



High-frequency field-deployable isotope analyzer for hydrological applications

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[1] A high-frequency, field-deployable liquid water isotope analyzer was developed that is capable of quantifying $\delta^{18}\text{O}$ and $\delta^2\text{H}$ to better than ± 0.17 and $\pm 0.32\%$, respectively, on over 90 samples/d. The instrument was deployed for 4 contiguous weeks in the H. J. Andrews Experimental Forest Long-term Ecological Research site in western Oregon, where it was used for real-time measurement of the isotope ratios of precipitation and stream water during three large storm events. We were able to document fine-scale changes in rainfall composition and damping effects in the stream channel continuously through these periods. We also performed a rain-on-snow experiment where we sampled leachate from a melting snow core continuously at 2 min intervals for 5 h. These data show remarkable fine-scale patterns of internal rain-snow mixing, patterns that would not have been detected without such high-frequency sampling. These two preliminary applications show proof of concept of the new field analyzer, a device that will ultimately provide hydrologists with insight into water flow dynamics with unprecedented frequency over long time scales.

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1. Introduction

[2] The use of isotope tracers in catchment hydrology has grown enormously over the past few decades [Kendall and McDonnell, 1998]. Following the early work with oxygen-18 and deuterium on the time source components of catchment storm runoff [Fritz *et al.*, 1976] and tritium-based analysis of surface water residence time [Martinec *et al.*, 1974], the scope of isotope applications in the hydrological sciences has greatly expanded [Aggarwal, 2002] for characterizing the recharge rates of groundwater systems, predicting the migration of contaminants, gauging the impact of climate change on water resources, and model calibration.

[3] Despite the widespread usage of isotope data in hydrology, the cost of analysis has been prohibitive in many cases [Burns, 2002] and consequently, sample frequency has been an issue. A recent development that has transformed this field is laser-based methods for quantifying $\delta^{18}\text{O}$ and $\delta^2\text{H}$ isotope ratios of collected water samples [Aggarwal *et al.*, 2006; Lis *et al.*, 2008; Brand *et al.*, 2009]. In this method, tunable diode laser absorption spectrometry in near-infrared [Kerstel *et al.*, 2002] or midinfrared [Sayres *et al.*, 2009] is used to directly quantify the molecular densities of the isotopomers (e.g., H_2^{16}O , $^1\text{H}^2\text{H}^{16}\text{O}$, and H_2^{18}O) of water vapor in an optical cell. In order to obtain absorption features that are large enough to quantify the isotopomers

to the required level, a high-finesse optical cavity can be used increase the optical path length to several kilometers [Baer *et al.*, 2002]. Unlike conventional methods (e.g., isotope ratio mass spectrometry), laser-based water isotope analyzers do not require extensive consumables, trained personnel, high vacuum, or sample conversion. Moreover, these instruments require lower power, and the cost per sample is substantially smaller. However, they are subject to erroneous readings if the water samples contain high levels of alcohols [Brand *et al.*, 2009] or other dissolved organic carbon [Singleton *et al.*, 2009]. Thus, this study focuses on relatively clean, freshwater samples.

[4] While laser-based techniques are poised to put isotope measurement in the hands of every hydrologist, we are still limited by the fact that samples must be collected in the field and transported to the lab for analysis. Kirchner *et al.* [2004] and others have noted that, while catchment studies of water flux are based on high-frequency (<1 h) data, studies of water particle movement (with chemical and isotopic tracers) are often much lower frequency (weekly or monthly). This dramatic difference in sampling frequency is due to the distinction between field-deployable measurements of water flux and laboratory measurements of chemical and isotopic parameters. Therefore, high-frequency isotope data have been limited to a few intensive studies of individual storm events.

