit to gray points in panel (a) – once normalized by isotopic standard for the four periods in which different standard bottles were used – indicate that the standards themselves may be drifting at Mauna Loa.

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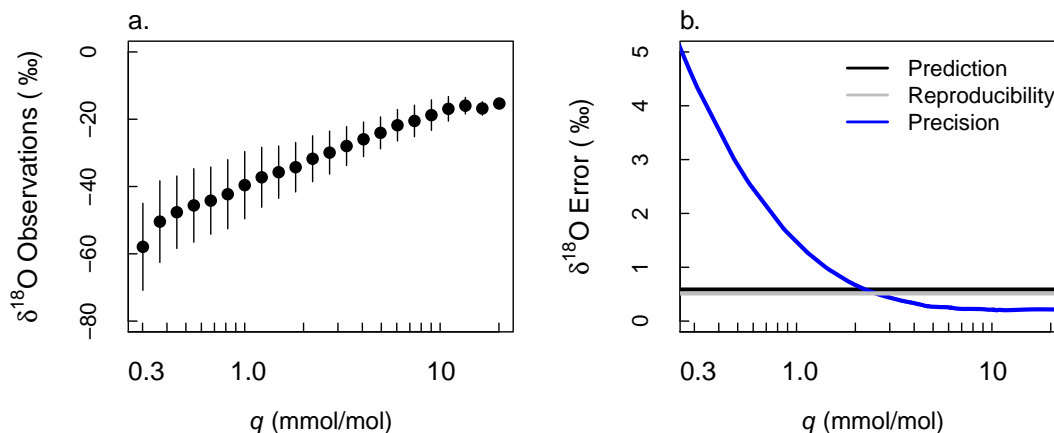


Figure 8. (a) The calibrated Mauna Loa $\delta^{18}\text{O}$ ambient data averaged as a function of the vapor volume mixing ratio (q), with one-sigma SDs given by vertical lines. (b) Sources of uncertainty in the $\delta^{18}\text{O}$ ambient data include the prediction errors from characterization of the total isotopic bias (black), measurement reproducibility errors (gray), and instrument precision (blue).

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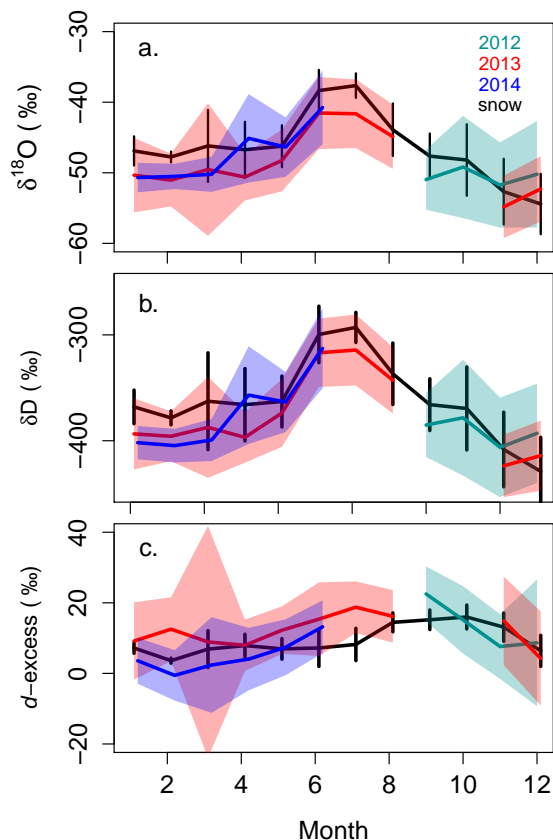


Figure 9. Gulper (Summit) mass-weighted monthly means of **(a)** $\delta^{18}\text{O}$, **(b)** δD , and **(c)** deuterium excess in vapor for 2012 (green), 2013 (red), and 2014 (blue). All monthly means represent > 20 days of sampling except for the October 2012 and June 2013 means, which represent 16 and 11 days of sampling, respectively. Shading represents one-sigma SDs. Monthly mean Summit surface snow values from 2013 (black, with vertical lines representing SDs) are plotted for comparison and offset by equilibrium fractionation factors of **(a)** -10 and **(b)** -80 ‰.

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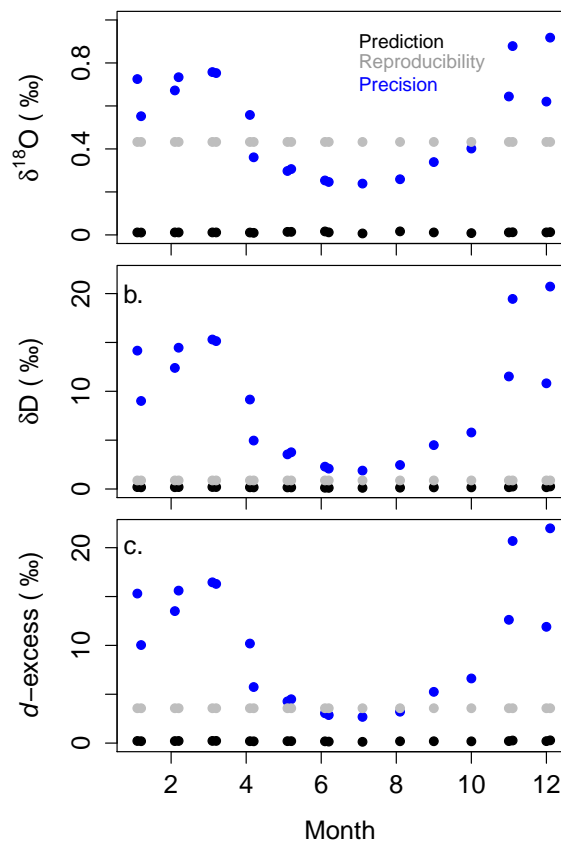


Figure 10. Contributions to uncertainty for Gulper at Summit include the prediction errors from the concentration-dependence characterization (black), measurement reproducibility errors (gray), and instrument precision (blue). These uncertainties are shown for (a) $\delta^{18}\text{O}$, (b) δD , and (c) deuterium excess.

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