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SAIL-Isotopologue (SAIL-iso) Field Campaign Report

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ARM

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Acronyms and Abbreviations

ARM	Atmospheric Radiation Measurement
IQR	interquartile range
iso	isotopologue
SAIL	Surface Atmosphere Integrated Field Laboratory
TRACER	Tracking Aerosol Convection Interactions Experiment
TWVIA	Triple Water Vapor Isotope Analyzer
VSMOW-SLAP	Vienna Standard Mean Ocean Water – Standard Light Antarctic Precipitation
WVISS	Water Vapor Isotope Standard Source

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1.0 Summary

The SAIL-iso project took place from November 19, 2022 to June 3, 2023 as part of the U.S. Department of Energy Atmospheric Radiation Measurement (ARM) user facility's Surface Atmosphere Integrated Field Laboratory (SAIL) project at the main project site in Gothic, Colorado. The project sought to use measurements of the stable isotopic composition of water vapor to better understand cloud-aerosol interactions in a remote mountainous watershed. Water vapor isotopologue and humidity measurements were determined using a Los Gatos Research Triple Water Vapor Isotope Analyzer (TWVIA). The instrument was deployed in the guest van and consists of three main components: a water vapor isotope analyzer, a Los Gatos Research Water Vapor Isotope Standard Source (WVISS), and a Los Gatos Research Dry Air Source.

Ambient air samples were collected through an inlet located about one meter above roof of the shipping container. Samples were then delivered to the analyzer through Teflon tubing by use of an external pump to minimize the transport time between the inlet and analyzer. The inlet tubing was surrounded by a Briskheat heat trace and insulating material to ensure ambient air samples did not fall below the dew point and result in condensation. The analyzer uses cavity ringdown spectroscopy to report isotopic ratios of ambient air samples at a frequency of 1 Hz. 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.

Multiple 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 2.3‰ for δD and 0.4‰ for $\delta^{18}O$.

2.0 Results

2.1 Humidity-Induced Bias Correction

A well-documented source of measurement bias can be 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. Such biases are especially prominent in dry settings, unlike the setting at La Porte, Texas during the Tracking Aerosol Convection Interactions Experiment (TRACER).

Several well-characterized water standards with a broad span of δ values were deployed with the analyzer (USGS45; USGS46; USGS47; USGS48.;W-64444-S). Standards were run throughout the instrument's deployment approximately monthly at mixing ratios spanning the range of local ambient humidity. The humidity-induced bias was corrected using standard methods.

2.2 Calibration to International Standards

Isotope observations must be calibrated to the international VSMOW-SLAP scale. This was accomplished by using measurements from the standard waters to generate linear fits for δD and δ18O plotting the known δ value as a function of the observed δ value.

2.3 Summary of Results

The corrected data are presented in Figure 1, and summary statistics are presented in Table 1.

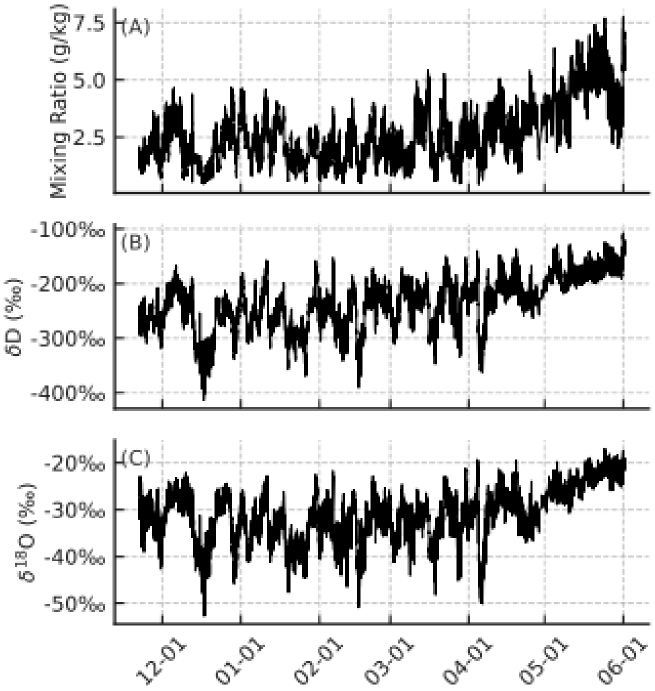


Figure 1. Water vapor measurements from the Los Gatos TWVIA during the SAIL-iso project. (A) Mixing ratio (g/kg); (B) δD (permil); (C) Water vapor δ18O.

