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Hydrogen isotope correction for laser instrument measurement bias at low water vapor concentration using conventional isotope analyses: application to measurements from Mauna Loa Observatory, Hawaii

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The hydrogen and oxygen isotope ratios of water vapor can be measured with commercially available laser spectroscopy analyzers in real time. Operation of the laser systems in relatively dry air is difficult because measurements are non-linear as a function of humidity at low water concentrations. Here we use field-based sampling coupled with traditional mass spectrometry techniques for assessing linearity and calibrating laser spectroscopy systems at low water vapor concentrations. Air samples are collected in an evacuated 2 L glass flask and the water is separated from the non-condensable gases cryogenically. Approximately 2 μL of water are reduced to H_2 gas and measured on an isotope ratio mass spectrometer.

In a field experiment at the Mauna Loa Observatory (MLO), we ran Picarro and Los Gatos Research (LGR) laser analyzers for a period of 25 days in addition to periodic sample collection in evacuated flasks. When the two laser systems are corrected to the flask data, they are strongly coincident over the entire 25 days. The $\delta^2\text{H}$ values were found to change by over 200‰ over 2.5 min as the boundary layer elevation changed relative to MLO. The $\delta^2\text{H}$ values ranged from -106 to -332 ‰, and the $\delta^{18}\text{O}$ values (uncorrected) ranged from -12 to -50 ‰. Raw data from laser analyzers in environments with low water vapor concentrations can be normalized to the international V-SMOW scale by calibration to the flask data measured conventionally. Bias correction is especially critical for the accurate determination of deuterium excess in dry air. Copyright © 2011 John Wiley & Sons, Ltd.

Water vapor, the most abundant greenhouse gas, plays a key role in climate forcing.^[1] To better understand climate dynamics and predict the consequences of future climate change, it is necessary to understand how water cycles through the atmosphere.^[2] Although atmospheric scientists have been using laser spectroscopy techniques for water vapor isotope measurements in the stratosphere,^[3] low-cost commercial laser spectroscopy instruments have only recently been developed by several manufacturers which can measure water vapor stable isotopes on-site in near real time. On-site laser spectroscopy measurements are less labor-intensive than flask sampling, in which a glass flask is evacuated, an air sample is collected, and the water in that sample is then isolated, reduced to H_2 , and analyzed on a mass spectrometer. The new laser systems also offer high

precision and temporal resolution. Ideally, they could be used to make on-site stable isotope measurements of low water vapor air samples at high altitudes in the subtropics, which are areas of great interest because the radiative balance of the atmosphere is critically dependent on changes in water vapor concentration.^[4] However, there is no simple method of calibration for the new laser spectroscopy instruments at low water concentrations. The only published tests of the water vapor analyzers at low water concentrations were made by injecting ≥ 0.1 μL liquid water into a vaporizing chamber prior to analysis, which corresponds to minimum water vapor concentrations of 2500 ppmv^[5] and 2000 ppmv^[6] respectively. The analytical accuracy at lower water vapor concentrations is unknown. This invites uncertainty into the performance of these systems at low water vapor concentrations and, since atmospheric water concentrations reach values far below 2500 ppmv, it is necessary to test the accuracy and precision of these systems in very dry air.

We measured the stable isotope composition of water vapor at the Mauna Loa Observatory (MLO) in Hawaii, USA, over 25 days in the fall of 2008. Two commercially available

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laser spectroscopy instruments from Picarro (Sunnyvale, CA, USA) and LGR (Los Gatos Research, Mountain View, CA, USA) were stationed at the observatory. We also used a low-cost flask-based method^[7] to accurately determine the $\delta^2\text{H}$ value of water vapor in samples from field tests at low atmospheric water vapor concentrations using conventional mass spectrometry techniques. We then tested a newly acquired laser system in the stable isotope laboratory at the University of New Mexico (Albuquerque, NM, USA) to determine how accurately it measured stable isotope values at low water vapor concentrations. We measured the $\delta^2\text{H}$ and $\delta^{18}\text{O}$ values of water vapor in controlled laboratory experiments in which we diluted the incoming air to determine if there is a concentration effect on the isotopic compositions. This work complements the thorough concentration experiments done by Schmidt *et al.*^[6] We also tested our flask method for storage effects to ensure that our correction method was valid at low water vapor concentrations. An empirical correction of the laser spectroscopy instruments to the flask data brings the two, otherwise discrepant, data sets into excellent agreement. Because the laser spectroscopy data collected at low water vapor concentrations require to be standardized, we propose that these data be normalized to IAEA (International Atomic Energy Agency) standard values, and we demonstrate how this can be done using the simple and inexpensive flask-based method.

