

Water Vapor Isotopic Composition from the Azores Field Campaign Report

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Acronyms and Abbreviations

ARM	Atmospheric Radiation Measurement
CSI	Center for Stable Isotopes
DOE	U.S. Department of Energy
ENA	Eastern North Atlantic
LGR	Los Gatos Research
LOWESS	locally weighted scatterplot smoothing
MBL	marine boundary layer
ppm	parts per million
RMSE	root-mean-square error
SST	sea surface temperature
TWVIA	triple water vapor isotope analyzer
UNM	University of New Mexico
VSMOW-SLAP	Vienna Standard Mean Ocean Water –Standard Light Antarctic Precipitation
WVISS	Water Vapor Isotope Standard Source

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1.0 Summary

Humidity and water vapor δD and $\delta^{18}\text{O}$ measurements were collected for one year (March 1, 2018 to February 28, 2019) at the U.S. Department of Energy (DOE) Atmospheric Radiation Measurement (ARM) user facility observatory on Graciosa Island, Azores. Continuous in situ measurements were collected in the boundary layer using a Los Gatos Research (LGR) triple water vapor isotope analyzer (TWVIA). Stable isotope measurements were corrected for humidity-induced bias, calibrated to international standards, accounted for time-drift, and are presented as 3-hour averages. The uncertainties in the data are 1.75‰ for δD and 0.95‰ for $\delta^{18}\text{O}$.

Measurements of water vapor stable isotopes (δD and $\delta^{18}\text{O}$) have been shown to be useful tracers of the atmospheric hydrologic cycle, providing more information than humidity measurements alone.^{1,2} The physical basis for using water vapor isotopes in hydrologic studies stems from the mass-dependent fractionation that takes place during phase change throughout the hydrologic cycle.³ Previous investigations have demonstrated the ability of water vapor isotopes to uniquely inform us about transport, mixing, and phase-change that water vapor undergoes in the atmosphere.^{2,4-14} As the climate warms, it is increasingly critical to better understand the current processes influencing the atmospheric portion of the hydrologic cycle to advance our understanding of how this cycle may change under future warming conditions.

The development of commercial laser-based spectroscopy has provided a key method to make continuous in situ measurements of stable isotopes of water vapor. Previous work has reported continuous measurements at a wide variety of locations. In 2017, cruise data were published that included measurements spanning from 4° South to 63° North between 2012 and 2015 in the Atlantic Ocean.¹⁵ In 2019, data from North America, Europe, Asia, Africa, Australia, Greenland, Antarctica, and oceanic measurements between Australia and Antarctica measured between 2004 and 2017 were published.¹⁶ In this paper, we present a one-year data set of water vapor stable isotope and humidity measurements from Graciosa Island, Azores, located in the North Atlantic Ocean (Figure 1).

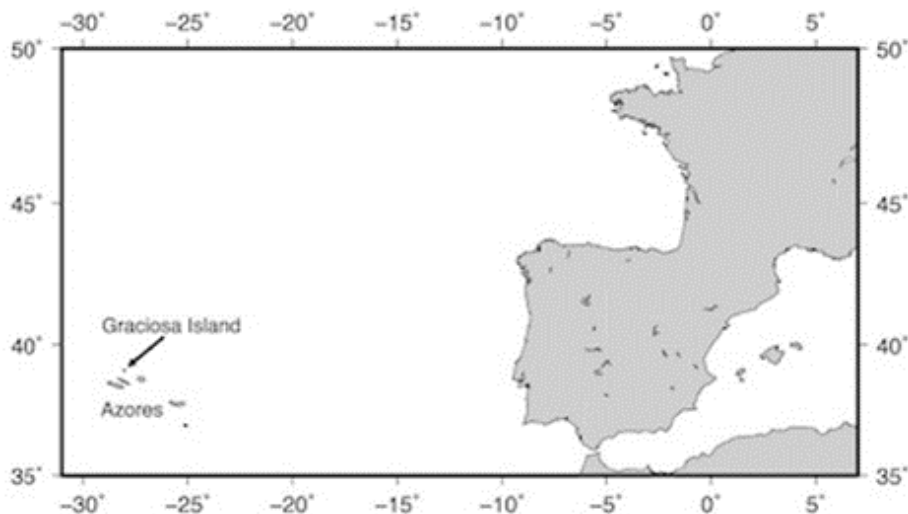


Figure 1. Location map of measurement site.

