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DOE/SC-ARM-19-027

Water Vapor Isotopic Composition from the Azores Field Campaign Report

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October 2019

ARM

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Work supported by the U.S. Department of Energy,
Office of Science, Office of Biological and Environmental Research

Acronyms and Abbreviations

ARM	Atmospheric Radiation Measurement
DJF	December-January-February
DOE	U.S. Department of Energy
ENA	Eastern North Atlantic
FT	free troposphere
JJA	June-July-Auguest
LGR	Los Gatos Research
MAM	March-April-May
MBL	marine boundary layer
SON	September-October-November
TWVIA	triple water vapor isotope analyzer
VSMOW-SLAP	Vienna Standard Mean Ocean Water –Standard Light Antarctic Precipitation

Contents

1.0 Summary

This study used one year of in situ water vapor isotopologue measurements collected at the U.S. Department of Energy (DOE) Atmospheric Radiation Measurement (ARM) user facility observatory located on Graciosa Island, Azores. Low clouds have an especially strong feedback over the ocean and previous studies have primarily focused on low clouds in the subtropics. This means that the Azores location in the transition between subtropical and mid-latitude oceanic areas represents an opportunity to study the connection between water vapor isotopologues and mixing processes that determine low-cloud feedback in an underrepresented setting with different seasonal dynamics. The DOE ARM facility on Graciosa Island presents the opportunity to complement water vapor isotopologue measurements with a suite of instruments capable of measuring changing atmospheric conditions.

Water vapor isotopologue and humidity measurements were determined using a Los Gatos Research (LGR) triple water vapor isotope analyzer (TWVIA). This instrument was deployed from March 2018 through February 2019 at the DOE ARM observatory on Graciosa Island, where it was housed in a shipping container. The instrument was connected to an uninterruptable power supply and consists of three main components: a water vapor isotope analyzer, calibration unit, and dry air source.

Ambient air samples were collected through an inlet located several meters above the shipping container. Samples were then delivered to the analyzer through tubing by use of an external pump to optimize the transport time between the inlet and analyzer. The tubing within the shipping container was surrounded by a heating cable and insulating material to ensure ambient air samples did not fall below the dew point and result in condensation. The analyzer uses laser-based off-axis integrated cavity output spectroscopy to report isotopic ratios of ambient air samples in 10-second averages. The calibration unit of the instrument was used in conjunction with the dry air source to periodically measure the δ values of standard waters. It uses a nebulizer to push small water droplets into a hot chamber that vaporizes the water without fractionation. This vapor was then transported to the analyzer using a built-in compressor and the dry air source, which allows each standard with known δ values to be measured at a wide range of humidity values for post-measurement calibration of ambient air samples.

Four sources of uncertainty are 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, and (4) Vienna Standard Mean Ocean Water – Standard Light Antarctic Precipitation (VSMOW-SLAP) calibration uncertainty. Uncertainty from each step is propagated in quadrature to calculate a total uncertainty of each isotopologue. Uncertainty was determined to be 1.8‰ for δD and 0.95‰ for $\delta^{18}O$.

An inverse model for mixing between surface fluxes and entrained air from the lower free troposphere (FT) was shown to match observations with mixing fractions between the marine boundary layer (MBL) and the FT that correspond to climatological cloud fields, suggesting that the isotopic composition of water vapor in the MBL may respond to the mixing processes that govern low-cloud feedbacks.

2.0 Results

Multiple data processing steps were taken 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.

2.1 Humidity-Induced Bias Correction

A well-documented source of measurement bias is caused by the tendency of the analyzer to report isotope ratios as a function of humidity. 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. Correcting for humidity-induced bias is highly important, as not doing so may lead to d-excess bias greater than 25‰.

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. Standards were run throughout the instrument's deployment at approximately 20-hour intervals, each of which included multiple periods of standard injections measured at 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 δ18O. The standard deionized water was chosen to generate this fit because its δ values were closer to 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, which corrects for humidity-induced bias as well as time drift in the analyzer's humidity-induced bias.