Principles of oxygen and hydrogen isotopes in water vapor

Stable isotope analyses of atmospheric water vapor are useful for constraining atmospheric circulation patterns and mixing.^[8–10] Water isotopologues in nature exist in nine combinations of stable oxygen and hydrogen isotopes.^[11] Because the isotopic composition of water vapor changes during a phase transition,^[12] measurements of water vapor associated with given air parcels indicate hydrologic pathways.^[13] Evaporation, condensation, mixing, and exchange are key processes that drive isotopic change in the hydrologic cycle.^[11] Evaporation is a kinetic process, unidirectional and incomplete in nature. Condensation is generally thought to be a near-equilibrium process that is controlled by temperature alone, and can be modeled through Rayleigh, or open-system, fractionation. In δ notation, Rayleigh fractionation can be written as:

$$\delta_{\text{vapor}} = (\delta_{\text{initial vapor}} + 1000) \times F^{(\alpha-1)} - 1000,$$

where F is the fraction of remaining water vapor, and α is a temperature-dependent fractionation factor. The rapid formation of ice in clouds may in fact be a disequilibrium process,^[14] and not follow simple Rayleigh distillation models. The isotopic ratios of air masses can also be influenced by mixing between two or more air masses, and by exchange between falling water droplets and the surrounding water vapor. In short, there are multiple processes that affect the $\delta^2\text{H}$ and $\delta^{18}\text{O}$ values of water vapor in a given air parcel, but there is great potential for these isotopes to provide insight into the hydrologic history of an air parcel.

Another isotopic parameter, deuterium excess (d-excess), is commonly used in paleoclimate studies and is considered to be a function mainly of sea surface temperatures and relative humidity at the moisture source area.^[15,16] The d-excess may also be controlled by kinetic effects along moisture pathways.^[17] d-excess is defined as $d = \delta^2\text{H} - 8\delta^{18}\text{O}$, and is a measure of the deviation from the Global Meteoric Water Line (GMWL).^[11] Surface water d-excess values have been mapped in the United States,^[18] but the explanation for the variation is not well understood, and there is a limited data set for d-excess measurements of water vapor.

The processes that affect stable isotopes in the water cycle have been studied for over 50 years; extensive analyses of ocean and meteoric water have been made, as samples are readily available.^[19,20] Models can incorporate water vapor H and O isotope fractionation physics to probe atmospheric circulation dynamics,^[21] but the number of existing stable isotope measurements of water vapor that can be used for model validation or application to natural assemblages is quite limited.^[22–24] There are only a handful of isotopic studies of water vapor samples with the goal of understanding atmospheric climate dynamics (e.g.^[25,26]). The paucity of water vapor isotope data has impeded our understanding of water vapor dynamics and links to atmospheric circulation. The lack of data is due to the difficulty in using traditional methods.

Water vapor can be collected for stable hydrogen isotope composition analyses by opening a previously evacuated glass flask and allowing it to fill with air. Flask-based studies of hydrogen isotope ratios in water vapor have been carried out in the southwestern United States and Hawaii,^[6,27] and provide insight into moisture source and large-scale mixing in the subtropics, respectively. The only previously published water vapor samples collected by flask of which we are aware were analyzed in the Stable Isotope Laboratory at the University of New Mexico (UNM). Analyses of water vapor for oxygen isotope and/or d-excess values are limited to air samples that are cryogenically trapped^[28] because a standard 2L flask will not trap enough oxygen for measurement. Larger flasks are prone to breakage and are impractical in the field.

EXPERIMENTAL

Sampling campaign

In October and November of 2008, we carried out a stable isotope sampling and measurement campaign of water vapor at the MLO in Hawaii, collecting water vapor samples in 2 L evacuated glass flasks following established methods.^[6,27] The flask samples were later analyzed for ^2H measurements using isotope ratio mass spectrometry at the University of New Mexico. In addition to the flask data, stable isotope measurements were made on-site using two commercially available isotope laser spectroscopy instruments manufactured by Picarro and LGR. Both instruments are based on the absorption of specific isotopologues of water at a specific wavelength of infrared radiation. The Picarro instrument measures the decay of the laser intensity with time (cavity ringdown),^[29] while the LGR instrument measures the

fractional change in transmitted intensity of a laser beam propagating through an optical cavity and the cavity ringdown while the laser wavelength is scanned over selected absorption lines.^[30] The $\delta^2\text{H}$ and $\delta^{18}\text{O}$ values of the local water vapor are calculated at 10 s intervals, and water calibration standards were measured every 8–12 h by injecting 2 μL of H_2O into a chamber. This injection method is appropriate for air samples with high water vapor concentrations, but may not be applicable to samples with low water vapor concentrations because of a concentration measurement bias (discussed below).

Dilution experiments

When making measurements at low concentrations, the magnitude of the background signal becomes more significant and introduces error. In order to determine whether or not the laser spectroscopy systems provide accurate water vapor stable isotope measurements at low concentrations, we constructed a bubbler apparatus. This apparatus generated a stream of undersaturated N_2 gas at chosen water vapor concentrations that bubbled through a beaker with 160 mL of water of known isotopic composition ($\delta\text{D} = -95.5\text{‰}$) at constant temperature ($24 \pm 1^\circ\text{C}$). Both the $\delta^2\text{H}$ and the $\delta^{18}\text{O}$ values of the produced water vapor were then measured with a Picarro system at the UNM Stable Isotope Laboratory (Fig. 1) which was acquired after the field sampling campaign. Although these experiments could not be done with the specific instrument used at MLO, it was necessary to gain an understanding of any potential bias that may exist as a function of water content in air for the laser analyzers. Dry nitrogen gas ($\text{N}_{2(\text{g})}$) was bubbled through water to produce a gas stream with constant water vapor concentration and D/H ratio. The concentration was diluted by mixing the $\text{N}_{2(\text{g})}$ -water mixture with varying amounts of dry $\text{N}_{2(\text{g})}$ that was first passed through a $\text{N}_{2(\text{l})}$ trap to remove all traces of H_2O . This allowed us to change the concentration without changing the $\delta^2\text{H}$ and $\delta^{18}\text{O}$ values of the dissolved water in gas. The relative flows were controlled with needle valves. A split of the gas mixture was drawn into the laser analyzer. We tested the fidelity of the system by placing a U-trap between the split and the laser analyzer. When cooled to liquid nitrogen (LN_2) temperatures, 100% of the water