Although similar measurements were recorded in the North Atlantic Ocean region during the STRASSE and RARA AVIS research cruises,¹⁵ those measurements took place over a much shorter period than our study. The measurements reported from the cruises also included constant locational changes whereas the measurements reported in this study keep a consistent location throughout the study period. The midlatitude region of the North Atlantic Ocean experiences pronounced seasonal changes with the build-up of the Azores-Bermuda high-pressure system in the late summer and early fall and the frequent crossings of the North Atlantic Storm Track between early fall and spring. The location of a DOE ARM observatory on Graciosa Island, Azores provides the opportunity to study how water vapor isotopes and humidity measurements change in response to annual, seasonal, daily, and sub-daily atmospheric dynamics recorded by the wide suite of instruments hosted at the facility.

Humidity and water vapor stable isotope measurements were recorded at the ARM facility on Graciosa Island (latitude 39.0916° N, longitude 28.0257° W, altitude 30 m, approximately 1 km from the coast) between March 1, 2018 and February 28, 2019. Measurements were recorded using an LGR TWVIA. Raw measurements were corrected for humidity-induced bias and calibrated to the Vienna Standard Mean Ocean Water – Standard Light Antarctic Precipitation (VSMOW-SLAP) scale. We additionally accounted for time-drift in the isotopic composition of standard waters and the LGR instrument. Humidity measurements recorded by the LGR were compared to local meteorological equipment¹⁷ to confirm accuracy. We compare consistency between trends in the data to similar North Atlantic measurements.¹⁸ Changes in humidity and water vapor isotopic composition are correlated to changes in sea surface temperature (SST).¹⁹

2.0 Results

Multiple data processing steps were completed to account for humidity-induced bias, calibration to international standards, time drift in the δ values of standard waters, and independent verification of the analyzer's humidity measurements, in accordance with standard procedures.²

A well-documented source of measurement bias is caused by the tendency of the analyzer to report isotope ratios as a function of humidity.^{20,21} This relationship is generally found to be non-linear and unique to the individual isotope analyzer, the isotope ratio measured, and the humidity at which measurements are recorded.^{20,22} Correcting for humidity-induced bias is highly important, as not doing so may lead to d-excess bias greater than 25‰.²³ Three secondary standards (Deionized Water, Greenland Meltwater, and South Pole Meltwater) with a broad span of δ values were deployed with the analyzer on Graciosa Island. The standards were run throughout the instrument's deployment at approximately 20-hour intervals with a range of mixing ratios spanning the range of local ambient humidity. Resulting measurements from Deionized Water were used to correct for the instrument's humidity dependence by generating three-dimensional surface fits for δD and $\delta^{18}O$. The standard Deionized Water was chosen to generate this fit because its δ values were closer to average ambient air δ values observed on Graciosa Island than the remaining secondary standards. The humidity-dependent surface fits plot bias (bias = known δ – measured δ) as a function of mixing ratio and the time the standard was run (Figure 2), which corrects for humidity-induced bias as well as time-drift in the analyzer's humidity-induced bias.

