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TRACER-iso Field Campaign Report

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Acronyms and Abbreviations

ARM	Atmospheric Radiation Measurement
IOP	intensive operational period
LGR	Los Gatos Research
TRACER	TRacking Aerosol Convection interactions ExpeRiment'
WVISS	water vapor isotope standard source
VSMOW-SLAP	Vienna Standard Mean Ocean Water – Standard Light Antarctic Precipitation

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1.0 Summary

The TRACER-iso project took place from June 1 to September 30, 2022, as part of the intensive operational period (IOP) of the U.S. Department of Energy Atmospheric Radiation Measurement (ARM) user facility's TRacking Aerosol Convection interactions ExpeRiment (TRACER) at the main project site at the La Porte, Texas, municipal airport. The project sought to use measurements of the stable isotopic composition of water vapor to better understand cloud-aerosol interactions in deep convection in a polluted urban setting.

A Picarro L2130 water vapor isotope analyzer determined water vapor isotopologue and humidity measurements. The instrument was deployed in the guest van and consists of three main components: a water vapor isotope analyzer, a Los Gatos Research (LGR) water vapor isotope standard source (WVISS), and a Los Gatos Research dry air source.

Ambient air samples were collected through an inlet about one meter above the roof of the shipping container. Samples were then delivered to the analyzer through Teflon tubing using 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 measure the δ values of standard waters periodically. 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 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 the total uncertainty of each isotopologue. Uncertainty was determined to be 2.3‰ for δD and 0.4‰ for δ18O.

2.0 Results

2.1 Humidity-Induced Bias Correction

A well-documented source of measurement bias can be caused by the tendency of the analyzer to report isotope ratios as a function of humidity. This relationship is generally found to be nonlinear 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.

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. Given the high humidity of the site and the relatively narrow range of mixing ratios (generally between 15-20 g/kg), there was no measurable humidity-induced bias.

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. The median values of mixing ratio (q), δD, δ18O, and deuterium excess were 18 g/kg, -75 permil, -11.4 permil, and 16 permil, respectively. The highest decile for these quantities was 19.5 g/kg, -66 permil, -10 permil, and 19 permil, respectively, values consistent with evaporation from nearby Galveston Bay. There were notable excursions associated with convective events on June 30, 2022, when δD dropped to -130 permil and δ18O dropped to -18.2 permil; and August 29, 2022, when δD dropped to -140 permil and δ18O dropped to -19.3 permil.

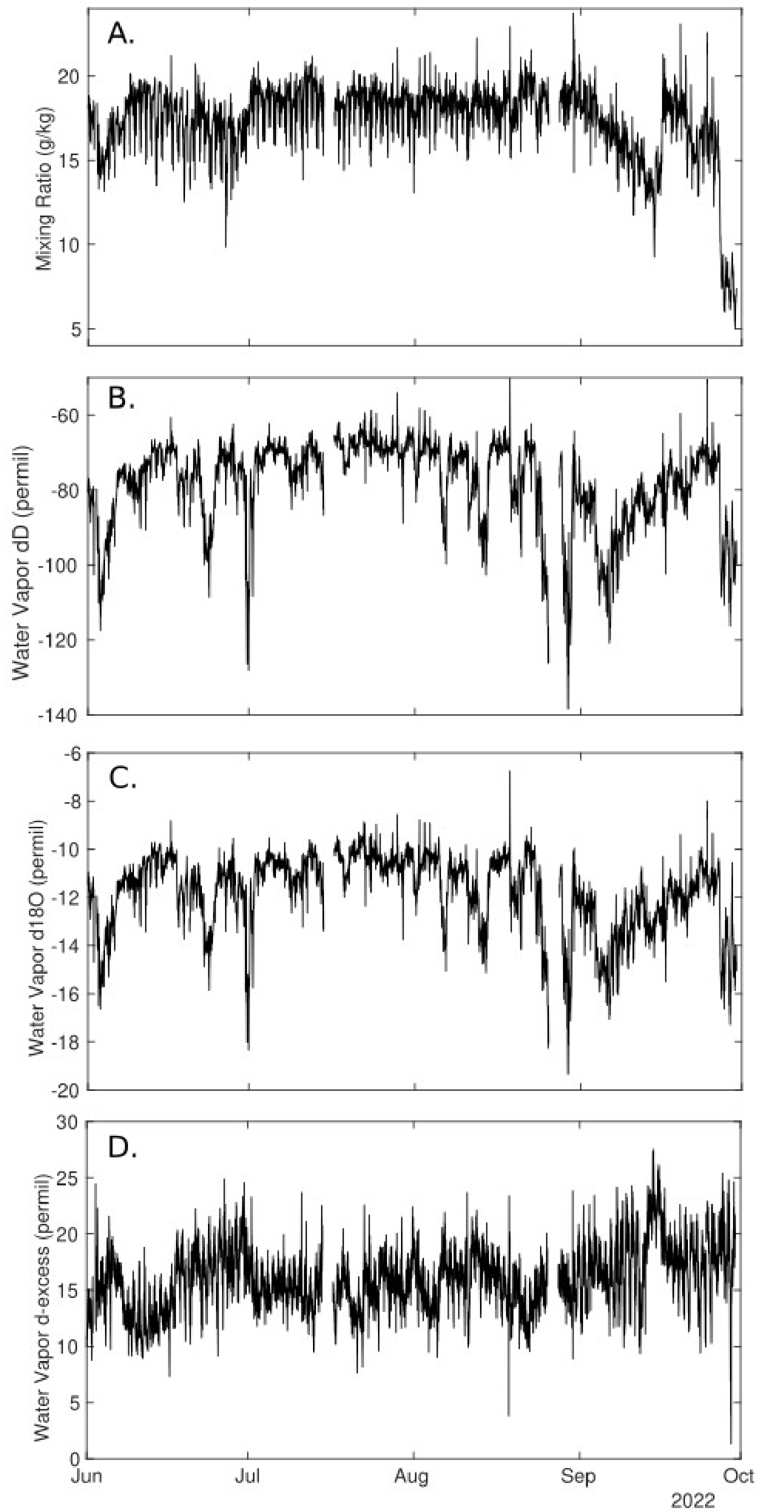

Figure 1. Water vapor measurements from the Picarro L2130 during the TRACER-iso project. (A) Mixing ratio (g/kg); (B) δD (permil); (C) Water vapor δ18O; (D) deuterium excess (permil).

3.0 Publications and References

Galewsky, J. Water vapor isotopic measurements during TRACER, TRACER Workshop, Houston, Texas, May 16, 2023.

4.0 Lessons Learned

Overall, the project proceeded relatively smoothly, with excellent operation from the Picarro. The extremely high humidity posed a few challenges; first, heating the inlet line was absolutely essential to prevent condensation, and we had to insulate the Swagelok connection between the Picarro and the inlet further to prevent condensation.

Second, calibrating the instrument at such high humidity was a challenge for the Los Gatos water vapor isotope standard source and dry air source. Reaching the maximum observed mixing ratios led to condensation in the unit and erroneous calibration results. Lowering the calibration mixing ratios led to more reliable results.

The USGS48 standard was the isotopically heaviest standard we used, and generally yielded very unreliable results, with substantial drift to positive delta values. It is unclear why this standard poses difficulties, but the USGS45 standard is nearly as isotopically heavy and yielded much more reliable results. The combination of the Picarro analyzer and the LGR calibration module generally works well, but the calibration module requires manual operation. Someone fluent in LabView could work out an automated connection between the Picarro and the LGR, and such a configuration would make the combination work very well in remote settings, requiring very little on-the-ground intervention.

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