[5] Lyon *et al.* [2008] used high-frequency isotope data from a series of rapid precipitation events to estimate the transit time distribution for a catchment located in the Santa Catalina Mountains. Thirty-two stream water and 24 precipitation samples were collected for 7 rainfall events that spanned 6 days. For one specific event, high-frequency samples were collected at frequencies ranging from one sample every 15 min during the rain event to one sample

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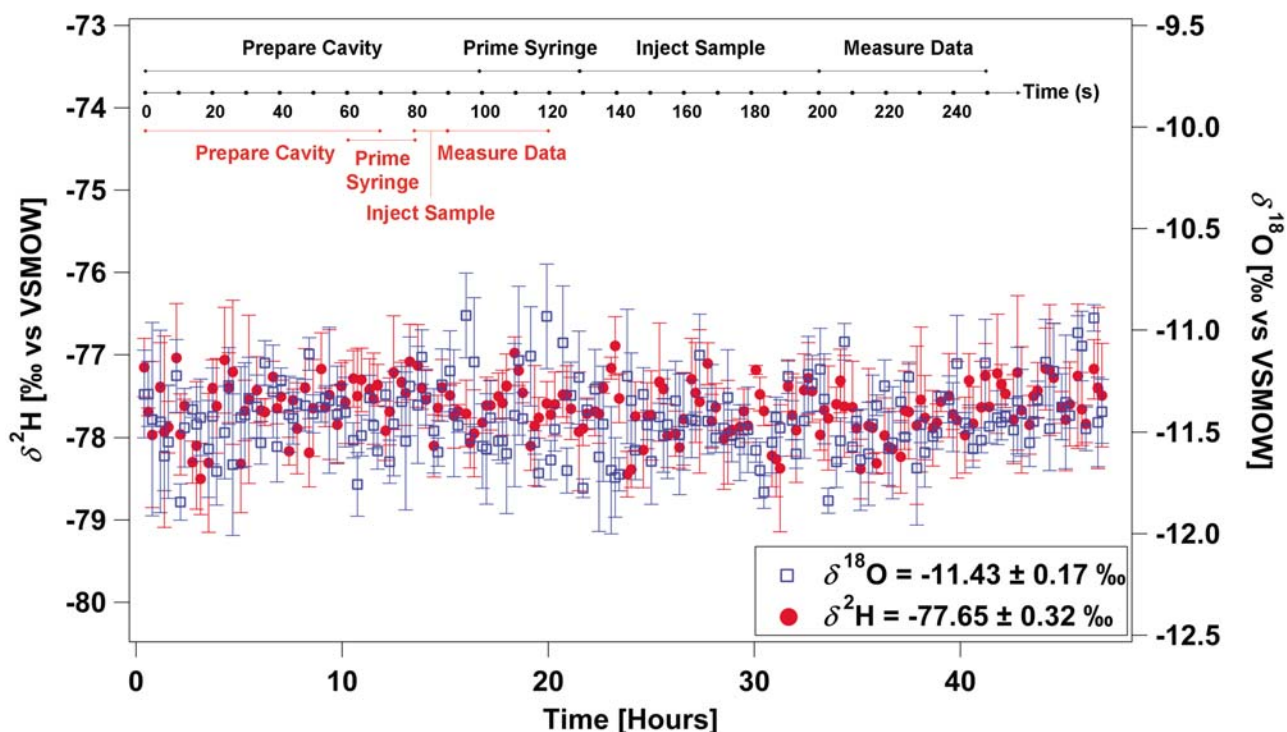


Figure 1. Measurement of 180 samples in 48 h. The instrument is capable of making 90 measurements of $\delta^{18}\text{O}$ (blue squares) and $\delta^2\text{H}$ (red circles) in liquid water per 24 h, as shown here with a precision of 0.17 and 0.32‰ (1σ), respectively. The throughput of a conventional Los Gatos Research LWIA was increased in a variety of ways as shown schematically in the inset. All isotope ratios are reported as ‰ versus VSMOW on the VSMOW-SLAP scale, where SLAP is defined as $\delta^2\text{H} = -428\text{‰}$ and $\delta^{18}\text{O} = -55.5\text{‰}$.