was trapped in the U-trap (as assessed by the zero water concentration measured in the water analyzer). The contents of the U-trap were transferred to a vacuum line, reduced to H_2 by a reaction with Zn from the Biogeochemical Laboratories at Indiana University (Bloomington, IN, USA)^[31] and analyzed on a Finnigan Delta Plus XL mass spectrometer (Thermo Fisher Scientific, Pittsburgh, PA, USA). The blank was determined by bypassing the bubbler and found to be below detection limits, even after trapping for several hours.

Flask experiments

During our Hawaii campaign, we collected air samples in 2 L evacuated glass flasks which were analyzed several weeks later in our laboratory in New Mexico. A total of 12 flask samples were collected and measured during the time when the two commercial laser spectroscopy systems were making measurements at MLO. During preliminary evacuation, the walls of the glass were heated with a gas-oxygen flame to remove adsorbed water from the flask walls. Isolation of the water sample for analysis follows the method of Strong *et al.*^[6] Upon return to the laboratory, the air sample was slowly passed through a LN_2 trap connected to the vacuum line over a period of ~ 2 h until the contents of the flask were completely transferred to the U-trap. Excess CO_2 was removed from frozen H_2O cryogenically by replacing the LN_2 trap with one filled with a dry ice/ethanol mixture. The remaining ice was transferred to a 6 mm Pyrex tube with ~ 50 mg of Zn. The sample tubes were sealed shut with a flame, and heated for 30 min at 500°C during which time the reaction $\text{H}_2\text{O} + \text{Zn} = \text{H}_2 + \text{ZnO}$ went quantitatively to completion.^[32,33] Volumes of 2 μL of liquid IAEA standards (GISP and SLAP) were added to evacuated flasks and analyzed in conjunction with the MLO sample flasks for standardization. The $\delta^2\text{H}$ values were measured on the Finnigan Delta Plus XL mass spectrometer. Values are reported relative to V-SMOW defined with $\text{V-SMOW} \equiv 0\text{‰}$, $\text{SLAP} = -428\text{‰}$.^[34] The reproducibility of this method is better than $\pm 2\text{‰}$.^[6]

In order to test the validity of our flask technique, we also added 5 μL capillaries of known water standards into the 2 L sample bulbs filled with dry N_2 gas, a water amount

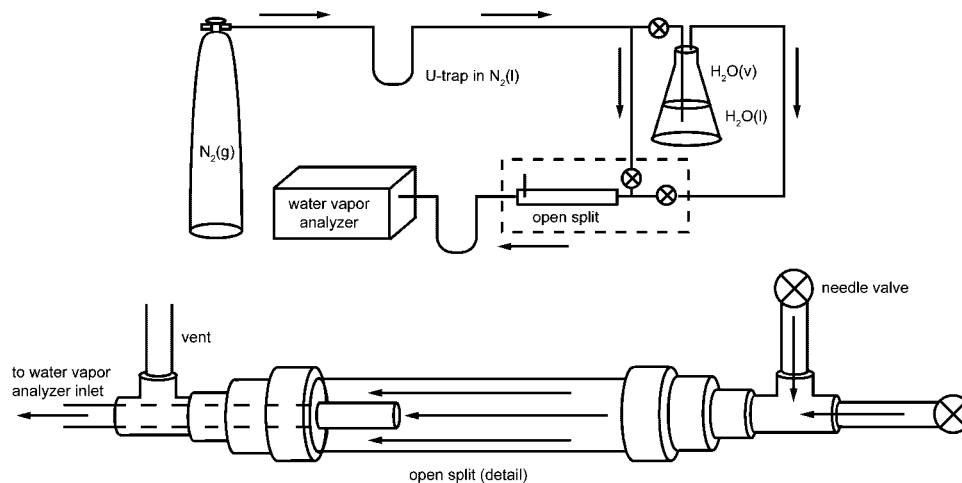


Figure 1. Experimental setup with inset showing open-split configuration.

equivalent to the average nighttime water vapor concentration measurements of ~ 5000 ppmv at ~ 3600 m (altitude of the MLO sampling site). This was accomplished by filling evacuated flasks with dry nitrogen, removing the stopcock and quickly adding a $5\ \mu\text{L}$ capillary filled with water of known isotopic composition. The standards included SLAP ($\delta^2\text{H} = -428\text{‰}$), GISP ($\delta^2\text{H} = -183.79\text{‰}$), and NM2, a calibrated, in-house lab standard ($\delta^2\text{H} = -95.5\text{‰}$). The stopcocks were quickly replaced and closed and the flasks were allowed to stand for different time intervals in order to evaluate any potential for isotopic exchange with the walls of the glass flasks. The amount of time that the water samples were stored in the flasks ranged from 0 (immediate sample transfer) to 21 days. The blank was determined by adding empty capillaries to a N_2 -filled flask. The H_2 concentrations for the blank samples were below detection limits (background noise ~ 10 mV; $2\ \mu\text{L}$ H_2O samples ~ 5000 mV) on the mass spectrometer. Three additional flasks with $2\ \mu\text{L}$ capillaries (equivalent to 2000 ppmv at MLO) of a known standard were allowed to sit for 21 days to ensure that our technique was valid for low water concentration samples.