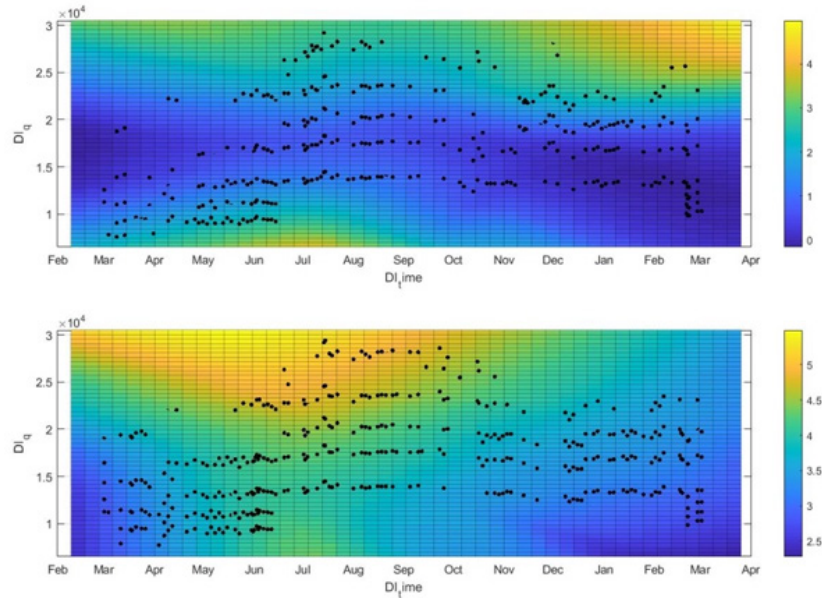


Figure 2. Surface fit developed to correct for humidity-induced bias. The surface fit is generated using individual measurements of the Deionized Water secondary standard recorded throughout the isotope analyzer’s deployment. Humidity-induced bias (δ) is reported as a function of humidity (mixing ratio, ppm) and time (February 2018 to March 2019). A surface fit of humidity-induced bias is developed using MATLAB’s curve-fitting toolbox (using locally weighted scatterplot smoothing (LOWESS) linear regression with span = 30, robust = bisquare, and center and scale = on). Panel a shows humidity-dependent bias for δD and Panel b shows humidity-dependent bias for $\delta^{18}O$. For δD , root-mean-square error (RMSE) = 0.9723. For $\delta^{18}O$, RMSE = 0.6374.

After correcting for humidity-induced bias, the isotope observations must be calibrated to the international VSMOW-SLAP scale. This was accomplished by using measurements from all three standard waters to generate additional surface fits for δD and $\delta^{18}O$ plotting the known δ value of the standard waters as a function of the humidity-corrected δ value and the time at which the standard water was measured (Figure 3).

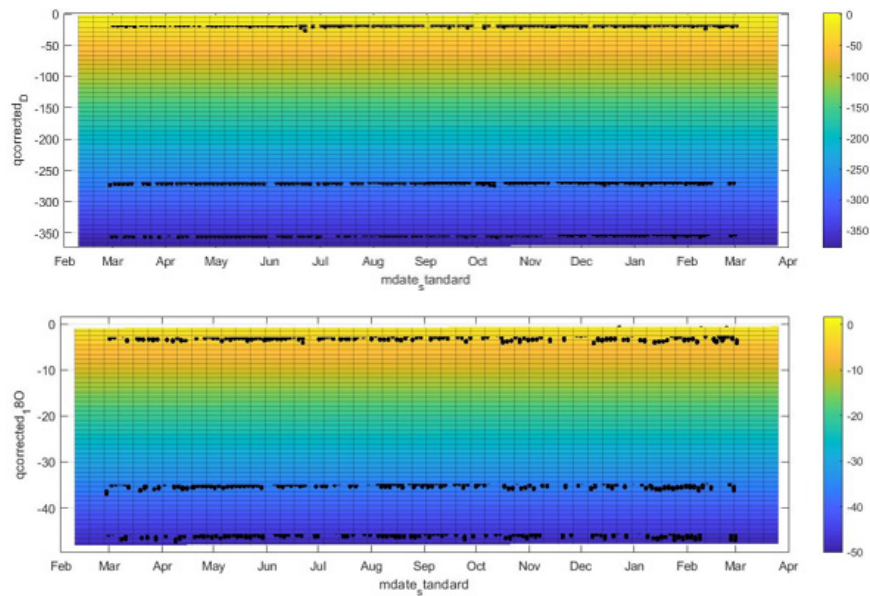


Figure 3. Surface fit developed to calibrate to the international VSMOW-SLAP scale. The surface fit is generated using individual measurements from all three of the standard waters recorded throughout the isotope analyzer’s deployment. The standard water’s known δ is reported as a function of the standard’s humidity-corrected measurement (δ) and time (February 2018 to March 2019). A surface fit of the VSMOW-SLAP calibration was developed using MATLAB’s curve-fitting toolbox (using a 1x1 polynomial, and robust = off, center and scale = off). Panel a shows VSMOW-SLAP correction for δD and Panel b shows VSMOW-SLAP correction for $\delta^{18}O$. For δD , RMSE = 1.221. For $\delta^{18}O$, RMSE = 0.6715.

