

# High-Frequency Field Deployable Isotope Analyzer for Hydrological Applications



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## Objectives and Performance

### Overview

The stable isotope ratios of liquid water ( $\delta^2\text{H}$  and  $\delta^{18}\text{O}$ ) are used in isotope hydrology to determine water flowpaths, residence times in catchments, and groundwater migration. Typically, discrete water samples are collected and transported to an IRMS lab for isotope characterization. Due to the expense and labor associated with such sampling, isotope studies are generally limited in scope and time-resolution. LGR has developed a field-portable, high-frequency Liquid Water Isotope Analyzer (LWIA) that quantifies  $\delta^2\text{H}$  and  $\delta^{18}\text{O}$  of multiple natural water sources (e.g. rain, snow, streams and groundwater) at a rate of over 132 unknown samples per day (>1000 injections per day). An instrument was deployed in the H.J. Andrews Experimental Forest for 4 continuous weeks, where it provided unique measurements of both stream water and precipitation every 40 minutes.

### Measurements using cavity enhanced laser absorption

LGR's Analyzers are based on high-resolution laser absorption spectroscopy and utilize LGR's patented cavity enhanced absorption technique in which a high-finesse optical cavity is used as the measurement cell. For more info, see: [www.LGRinc.com](http://www.LGRinc.com).



### Unprecedented Speed and Precision

The customized LGR LWIA provides high accuracy and precision measurements of both  $\delta^2\text{H}$  and  $\delta^{18}\text{O}$  simultaneously at unprecedented speeds of > 1000 injections per day.

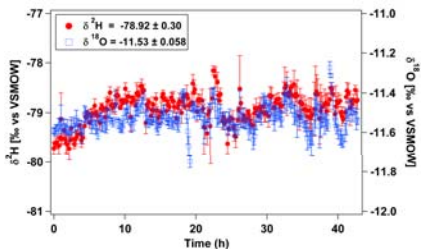


Figure 1. **Laboratory  $\delta^2\text{H}$  and  $\delta^{18}\text{O}$  measurements using the custom LGR LWIA.** 240 complete unknown sample measurements recorded in 43 hours with a precision of  $\pm 0.30$  ‰ in  $\delta^2\text{H}$  and  $\pm 0.058$  ‰ in  $\delta^{18}\text{O}$ . The average values ( $-78.92$  ‰ for  $\delta^2\text{H}$  and  $-11.53$  ‰ for  $\delta^{18}\text{O}$ ) agree with the actual values ( $-79.0$  ‰ for  $\delta^2\text{H}$  and  $-11.54$  ‰ for  $\delta^{18}\text{O}$ ) to within the instrumental precision.

### Post-Analysis Software

Los Gatos Research has recently released our new Post-Analysis Software for use with the LWIA. This software package is designed to increase user productivity and decrease data processing time. Key features include:

- Automatically processes sample measurements recorded by the LWIA to calibrated delta values
- Reads data directly from LWIA files
- Includes a suite of plots for data visualization
- Provides data diagnostics and report information
- Outputs processed data to tab-delimited text files.
- Filters the data using user-configurable data rejection and flagging criteria



## Field Deployment

See *Water Resources Research*, 2009, 45, W10201, doi:10.1029/2009WR008265

An LWIA was deployed at Watershed #1 gauging station in the H.J. Andrews Experimental Forest in Oregon from 3/5/09 – 4/3/09. A precipitation collector was placed atop the gauging station and a submersible pump was installed in the adjacent stream. Collocated equipment was used to log ambient temperature, local rainfall and streamflow. The isotope ratio measurement sequence interleaved water standards, stream water samples and precipitation samples resulting in 40 stream samples/day and 40 precipitation samples/day. Instrument readings were verified accurate to  $\pm 0.2$  ‰ and  $\pm 0.6$  ‰ for  $\delta^{18}\text{O}$  and  $\delta^2\text{H}$ , respectively, by taking 43 grab samples (approximately one every 12 hours) and analyzing them on a lab instrument.