We were unable to cryogenically trap enough water vapor at such dry conditions for oxygen isotope analysis. Standard techniques, however, are available for oxygen isotope measurements as well as for hydrogen.^[19]

RESULTS

The flask water vapor samples from MLO were collected at various times of day, and overlapped temporally with the Picarro and LGR time series. Two replicate samples were collected at two different times during the campaign to determine reproducibility, which was found to improve at higher water vapor concentrations (i.e. $\pm 7.8\text{‰}$ at 2500 ppmv, $\pm 2.1\text{‰}$ at 10500 ppmv). The isotopic values determined by the Picarro and LGR systems were similar to the flask data at high water vapor concentrations, but were consistently

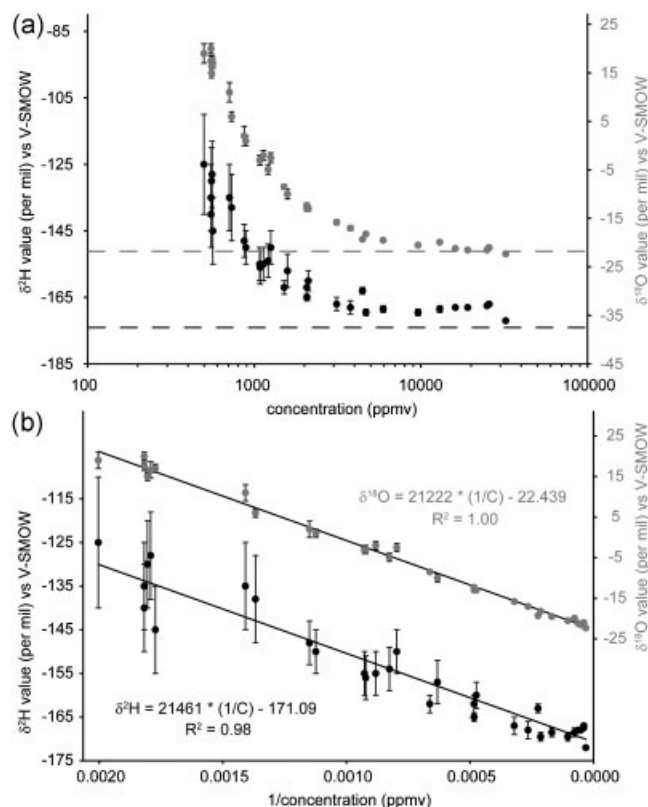


Figure 2. (a) $\delta^{18}\text{O}$ (gray, top) and $\delta^2\text{H}$ (black, bottom) values determined by Picarro during concentration experiments in the laboratory. Dashed lines represent calculated equilibrium values of vapor for $\delta^2\text{H}$ (-172‰ , black) and $\delta^{18}\text{O}$ (-22‰ , gray). (b) Same oxygen and hydrogen isotope measurements shown over $1/\text{concentration}$ ($1/C$). Variability increases significantly at lower concentrations. Vertical bars represent a range of values given by the Picarro instrument at a given concentration, and the data points represent the average value given. P -value of the slope is < 0.0001 .

Table 1. Measured and corrected flask ^2H data with corresponding Picarro and Los Gatos Research (LGR) data. All data are in δ notation ‰ relative to V-SMOW unless otherwise noted

Time and day of year (UTC)	Water vapor concentration (ppmv)	Measured flask	Corrected flask	Picarro	Corrected Picarro	LGR	Corrected LGR
day 285 07:00	3000	-266	-264	-276	-250	-265	-258
day 285 12:20*	2500	-269	-267	-280	-253	-262	-255
day 285 12:20*	2500	-258	-257	-280	-253	-262	-255
day 285 19:00	1500	-331	-325	-400	-346	-321	-310
day 286 01:11	11000	-93	-100	-96	-111	-94	-100
day 293 19:40	3000	-283	-280	-314	-279	-305	-295
day 294 00:00†	10500	-107	-114	-104	-117	-104	-110
day 294 00:00†	10500	-104	-111	-104	-117	-104	-110
day 296 21:27	1500	-290	-286	-315	-280	-299	-290
day 301 07:30	6000	-158	-161	-167	-166	-172	-172
day 302 12:00	7000	-193	-195	-189	-183	-181	-181
day 311 00:00	4500	-208	-189	-224	-210	-228	-224

†* dates averaged, plotted as one point in Figs. 7 and 8, ° sample from Mauna Kea.

† 'Corrected flask' refers to adjustment that was made based on the time between sample collection and subsequent analysis; see Fig. 3.

depleted in ^2H at low water vapor concentrations. To determine the cause of these discrepancies, we ran some experiments with both the laser spectroscopy system and the flasks, which were then used to provide the corrected data in Table 1. The results of the experiments are given below.