By incorporating time in the surface fits, long-term variability in the instrumental VSMOW-SLAP scale could be accounted for in the calibration of ambient air observations.¹⁸

Time-drift in the δ values of standard waters was monitored throughout the analyzer’s deployment. Some degree of change was expected due to fractionation associated with partial evaporation occurring during periodic opening and closing of standard water storage containers and bubbling of air into the water during the purge cycle of the Water Vapor Isotope Standard Source (WVISS) calibration unit during standard water analysis. Changes in the isotopic composition of standard waters was mitigated by storing waters in large volumes (1-gallon containers), decreasing the overall effect of fractionation. Standard waters were measured periodically throughout the field deployment and recorded changes were found to be within analytical uncertainty. Due to the lack of any recordable change in the δ values of the standard waters, an average value was calculated for each standard’s δ values (Table 1) and that average was used as the known δ value for the above-described humidity-induced bias correction and VSMOW-SLAP calibration.

Table 1. Average isotopic composition of secondary standard waters. To account for time-drift, the isotopic composition of three secondary standard waters was measured multiple times throughout the isotope analyzer’s deployment in the Azores. Any recorded time-drift was found to be within analytical uncertainty. The above values are averages from the different measurements times and are the values used to complete the humidity-induced bias correction and VSMOW-SLAP calibration.

Secondary Standard	δD (‰)	$\delta 18O$ (‰)
Deionized Water	-18.2	-2.94
Greenland Meltwater	-271.8	-35.10
South Pole Meltwater	-357.7	-46.00

The analyzer’s humidity measurements are compared to those recorded by the ARM meteorological station¹⁷ (met station). The isotope analyzer reports humidity in mixing ratio using units of parts per million (ppm), while the ARM met station records relative humidity, pressure, and temperature, which was converted to mixing ratio for comparison. During the field deployment, there was an average difference between the met station mixing ratio and the analyzer’s mixing ratio of 2.6% (Figure 4).

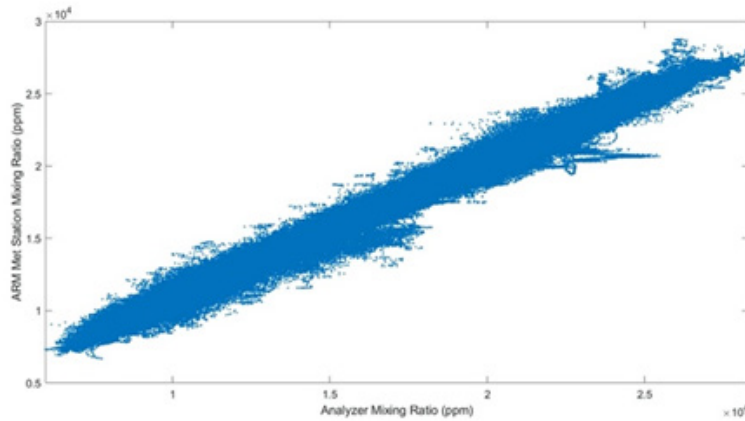


Figure 4. Mixing ratio (ppm) measured by the isotope analyzer compared to mixing ratio of the local ARM met station. Measurements are used to calculate the average percent difference between the two instruments, where the percent difference = $[(ARM \text{ mixing ratio} - \text{isotope analyzer mixing ratio})/ARM \text{ mixing ratio}] \times 100$. A period between September 5, 2018 and October 17, 2018 is removed from this calculation due to prolonged anomalously low mixing ratio values recorded by the ARM met station. Average percent difference = 2.6%.

2.1 Data Quality Control

The following data correction steps were considered to ensure the quality of the data presented in this paper:

1. Filtering time periods that may be influenced by memory.
2. Filtering time periods where external dew point was higher than the shipping container temperature.