every 3–4 h subsequent to the rainfall. A shift in the stream isotope ratio was observed followed by a slow decay back to its nominal value, and models were developed to relate these real-time measurements to the catchment's transit time distribution. High-frequency water isotope measurements have also been used in precipitation studies. For example, *Celle-Jeanton et al.* [2004] measured $\delta^{18}\text{O}$ of rainwater during 12 storm events with sampling frequencies approaching one sample every 5 min. The variation in $\delta^{18}\text{O}$ over the course of each rain event was then compared to a Rayleigh condensation model to assess the need for adding additional vapor sources or ice formation to explain the observed behavior. Similarly, *Coplen et al.* [2008] developed an automatic precipitation collector and studied high-frequency (1 sample every 30 min) isotope variations in a landfalling Pacific storm. They observed a remarkable shift in $\delta^2\text{H}$ over the course of the storm and related their observations to the precipitation temperature and condensed moisture fraction.

[6] Despite these demonstrations of the value of high-frequency isotope measurements, what is still needed is a field-deployable isotope measuring device for continuous field-based sampling of $\delta^2\text{H}$ and $\delta^{18}\text{O}$, comparable to what is used in stream chemistry studies for parameters like pH and EC. Here we present the first tests of a newly developed field-deployable laser spectrometer capable of making continuous, high-frequency measurements of $\delta^{18}\text{O}$ and $\delta^2\text{H}$ from multiple water sources. The objective of this paper is to outline the functionality of the new device and to show its

utility via a field-based deployment at the H. J. Andrews Experimental Forest Long-term Ecological Research site, where we deployed the analyzer for 4 contiguous weeks and used it for additional high-frequency experiments of rain on snow.

2. Experimental Method

[7] We developed a new field-deployable laser spectrometer around the Los Gatos Research liquid water isotope analyzer (LWIA), customized for field deployment by major changes to its throughput capabilities and external water source sampling capabilities. The standard LWIA uses near-infrared tunable diode laser absorption spectrometry with the laser coupled in an off-axis fashion to a high-finesse optical cavity to attain the necessary absorption path length [Baer et al., 2002]. This technique, termed off-axis integrated cavity output spectroscopy (off-axis ICOS), allows for highly accurate quantification of $\delta^{18}\text{O}$ and $\delta^2\text{H}$ in injected water samples in a relatively compact, robust instrument. Typically, the commercial instrument requires 250 s to inject a 1 μL sample and quantify its $\delta^{18}\text{O}$ and $\delta^2\text{H}$ isotope ratios. Each injection entails removing gas from the measurement cell (10 s), filling the cell with dry air (10 s), removing the air from the cell (80 s), injecting 1 μL of sample into the cell (30 s), waiting for full evaporation (70 s), and measuring the optical absorption spectra (50 s). Each sample is injected 6 times (25 min) and followed by a water standard that is analyzed in a similar manner (25 min).

Table 1. Accuracy of the High-Frequency Liquid Water Isotope Analyzer Confirmed by Measuring a Water Sample and Sending it out to Five Isotope Ratio Mass Spectrometry Laboratories^a

Instrument	$\delta^2\text{H}$	$\delta^{18}\text{O}$
High-frequency LWIA	-78.4 ± 0.5	-11.64 ± 0.19
IRMS 1	-79.4	-11.71
IRMS 2	-79.3	-11.51
IRMS 3	-79.5	-11.70
IRMS 4	-77.1	-11.53
IRMS 5	-77.1	-11.47
Mean IRMS	-78.8	-11.58

^aNote that the instrument agrees with the isotope ratio mass spectrometry (IRMS) mean value to within the measurement error of the instrument. All isotope ratios are reported as ‰ versus VSMOW on the VSMOW-SLAP scale, where SLAP is defined as $\delta^2\text{H} = -428\text{‰}$ and $\delta^{18}\text{O} = -55.5\text{‰}$.

Thus, the measurement procedure yields quantification of an unknown sample every 50 min and the instrument can process 29 samples/d.