To test concentration-based measurement bias with the Picarro system, the open-split method allowed us to make stable isotope measurements of air samples in the laboratory with water vapor concentrations ranging from $\sim 30\,000$ ppmv to less than 100 ppmv. The $\delta^2\text{H}$ and $\delta^{18}\text{O}$ values as well as the associated measurement errors increase dramatically at concentrations below 2500 ppmv (Fig. 2(a)). Plotted as $\delta^2\text{H}$ or $\delta^{18}\text{O}$ vs. $1/C$ (concentration) the data form linear arrays (Fig. 2(b)). Freezing out the water beyond the open split and measuring the $\delta^2\text{H}$ values using conventional mass spectrometry allowed us to check for any analytical fractionations caused by the open split. At water vapor concentrations of both 500 ppmv and 20 000 ppmv, the $\delta^2\text{H}$ values of the frozen water samples were indistinguishable within experimental error (-161.7‰ and -160.9‰). We then calculated the equilibrium $\delta^2\text{H}$ and $\delta^{18}\text{O}$ values of the produced water vapor for comparison. Since the water in the bubbler system is slowly removed in the form of vapor, the system is not under true equilibrium conditions; however, this calculation provides a decent approximation for our purposes. The calculated equilibrium $\delta^2\text{H}$ value of the water vapor, based on the equilibrium fractionation between the water (-95.5‰) and calculated water vapor using the fractionation equation of Horita and Wesolowski^[35] at 25°C , is -172‰ which is close to the measured value of our frozen sample, thus validating the technique. In contrast, the Picarro instrument at UNM produced $\delta^2\text{H}$ values that changed by nearly 50‰ between concentrations of 20 000 ppmv and 500 ppmv (Fig. 2(a)).

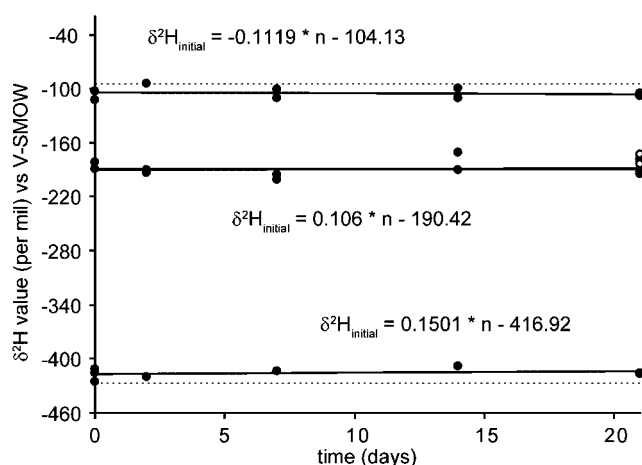


Figure 3. Experimental flask data and correction equations. Aliquots ($5\ \mu\text{L}$) of known water standards were added to flasks and then allowed to sit for different periods of time (n = number of days). The white circles indicate flask samples with $2\ \mu\text{L}$ of the GISP standard measured after 21 days. Three standards were used (SLAP $\delta^2\text{H} = -428\text{‰}$, GISP $\delta^2\text{H} = -183.79\text{‰}$, NM2 $\delta^2\text{H} = -95.5\text{‰}$, values indicated by dashed lines). A linear regression was used to determine corrected values. Values show minimal drift with time. P -values of intercepts are <0.0001 .

The laboratory control experiments for the flasks showed that there is very little change in the $\delta^2\text{H}$ values over a period of 21 days (Fig. 3). The values for the lightest waters (-428‰) increased by $\sim 3\text{‰}$ over 21 days, and for the heaviest waters (-95.5‰) decreased by $\sim 2\text{‰}$. The lightest samples yielded slightly heavier isotopic compositions and the heaviest samples yielded slightly lighter values than expected. This is presumably due to minor exchange with an irremovable monolayer of water on the surface of the glass^[36] despite efforts to fully evacuate the flasks before sampling. The MLO flask data was easily corrected for, however, by applying a stretching factor (see Sharp appendix^[11]) based on this experiment, where the data are normalized to the V-SMOW scale by plotting the true and measured $\delta^2\text{H}$ values and establishing a linear regression model. The initial $\delta^2\text{H}$ values at time zero for each sample were found, based on linear regressions of the experimental flasks for the three standards (y -intercepts from Fig. 3), and these values were corrected to the actual values of the standards to account for the effects of storage time. The equation that corresponds with this stretching factor ($\delta^2\text{H}_{\text{MLO flask actual}} = 0.9427 \times (\delta^2\text{H}_{\text{MLO flask measured}}) - 13$) was applied to the MLO flask data.

DISCUSSION

We were able to correct the $\delta^2\text{H}$ values of the laser systems based on the flask data collected at the same time (Fig. 4). Results from the dilution test were not included in the correction because the noted bias of the lab instrument could not be applied to the specific instrument used at MLO. The disagreement between the results from the flasks and those from the two commercial systems becomes greater at lower $\delta^2\text{H}$ values (and lower water concentrations). The linear