A common complication with isotope analyzers is the influence of memory on reported measurements.²⁰ This is especially true when switching measurements between sources that have very different isotopic values, such as between ambient air measurements and standard waters, or vice versa. The first standard measurement following a change of measurement source is typically the furthest from the final measured isotope ratio.^{20,22,24-26} To avoid the influence of ambient air memory on standard water measurements, we remove the first set of measurements of daily standard water measurements from consideration when constructing the surface fits for humidity-induced bias correction and calibration to VSMOW-SLAP. Similarly, periods of ambient air measurements immediately following daily standard measurements were removed from the data set to avoid memory from the standard waters influence on the δ value reported by the analyzer's ambient air measurement. It was determined that removing one hour of the data recorded following the daily standard measurements was sufficient to ensure no influence of memory.

In the transition from the spring to summer season, the outside ambient air dew point would occasionally rise above the temperature inside the shipping container housing the isotope analyzer. Under these conditions, and despite our best efforts to heat and insulate the entire system, condensation would rarely occur in the tubing between the inlet and the isotope analyzer, resulting in the analyzer reporting anomalous oscillations in the ambient air mixing ratio. Following observations of the oscillations on June 15, 2018, additional insulation was added to cover all fittings on the analyzer and WVISS. After adjusting the instrument set-up, humidity oscillations were no longer observed. Periods when the humidity oscillation had occurred were removed from the final data set and are recorded in Table 2.

Table 2. Time periods removed from data set due to humidity oscillations. The table documents the periods of time removed from the final data set due to the occurrence of humidity oscillations recorded by the isotope analyzer due to condensation occurring in the tubing between the inlet and where the tubing entered the shipping container. This issue was identified and the physical set-up of the equipment was adjusted in mid-June (the heating cable and insulating material was extended to cover all tubing between the analyzer and the inlet). After a lag following the fix, the analyzer consistently ran smoothly in late June.

Humidity Oscillation Time Periods
May 18 2018 09:46:21 – May 20 2018 17:19:52
May 25 2018 07:09:02 – May 25 2018 15:57:47
May 31 2018 21:00:50 – June 02 2018 19:38:05
June 03 2018 21:10:01 – June 06 2018 04:49:14
June 12 2018 07:01:21 – June 16 2018 21:53:55
June 19 2018 21:45:53 – June 20 2018 10:54:33
June 27 2018 05:59:48 – June 28 2018 11:00:33

2.2 Uncertainty Analysis

There are four sources of uncertainty introduced at different stages during the data collection and processing. These include:

1. Instrument precision.
2. Uncertainty in the secondary standards.
3. Humidity-correction uncertainty.
4. VSMOW-SLAP calibration uncertainty.

Uncertainty in the precision of the isotope analyzer is quantified using the standard error calculated from secondary standard injections (Equation 1).

$$\text{Standard Error} = \frac{\text{Average st.deviation of secondary standards}}{\sqrt{\text{number of samples collected per 3 hour period}}} \quad (1)$$

We divide the average standard deviation of the δD and $\delta^{18}\text{O}$ for all secondary standard measurements recorded throughout the analyzer's deployment by the square root of the number of 10-second samples that make up each final reported 3-hour average isotope measurements (1080 10-second samples are used to calculate a 3-hour average). The uncertainty from instrument precision was calculated to be 0.01‰ for δD and 0.005‰ for $\delta^{18}\text{O}$.

The isotopic composition of secondary standards was measured at the University of New Mexico's (UNM) Center for Stable Isotopes (CSI) laboratory using a Picarro L2140-I high-precision isotopic water analyzer. Instrument precision reported by UNMs CSI was generally 0.8‰ for δD and 0.2‰ for $\delta^{18}\text{O}$.

Uncertainty introduced by using surface fits to account for humidity-induced bias and calibrate to VSMOW-SLAP were quantified using the RMSE of each surface fit. The surface fit to correct for humidity-induced bias had an RMSE of 0.9723‰ for δD and 0.6374‰ for $\delta^{18}\text{O}$. The surface fit to calibrate to VSMOW-SLAP had an RMSE of 1.221‰ for δD and 0.6715‰ for $\delta^{18}\text{O}$.