[8] Here, our new instrument reduced the measurement time per injection from 250 s to 120 s (Figure 1). Foremost, the gas conductance out of the cell was increased by using a larger output orifice. This allowed the dry air to be removed from the cell in only 50 s. The software was modified to begin priming the syringe with water during this pump down time and the resultant injection time was reduced from 30 s to 10 s. Most importantly, the sample evaporation time was decreased from 70 s to 10 s by heating the injection port to $>80^\circ\text{C}$ and assuring that the injected water contacted only hot stainless steel surfaces. Finally, the data acquisition routine was modified to simultaneously collect and analyze spectra reducing the data analysis time from 50 s to 30 s. As before, each water sample is injected 6 times, however, this now requires only 12 min.

[9] In addition to reducing the measurement time per injection, the new instrument can measure more samples between standards while maintaining the same accuracy and precision. Conventionally, 3 samples and 3 standards are interleaved to yield quantification of 3 samples in 150 min. In the new analyzer, nine samples are interleaved between 3 standards (e.g., standard 1, sample 1, sample 2, sample 3, standard 2, sample 4, sample 5, sample 6, standard 3. . .) and the calibration curve spans 144 min for measurement of these 9 samples. Thus, the improved speed/injection yields a throughput of 90 samples/d.

[10] These modifications do not affect the instrument performance as empirically determined by quantifying a single water sample 180 times over 48 h and obtaining a measurement precision of $\pm 0.17\text{‰}$ and $\pm 0.32\text{‰}$ (1σ) for $\delta^{18}\text{O}$ and $\delta^2\text{H}$, respectively (Figure 1). The measurement accuracy was verified to be within the precision by sending a similar sample to several IRMS laboratories and comparing the results to those obtained by the enhanced liquid water isotope analyzer (Table 1).

[11] In addition to increasing the analyzer's throughput, a water handling system was developed to integrate stream and precipitation sampling into the analyzer's CTC LC-PAL autosampler unit (Figure 2). A submersible pump (31 mL/s against 3 m of head) was used to push stream water up to the instrument and a variable open split was used guide a small amount of water (10 mL/min) through 2 filters (140 μm and 2 μm stainless steel in-line particulate filters) and into a custom acrylic injection tray. The response time of the stream sampling system was estimated to be ~ 15 min and primarily limited by the flow through the open split. The rainwater was sampled using a large 50 cm \times 50 cm square funnel mounted 3 m above the instrument. Precipitation was collected by the funnel, flowed through a 140 μm stainless steel in-line particulate filter and into the acrylic tray through a separate channel from the stream water.

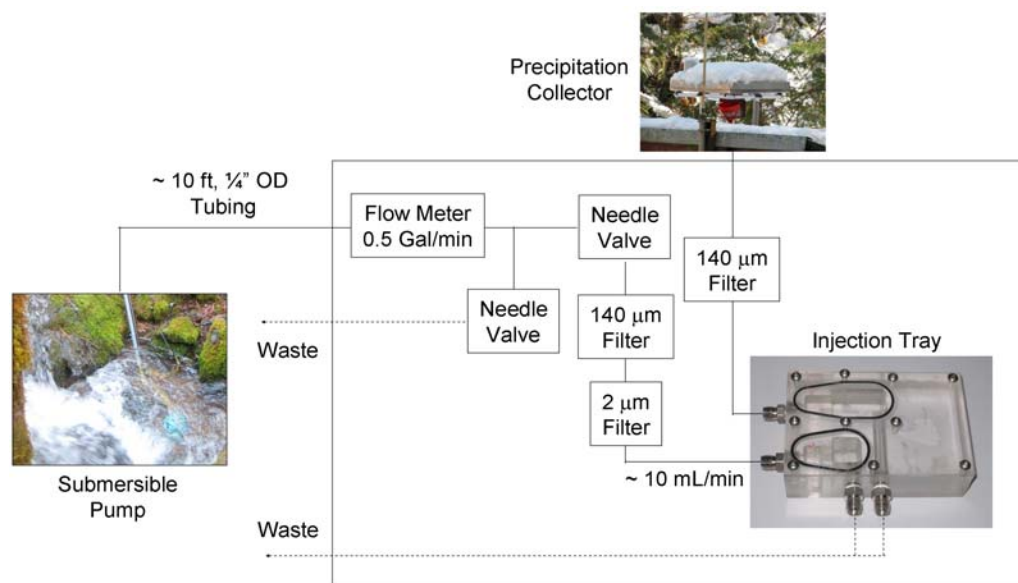


Figure 2. Schematic overview of the stream and precipitation sampling systems. The stream sampler utilizes a submersible pump to push water against ~ 3 m of head at a rate of 31 mL/s. A variable open split is used to sample ~ 10 mL/min of water through two filters and into the custom injection tray.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