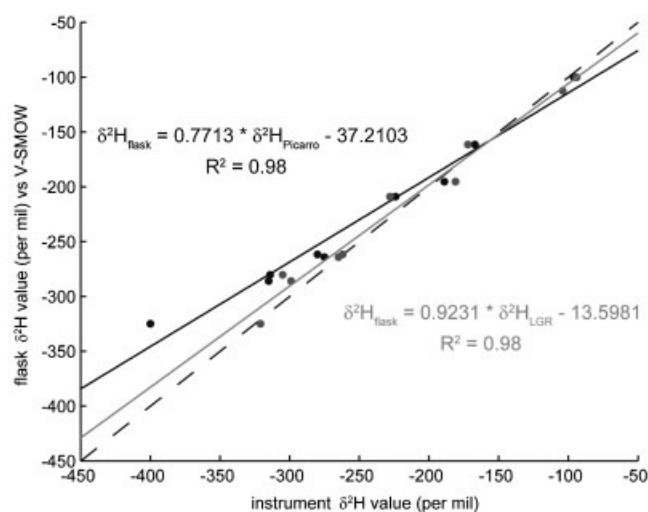


Figure 4. Illustration of initial flask measurement offset. Dashed line indicates 1:1 values. Black line indicates slope of flask data vs. Picarro data (uncorrected), gray line indicates slope of flask data vs. Los Gatos Research data (uncorrected). This assumes a linear relationship between water vapor concentration and stable isotope values is assumed, since the instrument used at MLO was not available for water vapor concentration dependence experiments. P -values of slopes are <0.0001 .

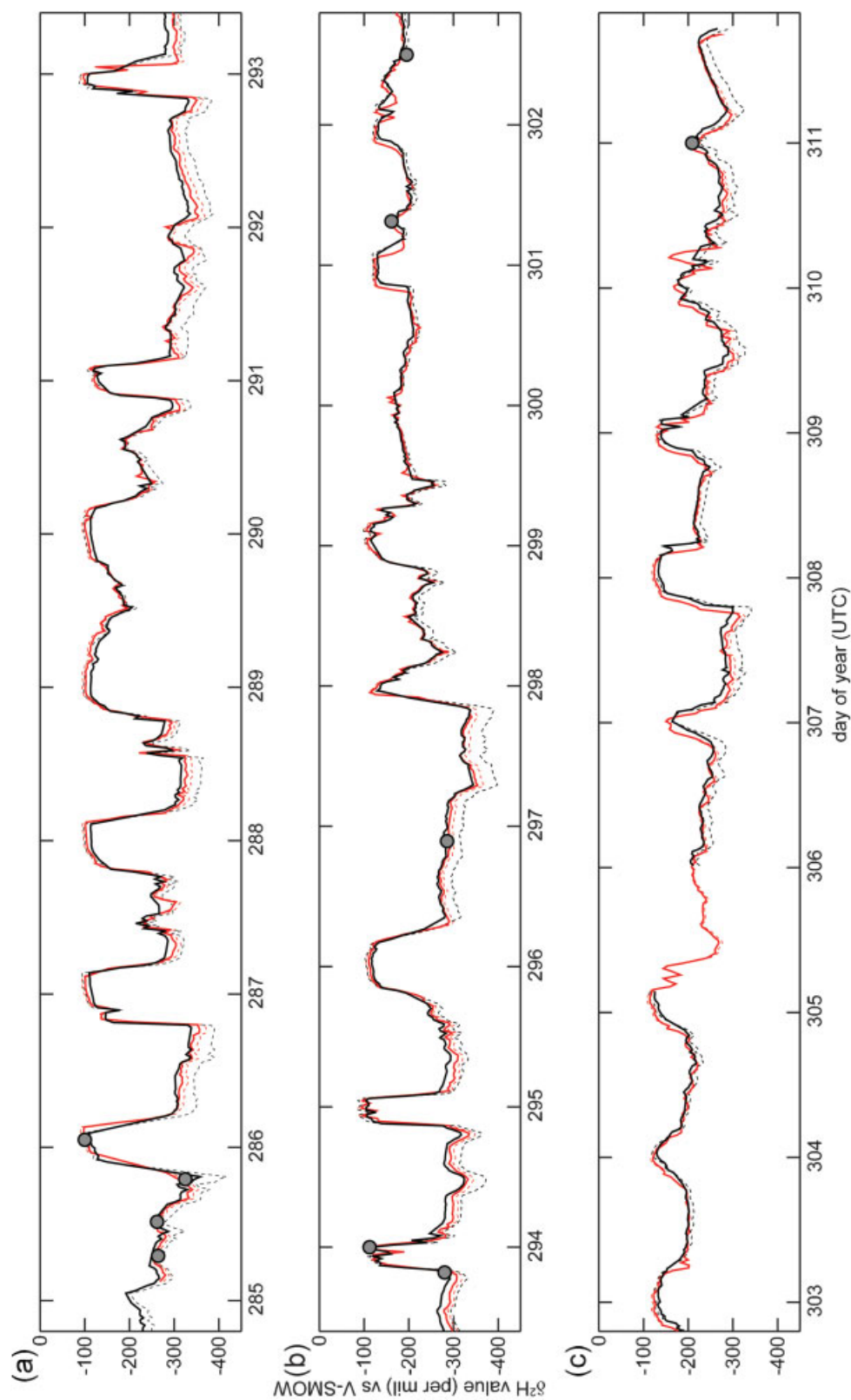


Figure 5. Continuous time series of initial $\delta^2\text{H}$ values measured by Picarro (dashed black) and Los Gatos Research (dashed red) instruments at MLO in 2008, shown in three sections (a, b, c) from day 285 (October 11) to 311 (November 5). Points in gray show corrected flask measurements. Corrected Picarro and Los Gatos Research data are plotted in solid black and red, respectively. These data can be found as Supporting Information.

