Capturing small-scale variations of water isotopes in ambient air and natural waters of California: Results of field measurements using Wavelength Scanned Cavity Ring-Down Spectroscopy

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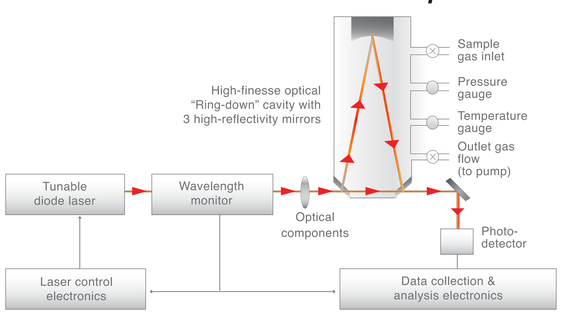
Abstract

Stable isotope analysis is a valuable tool for establishing links between ecology and hydrology. Measurements of stable isotopes in water vapor and liquid water are traditionally made with IRMS systems in core labs which preclude real-time field use. Recent advances in wavelength scanned cavity ring-down spectroscopy (WS-CRDS) have led to field-deployable instrumentation capable of making real-time high-throughput stable isotope measurements of water. Furthermore, the high precision of such instrumentation (typically <0.2‰ for δD and <0.07‰ for $\delta^{18}O$) allows for high-resolution measurements that enhance our understanding of the processes that govern natural variability in water isotopes.

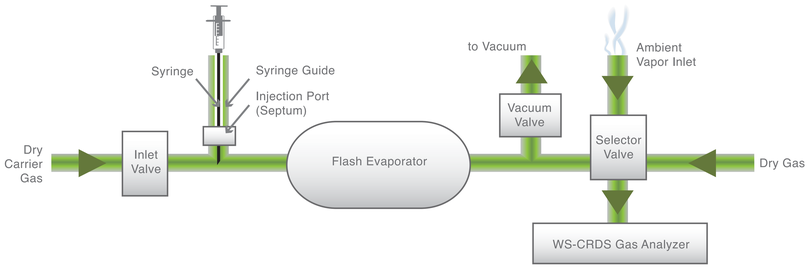
This presentation demonstrates the results from two different applications of the Picarro isotopic water analyzer. First, the analyzer was used to measure vertical gradients in ambient water vapor isotopes at Blue Oak Ranch Reserve, CA. The Picarro analyzer was deployed with a novel, field-durable and automated calibration system that introduces liquid water standards, as vapor, without fractionation effects. The results show clear gradients in water vapor isotopes during cooler nighttime periods, which subsequently break-up during daytime warming. The second set of results show measurements of liquid water samples collected from three different watersheds at Mammoth Lakes, CA. The data are comprised of samples collected from thirty different locations including snow melt lakes, creeks and rain water. The isotopic measurements shed some light on the dominating hydrological phenomena which affect the isotopic content of the water. However, and more importantly, the data demonstrate a complex relationship between the hydrological cycle, volcanic activity and hot springs contributions, and illuminates the fact that a simple explanation involving fractionation along water courses is not sufficient.

Schematic of Picarro WS-CRDS Isotopic Water Analyzer



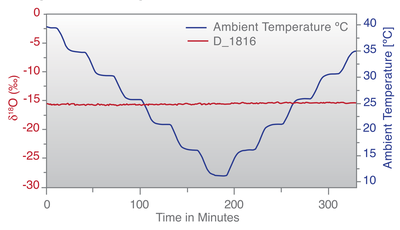
Schematic of Picarro WS-CRDS analyzer showing optical cavity and sample gas flow.

Instrument foot print: 54 cm x 60 cm
Instrument weight: ~ 40 Kg
Power consumption: 500 Watts @ 110V

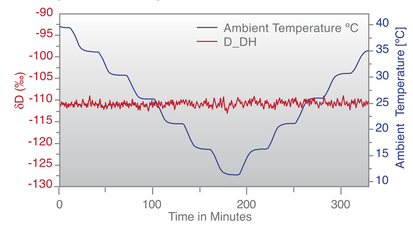


Schematic of flash evaporator which enables automated switching between liquid water and water vapor measurements

Temperature Dependance of $\delta^{18}O$ = 0.002 ‰/°C



Temperature Dependance of δD = 0.006 ‰/°C



Measurements of Vertical Gradients of Water Vapor Isotopes at Blue Oak Ranch Reserve

Vapor source at ~25 ft above ground level

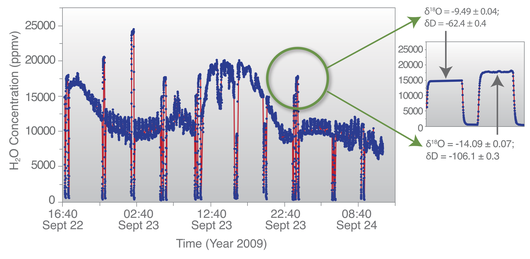
Analyzer alternated between measurements of vapor data from ground level source and elevated source every 15 minutes.

Every few hours, liquid water standards were injected using syringe pumps and measured for 25 minutes to calibrate the water vapor measurements.

