

Real-Time Field-Based Water Vapor Isotope Measurements with a CRDS Analyzer: Probing Cropland Evapotranspiration

PICARRO



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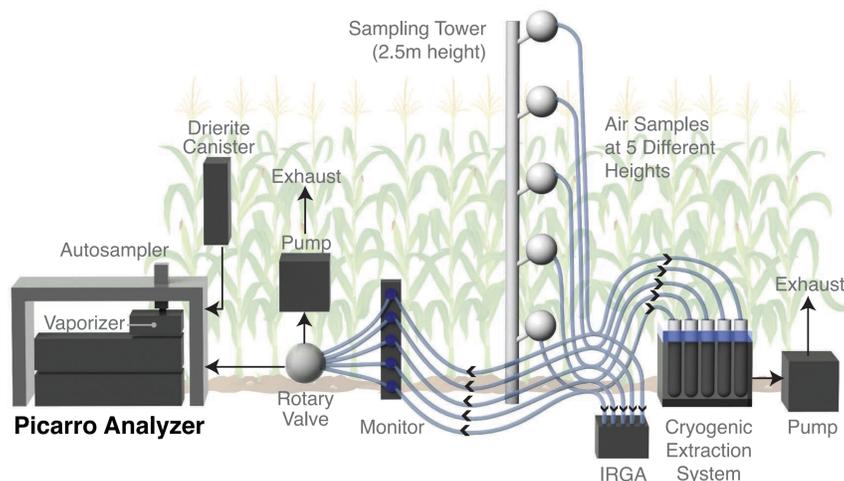
Abstract

While stable isotope techniques have been previously applied to partition evapotranspiration (ET) fluxes in crops, it has only recently become possible to take *in situ*, long-term, continuous (every 10 seconds) measurements of stable water vapor isotopologues. A Picarro water vapor isotope analyzer (L1115-*i*) based on cavity ringdown spectroscopy (CRDS) was recently deployed at China's National Experimental Station for Precision Agriculture during the FAO/IAEA 2nd Research Coordination Meeting on "Managing Irrigation Water to Enhance Crop Productivity under Water-Limiting Conditions using Nuclear Techniques." Measurements were conducted continuously over several days, sampling from five different heights within and above the canopy of a corn (*Zea mays*) ecosystem. The continuous measurements by the Picarro analyzer were complimented by additional measurements from the same sampling points, wherein the vapor was cryogenically trapped for later laboratory quantification of the water isotopologues. Stable isotope measurements were taken concurrently with conventional ET flux measurements. The isotope analyses can allow the partitioning of ET into its components: soil evaporation and leaf transpiration. Once daily, during the vapor measurements, liquid water isotope standards were measured by the Picarro analyzer using its included autosampler and subsequently used to calibrate the vapor-phase data. Described here are the analyzer and sampling system as well field data and comparison of the vapor-phase results with the off-line liquid analysis of the cryogenically-trapped vapor.

Instrumentation & Setup in Field Location

Air was drawn with a pump from five heights within and above the crop canopy through ~8m of Bev-a-Line tubing at ~3Lpm to a manifold and rotary valve, controlled by the Picarro analyzer, so that vapor was continuously measured for ~5min at each height sequentially. At the beginning and end of the day, the Picarro analyzer ceased measuring vapor and measured liquid standards (provided by IAEA and UWSIF as below) by using ambient air dried by a Drierite canister. This air was mixed with liquid standards, injected by the autosampler, and vaporized in the instrument's vaporizer module.