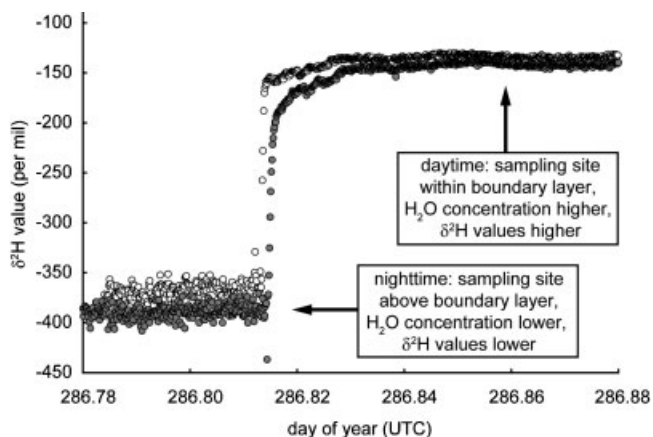


Figure 6. Section of Picarro (gray) and Los Gatos Research (white) data from MLO (uncorrected) illustrating diurnal pattern of stable isotope values corresponding with position of the boundary layer. Oxygen stable isotope data show a similar pattern.

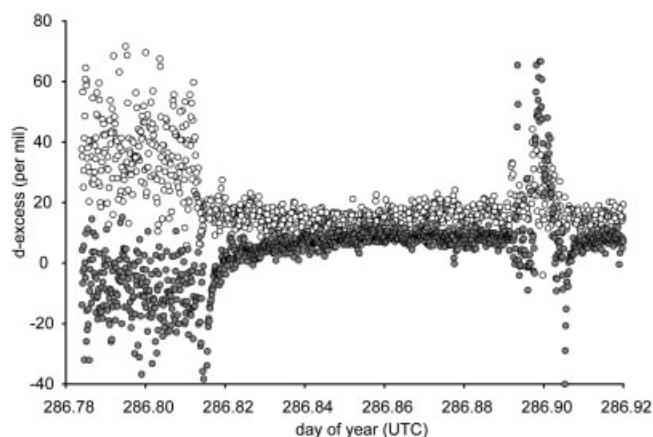


Figure 8. d-excess values determined from Picarro (gray) and Los Gatos Research (white) instruments over a 3.5 h time interval on October 12, 2008 (same as Fig. 6). Picarro d-excess values drop below -20 when water vapor concentration is below 2500 ppmv; Los Gatos Research d-excess values rise above $+40$ under the same conditions.

regression equations shown in this figure (Picarro $\delta^2H_{\text{flask}} = 0.7713 \times \delta^2H_{\text{Picarro}} - 37.2103$, $R^2 = 0.98$ and Los Gatos Research $\delta^2H_{\text{flask}} = 0.9231 \times \delta^2H_{\text{LGR}} - 13.5981$, $R^2 = 0.98$) were applied as correction terms to each of the two systems. This correction puts them into excellent agreement with each other and with the flask data (Fig. 5).

By using the corrected flask measurements as a basis for adjusting the laser spectroscopy data, it is possible to produce a time series of water vapor stable isotope data that is

not affected by instrument concentration bias and can be calibrated directly to the SMOW scale.^[11] This expands the utility of these new instruments, allowing data from different laboratories with different instruments to present data on the same scale. Interestingly, the Picarro system used in Hawaii appears to have a different bias from the one in our laboratory based on the MLO data; the Picarro data from Hawaii were lighter than the true values, whereas the data collected in our laboratory showed a bias towards higher δ^2H values at low