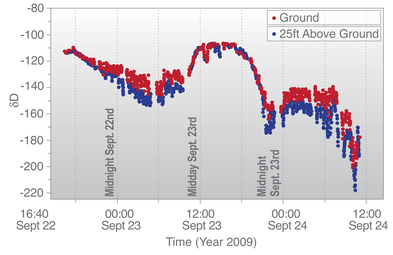
Vapor source at ground level

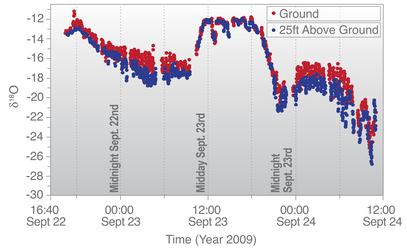
Field-deployable Picarro Isotopic water vapor analyzer with robust automated liquid calibration module installed on the top floor of the barn

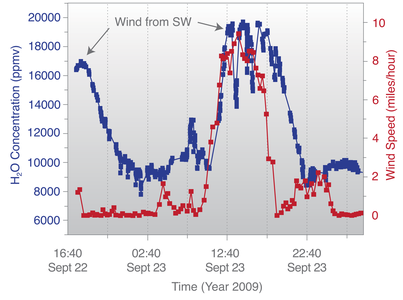
Water Vapor Data Interspersed with Liquid Water Calibrations



- Picarro analyzer demonstrates the necessary precision for resolving small gradients in water vapor isotopes in ambient air.
- The new auto-calibration system allowed for calibration with multiple standards at multiple concentrations resulting in highly credible data.
- The Picarro analyzer is robust and field-deployable, able to withstand large ambient temperature fluctuations, and can operate for weeks without human intervention!



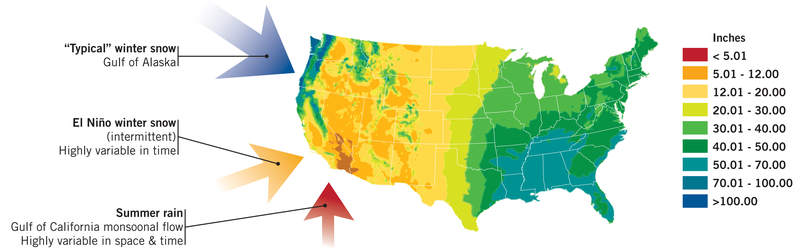




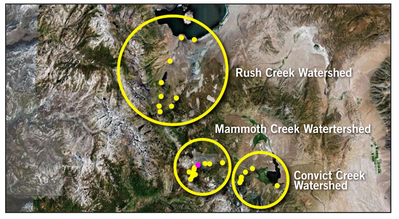
Conclusion and Future work

- Correlation between wind patterns and water vapor concentration indicate source-air mass effects.
- The isotopically heavier vapor near the ground suggests an evaporation source, while the isotopically lighter vapor aloft is likely influenced by plant water.
- Strong positive shifts in the ground data (e.g. from approx. 23:00 on Sept. 23rd to 06:00 on Sept. 24th), suggest a "condensation" fingerprint, where the vapor is sourced from condensation on ground-level surfaces.
- Future measurements will be aimed at studying the different small scale (evaporation vs. transpiration) and large scale (marine vs. urban vs. rural) source-air mass signatures.

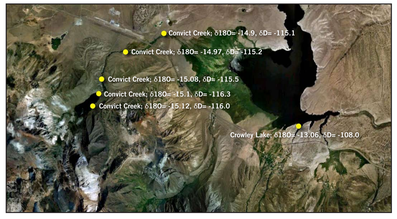
Picarro Isotopic Water Analyzer used to determine how surface flow fractionates meteorological water sources



- In water-limited terrestrial ecosystems of the western U.S., changes in precipitation patterns may be important for plant mortality, recruitment, biogeochemistry, and the emergent functions and distributions of ecosystems.
- Snow provides up to 80% of the annual hydrologic input of western ecosystems, and melt is a key timing event for the onset of physiological processes for many species.
- How altered snowfall patterns will affect the biogeochemistry of terrestrial ecosystems, and how vegetation responses will feedback on processes over multiple spatial and temporal scales are important scientific questions to be further explored.
- We aim to provide a better understanding and predictive ability of the effects of snow depth/melt manipulations on the spatiotemporal linkages between precipitation source, soil moisture, and plant water uptake of ecosystems at macro- and micro- spatiotemporal scales.
- The specific goal of this preliminary study was to better understand spatial variation in the fractionation of surface water stable isotopes in effluent streams in an arid shrubland. Spatial patterns will help interpret ongoing water sourcing efforts.

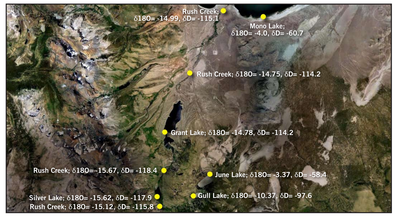


Watersheds Sampled



Convict Creek Watershed: Water fractionates due to evaporation as it flows along the short watershed from Convict Lake to Crowley Lake

Mammoth Creek Watershed: Isotopic measurements suggest significant evaporation from Horseshoe Lake. Intrusion of hot water from the magma chamber of the Long Valley Caldera may alter water isotopic signatures.



Rush Creek Watershed: Measurements indicate significant evaporation from June, Mono and Gull Lakes. The Mono Lake signature may also be affected by lake's mixing regimes, the unique chemistry (high levels of carbonates, sulfates, boron and potassium), and aquatic ecosystem feedbacks on water chemistry.

Conclusion and Future Work

- Deuterium and Oxygen isotope fractionation along watercourses was not as large as initially hypothesized.
- Spatial patterns were more complex than a simple linear fractionation along watercourses.
- Volcanic activity in Mammoth Creek, CO_2 vents in some lakes, and the unique biogeochemistry of Mono Lake appear to have contributed to the spatial complexity.
- Future measurements of vegetation water sources in this region will need to consider how the spatial pattern of effluent streams affect plant water composition.

We would like to thank Jeff Wilcox for his assistance with the set up at BORR.