Motivation
An accurate understanding of the relationships between the isotopic composition of liquid water and that of water vapor in the environment can help describe hydrologic processes across many scales. One such relationship is the isotopic equilibrium between falling raindrops and the surrounding vapor. The degree of equilibrium is used to model the isotopic composition of precipitation in isotope-enabled general circulation models and land-atmosphere exchange models. Although this equilibrium has been a topic of isotope hydrology research for more than four decades, few studies have included vapor measurements to validate modeling efforts. Recent advances in laser technology have allowed for in situ vapor measurements at high temporal resolution (e.g., >1 Hz). Here we present concomitant rain and vapor measurements for a series of 17 rain events during the “Continental” rainy season (June through August) at Mpala Research Center in central Kenya.

Field Site

Mpala Research Station, Laikipia District in Central Kenya
Vegetation type: open shrub savanna
Latitude: 0.485597°N, Longitude: 36.870089°E
Ground Surface Elevation: 1608 meters above sea level
Tower height above ground: 22.5 m

Data collection
- Rain samples from 17 rain events between June and August 2012
- Rain samples (n=218) were collected at intervals of 2 to 35 minutes (median of 3 minutes) depending on the rain rate (0.4 to 10.5 mm/hr).
- Vapor was measured continuously at ~2Hz (DLT-100, Los Gatos Research), with an inverted funnel intake 4m above the ground surface.
- Met data, in particular temperature, rain rate and relative humidity, was collected at intervals of 1 minute.

Temporal evolution of a single storm

The composition of the rain and the vapor exhibit a similar behavior during the storm. A matching pattern was observed by Risi et al. (2010). However, here we only see the first "V" of the W shape they observed: this tail observed by Risi et al. (2010) came from very depleted stratospheric air dragged down by the squall line. This is not the case here, because the rain events at our site are purely convective.

Δ^{18}O and ΔD as a measure of disequilibrium

Similarly we have: ΔD-Excess = ΔD-excess_vap - ΔD-excess_vap in equilibrium

The difference observed between the composition of the rain and the vapor can be explain by rain re-evaporation: as the rain drop fall, part of the drop re-evaporates into the atmosphere. If the liquid and the vapor are in equilibrium, we have ΔD = Δ18O = 0. Here we see that the first drop is in equilibrium with the vapor, but moves away from the equilibrium as the storm evolves, to eventually coming back towards equilibrium at the end of the storm. This result is very unexpected: we would expect the first drop to have re-evaporated almost entirely, since it is falling into very dry air.

Rain composition model

Here we show the results of the model against the actual rain composition for two different storms. Our model and the data are strongly correlated (correlation coefficient = 0.72, p = 3.10^{10} on top and 0.49 with p = 8.810^{-1} at the bottom) but the model fails to capture the magnitude of the variations. The output of the model is also strongly dependent of the choice of the V_{vapor}, the amount of water in the vapor reservoir, which is difficult to estimate precisely.

Water vapor model

As expected, the re-evaporation model leads to a more depleted atmospheric water vapor than the model without re-evaporation. For the two storms presented here, the model only captures the composition of the vapor at the very beginning of the rain event. Rayleigh fractionation is a good model for the composition of the rain under re-evaporation but this model is not complex enough to capture the variation of the composition of the vapor.

A possible explanation for this is the influence of evaporation from water accumulating on the ground. This large pool of water would have a more enriched composition and would therefore bring the composition of the vapor up, as observed on the data.

If the model is not quite capturing the composition of the vapor and the rain, the patterns shaping in this unique dataset show that rain re-evaporation is a complex phenomenon that new laser-based technology is now allowing us to study in more details.

Models of rain re-evaporation

Here we present a simple model for the rain re-evaporation to understand the different phenomenon observed in the data. Our model is based on a simple Rayleigh fractionation model for the evaporating raindrops. The water vapor in the atmosphere is seen as a reservoir with a sink (rain condensing) and a source (rain re-evaporation) from Mook (2006):

\[ R_{\text{rain}}(t) = \frac{1}{\Delta D} \ln \left( \frac{R_{\text{vap}}(t) \cdot R_{\text{rain}}(t) - 1}{R_{\text{vap}}(t) - 1} \right) \]

Where \( R \) is the ratio between input and output rates in the atmosphere, \( R_{\text{vap}} \) and \( R_{\text{rain}} \) are the isotope ratios of the vapor; the rain and the liquid condensing from the vapor with: \( R_{\text{cond}} = R_{\text{vap}} \) and \( \delta D_{\text{cond}} = 1 / \alpha \). The composition of the rain is given by a simple Rayleigh fractionation (from Ferronsky 1982):

\[ R_{\text{rain}}(t) = \frac{R_{\text{vap}}(t)}{R_{\text{rain}}(t)} \]

The case with no re-evaporation was also studied. In this case, the equation for the vapor stays the same, taking \( f = 1 \) (all output, no input) and the composition of the rain is the same as the one of the condensate.

\[ R_{\text{rain}}(t) = \frac{1}{\Delta D} \ln \left( \frac{R_{\text{vap}}(t)}{R_{\text{rain}}(t)} \right) \]