2.2 Calibration to International Standards

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 surface fits for δD and $\delta^{18}O$ plotting the known δ value as a function of the humidity-corrected δ value and the time at which the standard water was measured. 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.

2.3 Standard Water Isotopic Composition Time Drift

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 calibration unit during standard water injections. Changes in the isotopic composition of standard waters was mitigated by storing waters in large volumes, 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. Because of this, an average value was calculated for each standard's δ values and the average was used for the above described humidity-induced bias correction and VSMOW-SLAP calibration.

2.4 Independent Verification of Humidity

The isotope analyzer's humidity measurements are compared to those recorded by the DOE ARM facility's meteorological station (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 is converted to mixing ratio for comparison. During the field deployment, there was an average percent difference between the met station mixing ratio and the analyzer's mixing ratio of 3.8%.

2.5 Summary of Results

The annual averages for δD and $\delta^{18}O$ were -87.7‰ and -12.98‰, respectively. δD ranged between -156.4‰ and -67.5‰, and $\delta^{18}O$ ranged between -20.93‰ and -8.49‰. On the seasonal scale, June-July-August (JJA) had the highest average MBL δ value (-84.1‰) while December-January-February (DJF) had the lowest (-94.9‰). The highest variability (standard deviation) in MBL δ values was observed in DJF for both δD (13.5‰) and $\delta^{18}O$ (2.03‰), while the least variability in δD was observed in September-October-November (SON) (7.9‰) and least variability in $\delta^{18}O$ was observed in JJA (1.40‰). The annual average for d-excess was 16.1‰ with a standard deviation of 8.1‰. d-excess ranged between -19.5‰ and 41.0‰ during the deployment period. On the seasonal scale, average MBL d-excess was observed to be highest (18.8‰) and the least variable (1.7‰) during DJF and the lowest (13.1‰) during JJA with moderate variability (5.2‰). March-April-May (MAM) and SON had d-excess averages and standard deviations similar to that of the annual scale. The annual average and standard deviation of MBL-specific humidity was 10.2 g/kg and 3.0 g/kg, respectively. MBL-specific humidity ranged between 4.5 g/kg and 17.3 g/kg during the study period. On the seasonal scale, JJA had the highest average MBL-specific humidity (12.7 g/kg) while MAM had the lowest (8.0 g/kg), which was closely followed by DJF (8.2 g/kg). DJF had the least variability of MBL-specific humidity (1.7 g/kg) while SON had the most (2.8 g/kg).

While our initial studies focused on interpreting the isotopic results in terms of mixing between the lower FT and the marine boundary layer, we are now pursuing a line of study focused on the decoupling of the MBL from the cloud layer, with potential implications for better understanding how MBL humidity responds to decoupling.

3.0 Publications and References

Delp, J. 2019. An Estimation of Lower Tropospheric Mixing Derived from Inverse Modeling of Boundary Layer Water Vapor Isotopologues On Graciosa Island, Azores, MS Thesis, University of New Mexico.

Delp, J. and J. Galewsky. 2018. "Quantitative constraints on the relationships between lower tropospheric mixing and low-cloud cover on Graciosa Island, Azores, derived from stable isotopes in water vapor." Presented at the American Geophysical Union Fall Meeting. Washington, D.C.

Delp J., and J. Galewsky. 2017. "Water vapor isotopic measurements from the Atmospheric Radiation Measurement Site on Graciosa Island, Azores." Presented at the American Geophysical Union Fall Meeting. New Orleans, Louisiana.

4.0 Lessons Learned

The ENA site was a pleasure to work with. The staff were without exception professional, helpful, and responsive. We had a few hardware issues that the engineering staff helped us troubleshoot remotely, and we could not have succeeded without them. We also appreciate the logistical support with shipping the equipment. Again, all of the staff were professional and responsive. We have no complaints!

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