Air from each height in the vertical profile was pumped through a second parallel set of Bev-a-Line tubing to a LiCor 840 IRGA for determination of water vapor mixing ratios and then into Pyrex glass collection tubes for cryogenic trapping of the water vapor. The vapor traps were kept at -80°C by immersion in an ethanol bath cooled with liquid nitrogen. Cryogenic trapping of atmospheric water vapor was performed over two separate 60 min periods between 10:00 and 13:00h on several days prior to and after irrigation. The $\delta^2\text{H}$ and $\delta^{18}\text{O}$ values of the water vapor samples were determined at the University of Wyoming Stable Isotope Facility using a Los Gatos Liquid Water Isotope Analyzer. Analytical precision based on repeated analysis of laboratory check standards was 0.5‰ for $\delta^2\text{H}$ and 0.3‰ for $\delta^{18}\text{O}$. Values were normalized to the VSMOW scale using laboratory working standards directly calibrated to VSMOW and SLAP reference materials obtained from IAEA.



Sampling tower, Picarro (left) and cryogenic trap (right). Lowest-level sample inlet at ground level (lower right).



Cryogenic trapping setup and IRGA

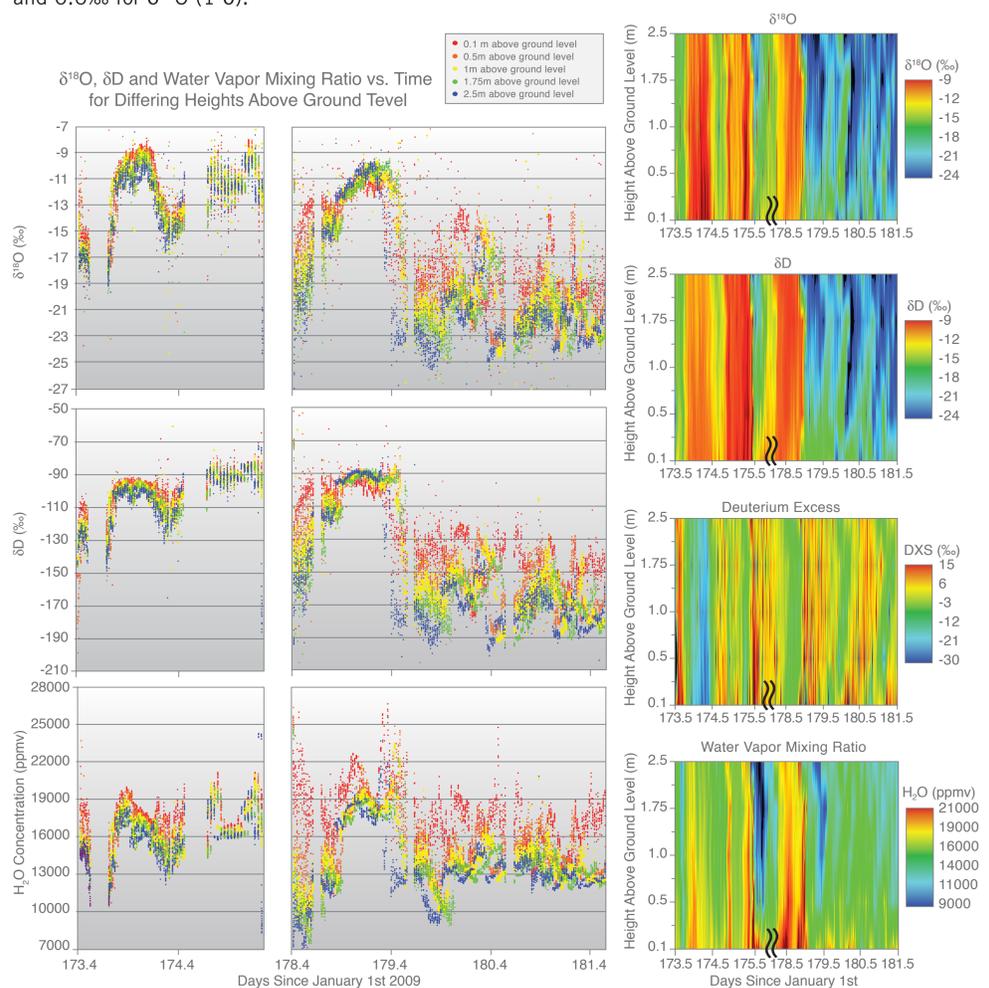


Picarro analyzer, sampling manifold, pump and rotary valve

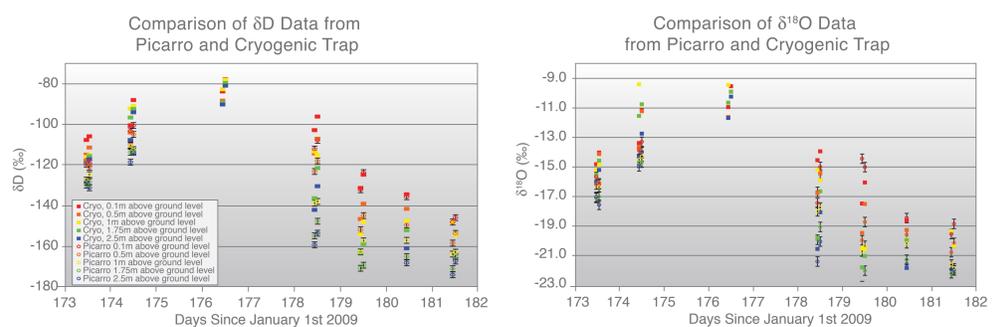
Data and Analysis

The continuous water vapor isotope and mixing ratio data for several days (June 23 – July 1, 2009) is shown here in the contour and time-series plots. The data has been scaled based on the measured standards described above and corrections have been added, where necessary, in the isotope data for temperature extremes (-19-42°C) experienced by the analyzer, imperfect drying of the air used in standards measurements and dependences on mixing ratio since all such parameters often ranged beyond the analyzer's stated specifications.

Isotope values for the cryogenically-trapped samples analyzed offline are compared here with the continuous Picarro data (averages weighted by mixing ratio), taken during the same interval (between 10:00 and 13:00h) on several days of the campaign. Estimates of error are shown for the Picarro data (precision of the analyzer is <0.6‰ for δD and <0.1‰ for $\delta^{18}\text{O}$ for water vapor and <0.2‰ for δD and <0.04‰ for $\delta^{18}\text{O}$ for liquid water standards). The error estimates account for instrument precision as well as errors due to the applied data corrections mentioned above and are 2.9‰ for δD and 0.6‰ for $\delta^{18}\text{O}$ (1- σ).