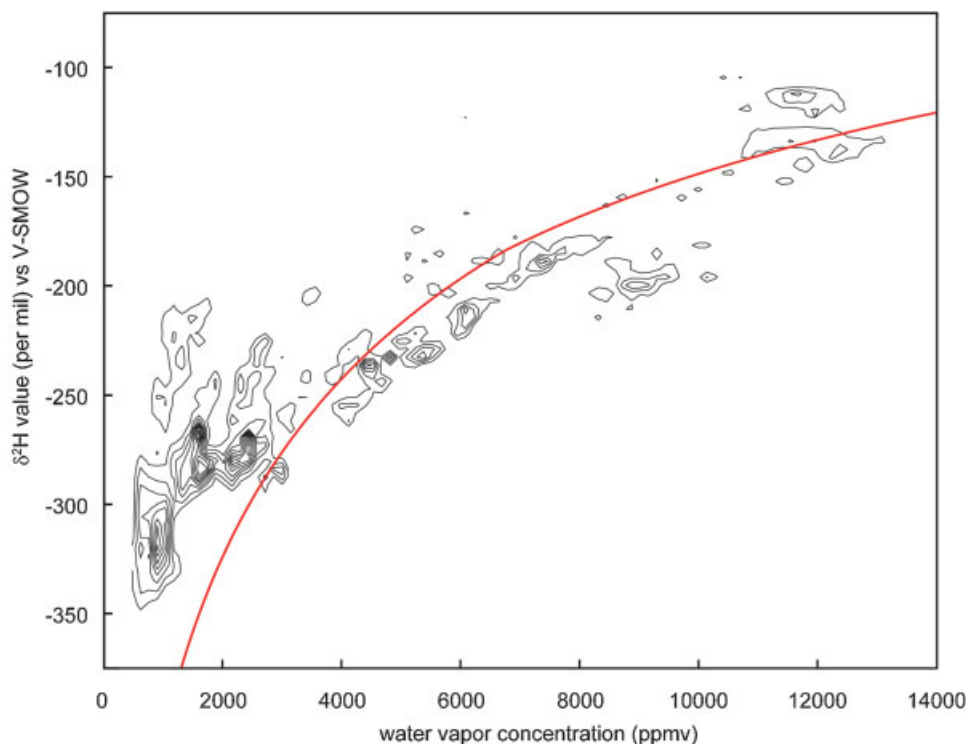


Figure 7. Water vapor concentration vs. δ^2H values as measured by the Picarro instrument at MLO, and corrected using the flask data. The contours indicate frequency of occurrence in 1% contour intervals. Outside contours are 1%. The relationship between these two variables is neither linear, nor fully described by a Rayleigh fractionation curve (red), demonstrating the need to accurately measure stable isotope values of water vapor for climatic interpretation.

water vapor concentrations. Variability exists among all instruments, so it is important to carefully characterize each one. By analyzing several flasks using the approach outlined here, $\delta^2\text{H}$ measurements field campaigns at low water vapor concentrations using a laser spectroscopy system can be corrected to the official IAEA V-SMOW scale.

The Picarro, LGR, and flask data have the same diurnal pattern over the sampling period. The sharp change in delta values corresponds to the rising and falling of the planetary boundary layer (Fig. 6). When the boundary layer drops below the MLO, the measured isotopic compositions are those of the subsiding free troposphere. Because the moisture associated with this layer is from a non-local source and part of the large-scale circulation,^[27] the stable isotope values associated with the water vapor are more depleted in the heavy isotope. Day-to-day variability in the $\delta^2\text{H}$ and $\delta^{18}\text{O}$ values of atmospheric water vapor at MLO is attributed to the temperature at which air parcels were last saturated in weather systems around the Pacific basin (J.V. Hurley, J. Galewsky, Z. D. Sharp, D. Noone, J. Worden, in preparation). While the water vapor concentration has a similar trend, it is important to note that the relationship between the concentration and the $\delta^2\text{H}$ values of the water vapor is not linear, nor can it be described by a simple Rayleigh curve (Fig. 7). Different atmospheric processes driving isotopic fractionation are responsible for this non-linear relationship, but we cannot yet fully define them. It is necessary to better understand the relationship between these two variables as measured via laser spectroscopy methods in order to describe atmospheric processes with greater certainty.

The flask data and laser spectroscopy data agree well at high water vapor concentrations, but diverge at low water vapor concentrations. The difference is more pronounced for the Picarro instrument used at MLO. The incongruous measurements become more evident when they are used to determine d-excess values. While the LGR instrument indicates large positive d-excess values at low water vapor concentrations, the Picarro instrument indicates large negative d-excess values (Fig. 8). Because we do not have a flask correction for the $\delta^{18}\text{O}$ values of the laser spectroscopy systems, we are unable to determine the correct d-excess values at this time. However, it is important to note that without instrument reconciliation, d-excess determination is not possible.

CONCLUSIONS AND FUTURE WORK

The laser systems are invaluable new analytical devices that offer unprecedented temporal resolution and sampling ease at low cost, but care must be taken at low water vapor concentrations to normalize the data to V-SMOW. Samples collected in 2 L evacuated flasks and analyzed conventionally give $\delta^2\text{H}$ values that are nearly free from size bias and can be corrected to true values on the V-SMOW scale by applying a simple linear correction. The flasks offer a low-cost method of making the correction. Alternately, one could make a correction based on the open-split method in which the laser is calibrated for changes in concentration, although this method requires that the bias does not change with time,

altitude, or temperature. A correction needs to be made for each individual machine.

LGR endorses the need to calibrate the analyzers at low concentrations and since our field campaign, another method has been developed for doing so (D. Baer, personal communication, August 31, 2010). LGR has developed a Water Vapor Isotope Standard Source (WVISS, model: 908-0004-9001), essentially a robust nebulizer, that provides a controllable flow of water vapor of known isotopic composition over the entire measurement range of mixing ratios. The WVISS thus enables automatic and full characterization of the LGR Water Vapor Isotope Analyzer to correct for drift and concentration dependence, if necessary.^[37] For the Picarro machine, dilution tests down to 2500 ppmv show very little variation with concentration. Below 2500 ppmv, instrument bias may become significant depending on the individual machine. In our tests, we found a change in $\delta^2\text{H}$ ($\delta^{18}\text{O}$) value of $\sim 12\%$ (20%) at 1000 ppmv and $\sim 30\%$ (40%) at 500 ppmv. This bias is recognized by the manufacturer (C. Rella, personal communication, June 18, 2010), and algorithms can be applied to reduce the $\delta^2\text{H}$ and $\delta^{18}\text{O}$ measurement bias at low concentrations (C. Rella, personal communication, June 18, 2010).

Because areas of low water vapor concentration are of great climatic interest and better accuracy is required, especially for d-excess determinations, we suggest that the $\delta^2\text{H}$ data from laser instruments can be corrected to an internationally recognized water sample related to V-SMOW by making flask measurements. For some spatial and temporal sampling campaigns, flask sampling may still be the most efficient means of collecting the required water vapor samples. The method is simple and easy to implement in the field. Once made, a long-time series could be corrected to the V-SMOW scale.

SUPPORTING INFORMATION

Additional supporting information may be found in the online version of this article.

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