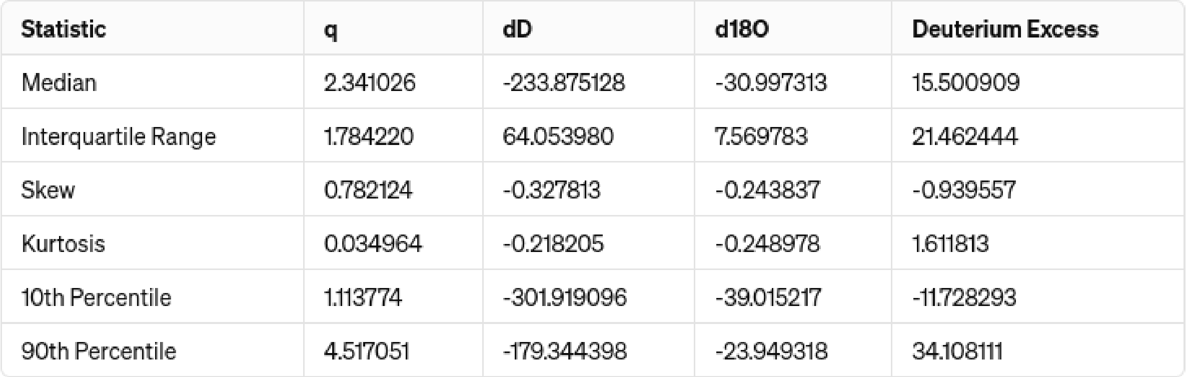
As expected for wintertime measurements in a high-altitude watershed, the mixing ratios and water vapor delta values are generally quite low, with increases only occurring in the spring. The lowest `dD` value in the data set is approximately -413.89 permil, and it occurred on December 17, 2022 during an unusually cold period. The highest `dD` value recorded in the data set is approximately -107.33 permil, and it occurred on May 31, 2023, consistent with warming and increased humidity. The highest deuterium excess value was 86.93 permil, and it occurred on March 28, 2023. The lowest deuterium excess value was approximately -116.28 permil, and it occurred on February 10, 2023.

The median mixing ratio is 2.34 g/kg. The median values for `dD` and d18O are -233.88 permil and -30.997 permil, respectively, which represent the midpoint in the isotopic ratios' distribution, providing a central point around which the data varies. The deuterium excess has a median of 15.50 permil, offering insight into the typical excess deuterium relative to what is expected from the global meteoric water line.

The interquartile spread for these variables ranges from 1.78 for the mixing ratio to 64.05 for `dD`, indicating the middle 50% of the data's spread. A wider interquartile range (IQR) in `dD` suggests more variability in the deuterium content of the water vapor compared to the mixing ratio.

The skewness values indicate the degree of asymmetry in the distribution of the data set. The mixing ratio exhibits a positive skew (0.78), indicating a tail that stretches towards higher values; this suggests a concentration of lower values with fewer high values, consistent with the relatively brief period of humid conditions during spring. Along the same lines, slight negative skew in `dD` (-0.33) and d18O (-0.24) points to a distribution with a tail extending towards lower values. Deuterium excess shows a notable negative skew (-0.94), highlighting a tail towards lower excess values. The kurtosis measures the "tailedness" of the distribution. A kurtosis near zero for `dD` and d18O suggests a distribution with tails similar to that of a normal distribution. The positive kurtosis (1.61) for deuterium excess implies heavier tails, indicating more extreme values (both high and low) than a normal distribution would exhibit.

Table 1. Descriptive statistics of water vapor isotopic measurements during SAIL.



Statistic	q	dD	d18O	Deuterium Excess
Median	2.341026	-233.875128	-30.997313	15.500909
Interquartile Range	1.784220	64.053980	7.569783	21.462444
Skew	0.782124	-0.327813	-0.243837	-0.939557
Kurtosis	0.034964	-0.218205	-0.248978	1.611813
10th Percentile	1.113774	-301.919096	-39.015217	-11.728293
90th Percentile	4.517051	-179.344398	-23.949318	34.108111

3.0 Lesson Learned

Overall, the project proceeded quite smoothly, with excellent operation from the Los Gatos Research instrument. The extreme cold and remoteness of the site could have been a source of significant challenges during this project, but the technical staff from ARM were extremely capable and allowed us to collect a remarkable data set under difficult conditions.

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