



Wavelength-Scanned Cavity Ring Down Spectroscopy: Opening new doors for tracing water isotopes in the hydrosphere, biosphere and atmosphere.

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Stable isotopes of water are proven indicators, tracers and recorders of processes that affect the hydrologic cycle. Measurements of stable isotopes (dD and d18O) in water are typically done with IRMS systems in laboratories that preclude real-time field use. In practice, this limits the spatial and temporal density of samples that can be taken, and thus also limits the utility of isotopes as a tool to validate models of water transport. A prominent example of this problem is isotopes in atmospheric water vapor. While the isotopic concentration of water vapor in the free troposphere is known to contain information about global moisture transport, mixing processes, and evaporation and transpiration fluxes, measurements of water vapor are labor intensive and difficult to make in the field, because of reliance upon off-line cryogenic extraction methods and traditional laboratory IRMS. This has seriously limited their utility in validating models, as well in tracking and quantifying processes in nature. A new measurement technique, based on Wavelength-Scanned Cavity Ring Down Spectroscopy (WS-CRDS), has recently become available to enable high-throughput, stable isotope ratio measurements in water and water vapor. The instruments are small and portable enough to enable field use. Lab tests analyzing both known and unknown waters have shown that the reproducibility of the system is competitive with IRMS systems. The typical precision of this technique is conservatively <0.8 permil for dD and <0.1 permil for d18O (2 sigma), and is sufficient to allow accurate determination of deuterium excess. Both liquid water and water vapor measurements are calibrated by injecting known liquid waters in the field. Here we show an example of water vapor isotopes measured in the field at Woods Hole, Massachusetts (20m amsl). The temporal resolution is 15 minutes, allowing one to see remarkable variability masked by the traditional sampling which collects vapor over long time periods. We examine the data in the context of mixing models of air. Similar field based, high frequency sampling of liquid water, for example stream flow is also possible, as are real time analyses of ice cores.