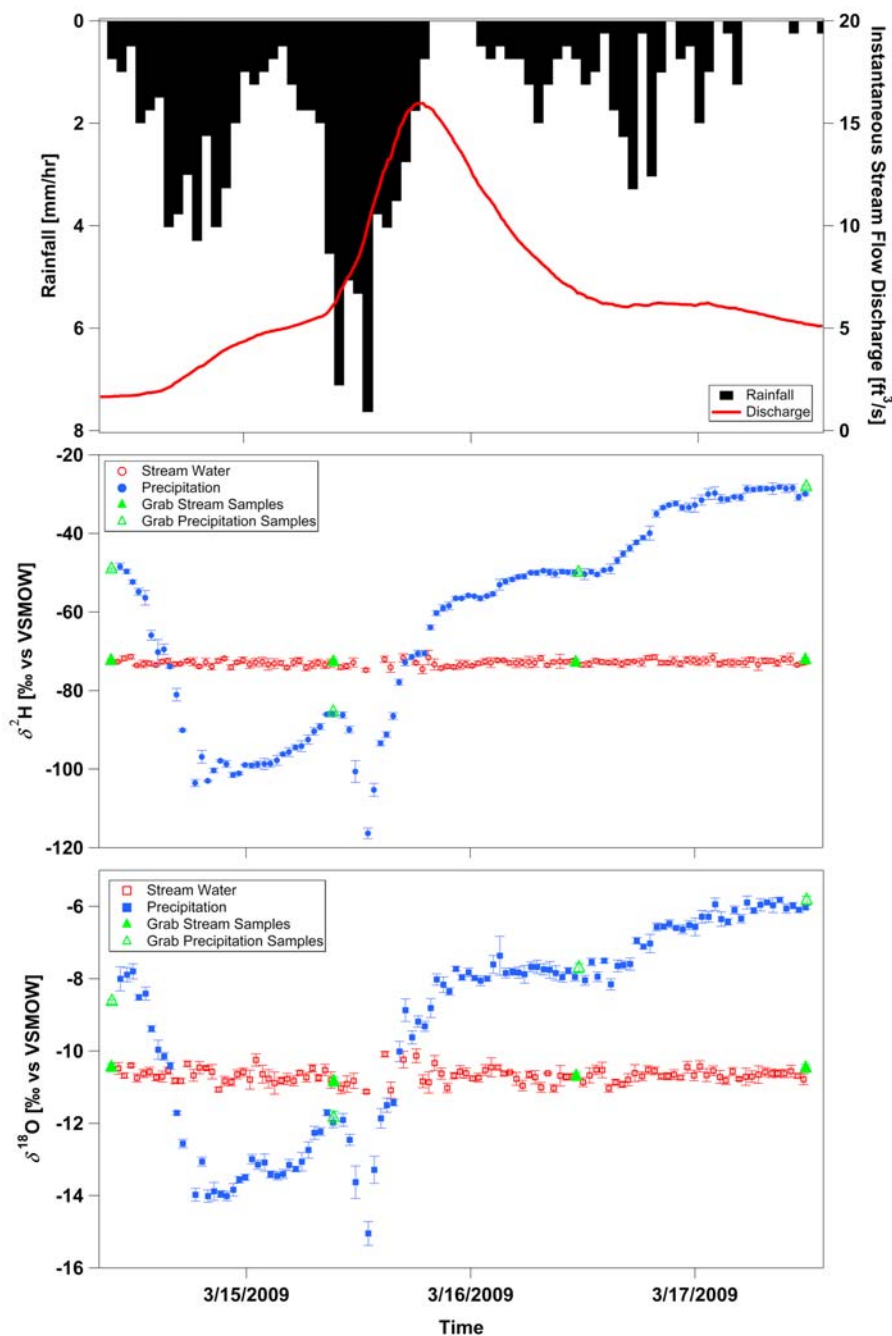


Figure 3. High-frequency measurements of (bottom) $\delta^{18}\text{O}$ and (middle) $\delta^2\text{H}$ taken during a large rain event. (top) The $\delta^2\text{H}$ excursion in the rain spans over 90‰ and changes during the event as the rainfall increases. There is no measurable shift in the stream isotope ratio despite a sizable change in the stream discharge. The data were validated by taking periodic grab samples (green markers) of both water sources and measuring them with a laboratory analyzer.

Empirical tests suggest a response time of <5 min for the precipitation collector.

[12] Both water samples flow into an acrylic tray that fits into the CTC LCPAL autosampler (Figure 2). The filtered water flows into the tray, and, after approximately 1–2 mL of water enters the appropriate channel (stream or precipitation), it overflows into the drain. This configuration allows for frequent sample flushing while retaining a constant water column height, which results in more consistent injected volumes. The tray is positioned into the autoloader such that the sampled stream water and precip-

itation can be drawn into the syringe as if they were vial 11 and vial 38 in tray 01, respectively. Note that the tray can be readily modified to accept additional water input channels, allowing for sampling of multiple water sources (e.g., groundwater, well water, multiple points along a stream, etc.).

3. Field Testing

3.1. H. J. Andrews Deployment at WS 1

[13] We deployed the analyzer at the watershed 1 gauging station in the H. J. Andrews Experimental Forest in Western