Uncertainty from each step is propagated in quadrature (Equation 2) to calculate a total uncertainty of each isotopologue measurement. Final uncertainty was determined to be 1.75‰ for δD and 0.947‰ for $\delta^{18}\text{O}$.

$$\text{Propagated Uncertainty} = \sqrt{(\text{instrument precision})^2 + (\text{standard uncertainty})^2 + (\text{humidity induced bias uncertainty})^2 + (\text{VSMOW SLAP uncertainty})^2} \quad (2)$$

2.3 Technical Validation

The data presented in this study has undergone all standard procedures,² including correcting for humidity-induced bias, calibrating to the international VSMOW-SLAP scale, accounting for time-drift in the isotope analyzer,¹⁸ and verifying humidity measurements (Figure 5).

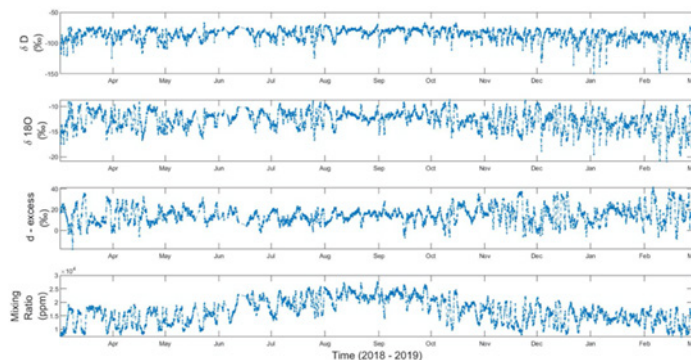


Figure 5. Timeseries of δD (‰), $\delta^{18}O$ (‰), d-excess (‰), and mixing ratio (ppm) for March 1, 2018 through February 28, 2019. δD and $\delta^{18}O$ have been corrected for humidity-induced bias and calibrated to the international VSMOW-SLAP scale. The deuterium excess parameter is calculated from the corrected/calibrated δD and $\delta^{18}O$.

The secondary standards in this study were calibrated to the international VSMOW-SLAP scale. They were additionally monitored throughout the instrument's one-year deployment for time-drift due to partial evaporation occurring during periodic opening and closing of standard water storage containers and bubbling of air into the water during the purge cycle of the calibration unit during standard water injections.

We compare trends in the data from Graciosa Island to the most similar oceanic study location with published data to inform certainty of trends observed on Graciosa Island, Azores. Previous work¹⁸ reported 500 days of continuous humidity and water vapor isotopic measurements from the Bermuda Islands between November 2011 and June 2013. A comparison of the two data sets indicates similar averages, ranges, and seasonal trends in the reported δ values. In 2012, the Bermuda data set had an annual average δD ($\delta^{18}O$) of -80.8‰ (-11.81‰) whereas the Azores data set had an annual average δD ($\delta^{18}O$) of -86.7‰ (-12.71‰) between March 2018 and February 2019. The range of observed isotopic values was similar between the two study locations, but Graciosa Island observations were slightly broader. For example, Graciosa Island (Bermuda) $\delta^{18}O$ ranged between -20.90‰ and -8.72‰ (generally between -16‰ and -8‰). The more isotopically depleted averages and broader isotopic range observed on Graciosa Island compared to Bermuda can be explained by the location of the Azores further north with the latitude effect,³ whereby δD and $\delta^{18}O$ values decrease with increasing latitude. The observed relation of δD and $\delta^{18}O$ (d-excess) maximums (minimums) in the summer and minimums (maximums) in the winter are consistent between both study locations. Additionally, we observe a notable correlation ($R^2 = 0.56$) between SST¹⁹ and the mixing ratio recorded by the isotope analyzer on Graciosa Island. Comparing SST with observations of δD and $\delta^{18}O$ values indicate these measurements have a much smaller dependence on SST ($R^2 = 0.12$ for δD and $R^2 = 0.09$ for $\delta^{18}O$). Previous work⁶ has observed similar shifts in humidity in response to changes in SST when considering cruise data from the North Atlantic Ocean in 2012 and 2015¹⁵ as well as the data set from Bermuda.¹⁸

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