Significant diurnal changes in isotope ratio values are observed as well as a vertical gradient due to increased mixing of the canopy vapor with the more depleted background air with increasing height. The field was irrigated on the evening of June 27 (DOY 177). The significant difference in the pre- and post-irrigation signals may or may not be due to the irrigation itself, but rather, may be due to a shift in the source of the regional air mass. Further analysis of the meteorological measurements and leaf and soil isotope signatures taken during the campaign will aid in this understanding and require further study.



Conclusion

High-frequency, real-time measurements of atmospheric water vapor concentration and isotopic ratios using the Picarro CRDS analyzer in an irrigated crop system compared favorably with those from conventional IRGA and cryogenic sampling techniques.

The Picarro analyzer was capable of monitoring rapid changes in $\delta^2\text{H}$ and $\delta^{18}\text{O}$ ratios of water vapor in canopy air associated with irrigation over a 2.5m vertical profile. Together with information on the isotopic signature from different evaporation sources, the Picarro measurements will allow high-frequency estimates of the proportion of evaporation to transpiration water losses at the crop scale.

Additional analyses are aimed at better understanding the discrepancies between the continuous vapor measurements of the Picarro analyzer and the cryogenically trapped samples. Slight offsets in the $\delta^2\text{H}$ and $\delta^{18}\text{O}$ ratios between the two methods were likely associated with the method of comparing the real-time Picarro data and hour-long averages of the cryogenic trapping. It is also possible the degree of fractionation within the sample delivery systems was different for the two systems, perhaps exacerbated by temperature gradients over the period of comparison.