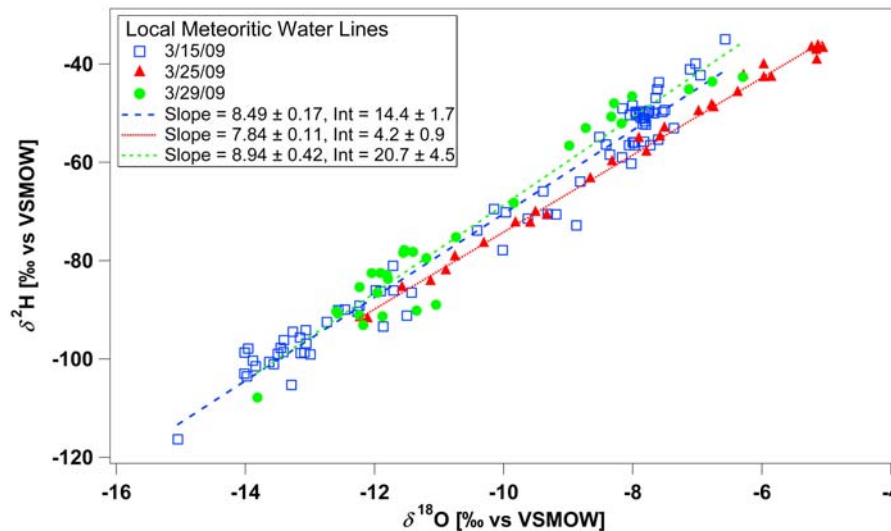


Figure 4. Local meteoric water lines generated for three distinct large-precipitation events that occurred during the deployment period.

Oregon from 5 March 2009 to 3 April 2009. We used the existing gauging station to measure streamflow from the $\sim 1 \text{ km}^2$ watershed and one of the primary meteorological sites ($< 1 \text{ km}$ away) for rainfall inputs and local meteorological variables. The analyzer and autosampler were housed in Plexiglas enclosures and placed in the small gauging station that housed the stilling well and water level recorders. The station was nominally heated to $\sim 9^\circ\text{C}$ by a small propane heater to prevent freezing. A precipitation collector was placed atop the station and a submersible pump was installed in the adjacent stream to move water from the stream to the analyzer. In addition to measuring water isotope ratios, collocated equipment was used to log the ambient temperature and local rainfall amount. The measurement sequence was altered slightly to interleave water standards, stream water samples and precipitation samples (e.g., standard 1, stream, precipitation, standard 2, stream, precipitation...), resulting in 40 stream samples/d and 40 precipitation samples/d. The instrument readings were verified to be accurate to within $\pm 0.2\text{‰}$ and $\pm 0.6\text{‰}$ for $\delta^{18}\text{O}$ and $\delta^2\text{H}$, respectively by taking over 43 periodic grab samples (approximately one every 12 h) and analyzing them on a laboratory liquid water isotope analyzer within 2 weeks of collection.

