

High-frequency isotopic analysis of liquid water samples in the field – initial results from continuous water sampling and cavity ring-down spectroscopy

Jana von Freyberg (1), Bjørn Studer (1), James Kirchner (1,2)

(1) Institute of Terrestrial Ecosystems, Environmental Systems Science, ETH Zurich, Switzerland
(jana.vonfreyberg@usys.ethz.ch), (2) Swiss Federal Research Institute WSL, Birmensdorf, Switzerland

Studying rapidly changing hydrochemical signals in catchments can help to improve our mechanistic understanding of their water flow pathways and travel times. For these purposes, stable water isotopes (^{18}O and ^2H) are commonly used as natural tracers. However, high-frequency isotopic analyses of liquid water samples are challenging. One must capture highly dynamic behavior with high precision and accuracy, but the lab workload (and sample storage artifacts) involved in collecting and analyzing thousands of bottled samples should also be avoided. Therefore, we have tested Picarro, Inc.'s newly developed Continuous Water Sampler Module (CoWS), which is coupled to their L2130-i Cavity Ring-Down Spectrometer to enable real-time on-line measurements of ^{18}O and ^2H in liquid water samples. We coupled this isotope analysis system to a dual-channel ion chromatograph (Metrohm AG, Herisau, Switzerland) for analysis of major cations and anions, as well as a UV-Vis spectroscopy system (Scan Messtechnik GmbH, Vienna, Austria) and electrochemical probes for characterization of basic water quality parameters.

The system was run unattended for up to a week at a time in the laboratory and at a small catchment. At the field site, stream-water and precipitation samples were analyzed, alternating at sub-hourly intervals. We observed that measured isotope ratios were highly sensitive to the liquid water flow rate in the CoWS, and thus to the hydraulic head difference between the CoWS and the samples from which water was drawn. We used a programmable high-precision dosing pump to control the injection flow rate and eliminate this flow-rate artifact. Our experiments showed that the precision of the CoWS-L2130-i-system for 2-minute average values was typically better than 0.06‰ for $\delta^{18}\text{O}$ and 0.16‰ for $\delta^2\text{H}$. Carryover effects were 1% or less between isotopically contrasting water samples for 30-minute sampling intervals. Instrument drift could be minimized through periodic analysis of external standards, as well as by maintaining constant physical conditions within the system. Our automated system combines isotope and water quality analysis, allowing on-site monitoring of highly dynamic hydrochemical behavior at sampling frequencies that would make traditional sample collection and analysis impractical.