CONTINUOUS ISOTOPIC WATER SAMPLING CAVITY RING-DOWN SPECTROSCOPY (CIWS-CRDS) FOR REAL-TIME MEASUREMENTS OF WATER ISOTOPES

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Stable isotopes of water (δ^2H, $\delta^{18}O$) are unique tracers of many hydrological processes including evaporation, precipitation, reservoir mixing and residence time. Historically, discrete water samples have been collected and analyzed via either Isotope Ratio Mass Spectrometry, or more recently laser-based spectroscopic methods, such as Cavity Ring-Down Spectroscopy (CRDS). However, the analysis of discrete samples precludes the ability to construct high resolution water isotopes data sets through time and space. Previously, research groups have developed laboratory-built diffusive samplers for extracting water vapor from liquid [1,2] and then analyzed that vapor via CRDS instruments, whose continuous flow design and high frequency measurement interval (< 1 Hz) makes them uniquely suited to real-time, high throughput measurements. Here we present details of the first commercially-available and field-deployable Continuous isotopic Water Sampler (CiWS) coupled to a Picarro L2130-*i* for isotopic water analysis. The CiWS device utilizes an expanded polytetrafluouroethylene (ePTFE) membrane to extract water vapor into a dry air stream. The resultant water vapor is analyzed by a Picarro L2130-*i* for δ^2H and $\delta^{18}O$. An automated software program provides user-specified time-averaged data and switches between four ports to enable easy calibration. Tight temperature and flow rate control regulates fractionation across the membrane. In-lab testing demonstrates that the system can achieve a raw precision (1σ of 3 minute average) better than 0.05/0.15 ‰ ($\delta^{18}O/\delta^2H$), respectively, and a reproducibility of 0.15/0.5 ‰ ($\delta^{18}O/\delta^2H$) over seven days, even under variable ambient air and water temperature conditions.