[14] We found that the Teflon-silicone-Teflon injection septum could handle typically 750–1000 injections before resealing improperly. The septum was changed daily to avoid air leakage. Similarly, depending on the turbidity of the stream water, the stream sampling filters became partially clogged every 1–3 days, reducing the sample flow rate. When the flow rate became visibly slower, these filters were removed, thoroughly rinsed, and replaced. Throughout the entire deployment period, the precipitation filter was also replaced once because of insufficient flow. Because of the small injected volumes (e.g., $\sim 1 \mu\text{L}$), a $1.2 \mu\text{L}$ syringe is used in the system. This syringe is especially prone to damage from particulates and precipitates, and especial care was taken to extend the syringe lifetimes. Foremost, the syringes were manually rinsed with distilled water prior to insertion. Then, they were operated continuously to prevent

them from drying out and becoming jammed. Last, syringes were replaced on approximately a weekly basis to preclude any injected volume fluctuations. The vials containing water standards were also replaced on a daily basis to avoid any shift in the standards due to evaporation.

[15] There were 3 large storm events and several days of snow accumulation over the course of the deployment. The 3 storm events took place from 14 to 17, 23 to 25, and 28 to 29 March with total rainfalls of 111 mm, 48 mm, and 32 mm, respectively. The data taken during the largest event (14–17 March) are shown in Figure 3 and depict 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 [Kirchner, 2003] 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. Previous residence time analysis of H. J. Andrews waters have shown that these waters range in mean residence time from approximately 1–3.5 years [McGuire *et al.*, 2005].

[16] Because of the high rainfall measurement frequency, two distinct decreases in isotope ratio are clearly resolved, possibly suggesting rainfall from multiple storm fronts. Moreover, the instrument's continuous operation for long deployment periods allows for multiple storms to be individually examined. For example, a local meteoric water line can be generated for each storm event and provide information about the precipitation source water (Figure 4).

3.2. H. J. Andrews Rain-on-Snow Experiment

[17] Rain on snow is the key flood-producing runoff generation mechanism in the Pacific Northwest [Harr, 1981]. Nevertheless, little is known about how rain mixes with snow within the melting pack to generate and deliver water to the ground surface [Mazurkiewicz *et al.*, 2008]. In this study, we extracted a large, 200 mm diameter, intact, isothermal snow core from watershed 7 at the H. J. Andrews and transported it to the H. J. Andrews headquarters. The

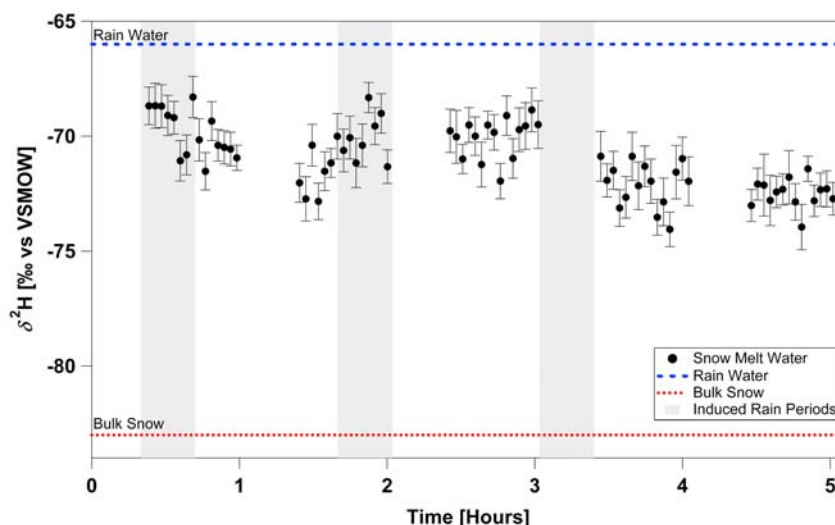


Figure 5. Isotope measurements of water eluting from a melting snow column measured every 2 min. Melting was induced via artificial rain periods. Isotope ratios of the rainwater and bulk snow are also indicated.