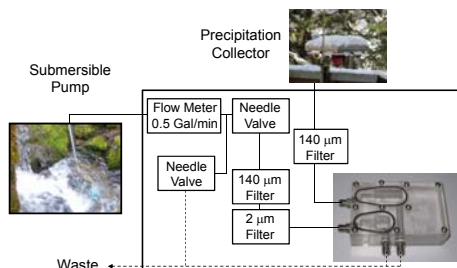


Figure 2. Schematic diagram of stream and precipitation sampling systems. The stream sampler utilizes a submersible pump to push water against 3 meters of head at 31 mL/s rate. A variable open split is used to sample 10 mL/min of liquid through two filters and into the injection tray. The precipitation sampling utilizes a funnel atop the gauging station to flow water through a single filter and into the injection tray.

There were 3 large storms and several days of snow during the deployment. Data taken during the largest event is shown below (Figure 3) and depicts a large excursion in rainwater isotope ratio with no correlated shift in the stream. The lack of response of stream  $\delta^{18}\text{O}$  and  $\delta^2\text{H}$  is a classic example of the old water paradox whereby the pressure propagation through the watershed is immediate (i.e. flow in the stream) whereas particles carried with the water (i.e.  $\delta^{18}\text{O}$  and  $\delta^2\text{H}$ ) represent water stored in the watershed for months to years prior to the event. Due to the high measurement frequency, two distinct decreases in isotope ratio are clearly resolved, suggesting rainfall from multiple storm fronts. Moreover, the instrument's continuous operation for long deployment periods allows for several storms to be examined individually. For example, a Local Meteoric Water Line has been generated for each storm and provides information about the precipitation source water (Figure 4).

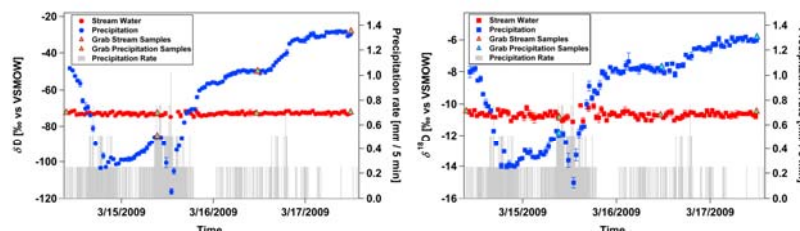


Figure 3. **High-frequency  $\delta$  measurements** taken during a large rain event.  $\delta^2\text{H}$  in rain spans 90 ‰ and changes during the event as rainfall increases. Note that the high measurement frequency allows resolution of two distinct storm fronts. No measurable shift is seen in stream isotope ratios despite a sizable change in stream discharge.

## Conclusions

**New Liquid Water Isotope Analyzer with novel injection tray enables continuous sampling of natural waters:**

- **Rapidly quantifies  $\delta^2\text{H}$  and  $\delta^{18}\text{O}$**  in rain, snow, streams, groundwater, and other natural waters
- **High precision and reliability** demonstrated in the field over long durations, changing temperatures and difficult conditions
- Resolves **dynamic changes in  $\delta$  quickly** (minutes) and **over long time scales** (weeks, months)
- The customized LWIA measures **>132 unknown samples per day** (6 injections per sample, >1000 injections per day, >166 total unknown and reference samples per day). The commercial V2 LWIA measures 90 unknown samples per day.
- Allows studies of **water flow dynamics** over unprecedented time scales
- Enables studies of mixing dynamics in snowmelt, canopy throughfall, stream mixing, and with natural & labeled injections
- Allows for **individual precipitation events** to be independently studied
- **Post-Analysis Software** streamlines data processing and provides data visualization and diagnostics

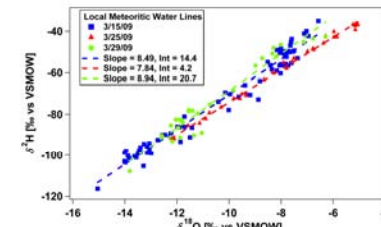


Figure 4. **Measured Local Meteoric Water Lines** generated for 3 distinct, large precipitation events that occurred during the LWIA deployment showing differences in source water.