Isotope Hydrology: Monitoring Rainfall Events in Real Time

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Introduction
At the Hillslope and Watershed Hydrology Laboratory at Oregon State University, we have been working with LGR to optimize the high frequency capabilities of their analyzer (model LWIA-24d) for hydrological applications. This is a dual isotopic water analyzer that measures $\delta^{18}O$ and $\delta^2H$ in real time. This case study describes how the automation and speed of this analyzer are enabling us to track stable isotope ratios during rain events with unprecedented temporal resolution. This ongoing study has already revealed some unusual data about isotopic variability during single events (rainstorms). We hope to use such detailed isotopic data for an improved assessment of hydrological flowpaths.

Isotope Hydrology Background
In isotope hydrology we study the interrelationships between the components of the water cycle, such as evaporation, rainfall, run-off, plant uptake, plant transpiration, and so on. In particular, we use the stable isotopes $^2H$ (D, deuterium) and $^{18}O$ (oxygen-18) to track water through the water cycle. As in most other stable isotope applications, we measure the abundance of each isotope and express its concentration relative to a standard for those atoms, in units of per mill (per thousand, ‰). These ratios are written as $\delta^2H$ (or $\delta D$) and $\delta^{18}O$. The standard for natural water samples was originally “standard mean ocean water” (SMOW) as defined in the landmark 1961 study by Craig. But today we more commonly use a newer standard, specifically the Vienna standard mean ocean water (VSMOW).

In his well-known study, Craig showed that in most nascent rainwater (i.e., before any evaporation) the isotopic ratios $\delta^2H$ and $\delta^{18}O$ vary with temperature controlled fractionation. That is, water containing heavier isotopes evaporates and condenses at slightly different fractional rates because of the mass difference. More importantly, Craig showed that the interrelationship between $\delta^2H$ and $\delta^{18}O$ in rainwater is virtually independent of temperature all over the globe and follows a simple, linear formula: the so called “Global Meteoric Water Line”. The average relationship is $\delta^2H = 8 \times \delta^{18}O + 10$, presented in figure 1. Notice that the line usually only covers negative values of $\delta^2H$ and $\delta^{18}O$, i.e., water that is more depleted in heavy isotopes than the VSMOW standard. This is because all rainwater originates in some type of evaporation process. Therefore, with very rare exception, it is more depleted than seawater.

Figure 1. Plotting the stable isotope ratios of $\delta^2H$ and $\delta^{18}O$ against each other yields a characteristic straight line plot, the meteoric water line.
Discrete showers and rainstorms are called rainwater events, and can last hours or even tens of hours. The ambient temperature can vary during this period, but all the data should scatter around a regression line called the local meteoric water line (LMWL). This geographically biased line gives us a local mean value with which different individual events can then be compared; a baseline, if you like. This LMWL can be slightly different from the Global Meteoric Water Line, in terms of slope and intercept (e.g. Gibson et al., 2008), and individual events will typically have a line different from the LMWL.

In isotope hydrology, we use another important parameter called d-excess. This metric amplifies the small differences between the observed isotope ratio (δD and δ18O) at individual data points and what would be expected from the Craig relationship. This was originally defined by Dansgaard in 1964 as d-excess (in permil) = δ2H - 8 δ18O. Referring back to the water line equation of Craig, we can see that “average” rainwater should have a d-excess of 10. There are many factors that can affect d-excess values, but these mainly reflect differences in conditions at the source area for the water vapor in an airmass, and the nature of the airmass prior to the moisture falling as rain or snow (refs Clark and Fritz, 1997, Froehlich et al, 2002).

**High Frequency Assessment of Inter and Intra Event Variability**

Until the advent of automated, laser-based instruments, such as the LWIA-24d from LGR, measuring stable isotopes from water was a cumbersome, relatively expensive and time-consuming affair. Captured rainwater samples were sealed (to prevent any evaporative bias) and taken back to the laboratory (or sent to a specialty isotope laboratory) for processing days later using isotope ratio mass spectrometry (IRMS). The samples had to be separately chemically processed for both oxygen and hydrogen; an IRMS should never be exposed directly to water samples as this molecule is “sticky” and will persist in trace amounts in this high-vacuum instrument for a long time. The cost, in terms of time and complexity, limits the number of data points that can be realistically attempted in a rainwater study. For example, it is normal to report only a single average value of the d-excess for each event or even a week/month.

In contrast, the LWIA-24d analyzer is a fully automated instrument that can continuously operate in real time. This is enabling us to measure rainwater directly using unmanned operation of the instrument in Corvallis, Oregon (44°34’14.81”, N 123°16’33.59”W 1). In the study reported here, we have so far analyzed 3000 rainfall isotope measurements (for both D and 18O) over the period from November, 2011, to February, 2012. The LGR analyzer was positioned on a platform 1 meter above the ground, and the isotopic composition of rain water measured at 2 minute intervals using a flow-cell as originally described in Berman, et al. (2009). Allowing overhead for automated purging and calibration, this comfortably enables an average sample frequency of 15 measurements per hour, clearly improving precipitation analysis.

**Data and Interpretation**

Figure 2 presents six selected rainfall events, numbered 1-6 in chronological order. Total rainfall in these events ranged from 4.2 mm (event 4) to 148.2 mm (event 5). For each event, we took the isotope ratio data points and constructed an event water line. The six events are presented together with the LMWL (all observations) that has a slope of 8.1 and a d-excess of 15.2.
Several aspects of this graph are interesting. First, the variability of the values enabled excellent fitting, with linear regressions of 0.978 or better. And, as expected, each line is somewhat different from the LMWL, since each event can be expected to have a slightly different history. And, not surprisingly, the shortest and longest events (events 4 and 5) show the largest slope deviations from the LMWL, with slopes of 5.1 and 9.2 respectively.

However, some of our data is definitely quite surprising. The long duration of event 5 and the high frequency sampling capability of the analyzer enabled a highly detailed plot of d-excess for this event (see the inset to figure 2). For a single event, only minor variations of d-excess would be expected over the event duration, with d-excess somewhere in the range 5-15‰ for the northern hemisphere, relative to the global meteoric water line. But, figure 2 shows the d-excess for this prolonged had high temporal variability. A potential explanation of this is the contribution of different water vapor sources through a single event, one with a d-excess close to 25‰ and the other in the 5-10‰ range.

Future Work

Looking to the immediate future, we plan to continue analyzing rainfall events at this location, with particular emphasis on d-excess, to see how frequently (or infrequently) events like event 5 occur. And, now that we have demonstrated the ease of fully analyzing the isotopic signatures of events, we plan to account for the inter and intra event variability in hydrological processes research.

References