core represented 125 mm of snow water equivalent and weighed 1512 g. The core was packed in ice to prevent melt along the sidewalls. The core was mounted outside a room that housed a second field-deployable, high-frequency liquid water isotope analyzer and autoinjection unit. Rainfall was applied at a rate of ~ 10 mm/h using a backpack spray unit. The isotope analyzer was operated in a similar manner to that presented above (i.e., 2 min/injection); however, the run sequence was altered to 6 injections of a water standard alternating with 18 injections of snowmelt water. The first two injections between sample alternations were discarded to account for memory and the rest of the injections of snowmelt water were treated as individual measurements because of the slowly varying nature of the isotope signature (i.e., the memory effects between adjacent snowmelt water samples could be ignored). In this configuration, the instrument provided a unique data point every 2 min with an empirically determined measurement precision of $\pm 0.22\text{‰}$ and $\pm 0.8\text{‰}$ for $\delta^{18}\text{O}$ and $\delta^2\text{H}$, respectively.

[18] Three 22 min rain pulses were simulated over the course of a 5 h melt event spaced 1 h apart. At the end of the 5 h experiment, 41% of the total snow water equivalent was lost. Figure 5 shows the high-frequency mixing dynamics in $\delta^2\text{H}$ between the rain source (-66‰ versus VSMOW) and the preevent bulk snow composition (-83‰ versus VSMOW). The gap in the measurements is due to the quantification of water standards. While detailed discussion of this experiment is beyond the scope of this paper, Figure 5 shows how rainfall infiltrates the isothermal, granular snowpack and dominates the outflow from the base of the snowpack. Melt from the core is $>80\%$ rainfall in the first rain-on-snow episode and decreases to a blend of approximately coequal amounts of rain and prerin snow by the end of the 5 h experiment. The fine-scale features of melt are striking in terms of the trajectory of the melt $\delta^2\text{H}$ signature during the three rain pulses: a progressive hydrogen-2 depletion in rain pulse one, followed by a steady hydrogen-2 enrichment in rain pulse two and largely unchanging melt composition in rain pulse three. While the error bands plotted in Figure 5 show considerable overlap in

successive 2 min samples, the high-frequency data show a robust pattern over the course of tens of minutes and reveal new information on the mixing between the rainfall wetting front and prerin snow.

4. Future Directions

[19] Our first field use and testing of the field-deployable liquid water isotope analyzer has shown considerable promise by providing high-frequency, real-time isotope hydrology data over long field deployment periods. Notwithstanding, the instrument still requires daily servicing to change the injection septa and clean the stream sampling filters. Future developments will be focused on increasing the service interval to several weeks and will include using a longer-life injection septum, cyclone filtration prior to the cartridge filters, and automatic filter back flushing. Moreover, we expect that the instrument measurement time can be further decreased to ~ 90 s/injection by improving the gas conductance (e.g., reducing gas fill and pump out times) and evaporation times (e.g., heating the injection port to 150°C). The analyzer should then be able to quantify 133 samples/d and provide unique measurements of water sources every 11 min.

[20] New measurements are often what drives science forward [Kirchner *et al.*, 2004]. The development of a high-frequency, field-deployable liquid water isotope analyzer will enable hydrologists to study rapid water flow dynamics over long time scales. We anticipate many breakthroughs in the future where such high-frequency, field-based measurements can be used to resolve complex mixing dynamics in snowmelt, canopy throughfall, stream mixing, etc. . . with natural and labeled injections.

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