Spatial Variability of ^{17}O-excess in Meteoric Water in the Pacific Northwest

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Motivation for Study

Recent advances allowing for high-precision triple oxygen isotope analysis of water have given rise to a new second-order parameter, ^{17}O-excess (Δ^{17}O) which describes the deviation from a reference relationship between δ^{18}O and δ^{17}O. This tracer, like d-excess, reflects the degree of kinetic fractionation that has occurred during phase changes within the hydrologic cycle. However, Δ^{17}O in liquid precipitation does not vary with temperature and is less sensitive to temperature at the evaporative source, making it a useful tool to constrain the mechanisms driving the evolution of d-excess. We present δ^{18}O, δD, and Δ^{17}O data from stream waters along multiple east-west transects in the Pacific Northwest to develop a regional isoscape and explore the sensitivity of Δ^{17}O to changes in elevation and relative humidity and its relationship to d-excess and other isotopic parameters.

Methods

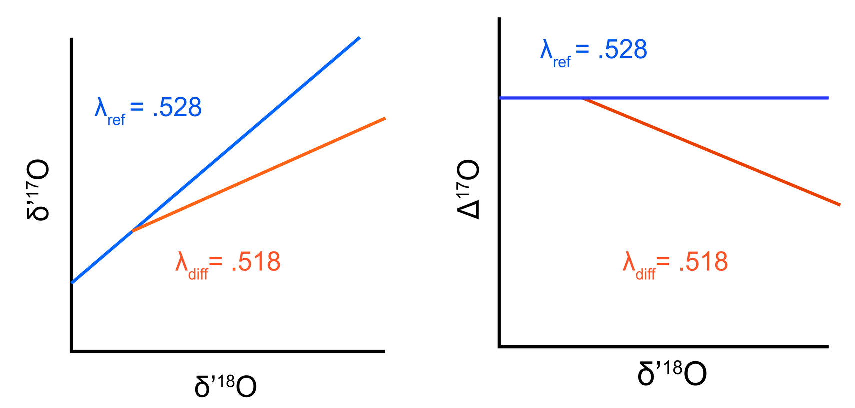
Samples were collected from surfaces waters along two transects spanning Oregon and Washington in the United States. When possible, smaller tributaries were targeted, as they represent an integrated local record of precipitation. However, in arid regions where active tributaries are scarce in summer months, water from larger rivers was collected instead.

High-precision triple oxygen and deuterium measurements were obtained at the University of Washington's Isolab with a Picarro L2140-i, a cavity ring-down spectroscopy analyzer with laser-current-tuned cavity resonance. Data were normalized according to the VSMOW-SLAP scale (Schoenemann et al. 2013), which assumes SLAP values of δ18O = -55.5, Δ^{17}O = 0‰, and gives a reference slope (λref) between δ^{18}O and δ^{17}O of 0.528. Measurement precision on internal standards for δ^{18}O, δD, δ^{17}O, and Δ^{17}O are <0.03 ‰, <0.2 ‰, <0.02 ‰, and <8 per meg respectively, where precision (±) is the standard error (σ/n) (Steig et al., 2013).

Study Site

Figure 1. Map of the study area. Black circles depict sample locations. Water samples were collected in the summer of 2015 and October of 2016 (Olympic samples only). Both transects dessucate two major mountain ranges, the Coast Range and High Cascades in OR and the Olympics and High Cascades in WA. Moisture influx is often controlled by Westerlies with a substantial rainshadow extant east of the Cascades. The satellite derived ground cover was obtained from Natural Earth (www.naturalearthdata.com).

Triple Oxygen Isotopes in Water



Changes in the ratio of water isotopes are generally expressed with respect to the VSMOW standard as $\delta = R_{sample}/R_{VSMOW} + 1$ in parts per mil (‰). However, in triple oxygen isotope studies, a modified δ is used, designated δ', where $\delta'^{x}O = \ln(\delta^{x}O + 1)$.

Δ^{17}O denotes the divergence from a reference relationship between δ^{17}O and δ^{18}O, and is defined: $\Delta^{17}O = \delta'^{17}O - \delta'^{18}O$, where λ_{ref} = .528. Δ^{17}O values are reported in parts per meg.

The slope λ varies slightly depending on the degree of the different fractionation processes. For equilibrium fractionation λ_{eq} = .529 and for purely diffusive fractionation λ_{diff} = .518 (Barkan and Luz, 2007).

Longitudinal Profiles of Δ^{17}O and d-excess

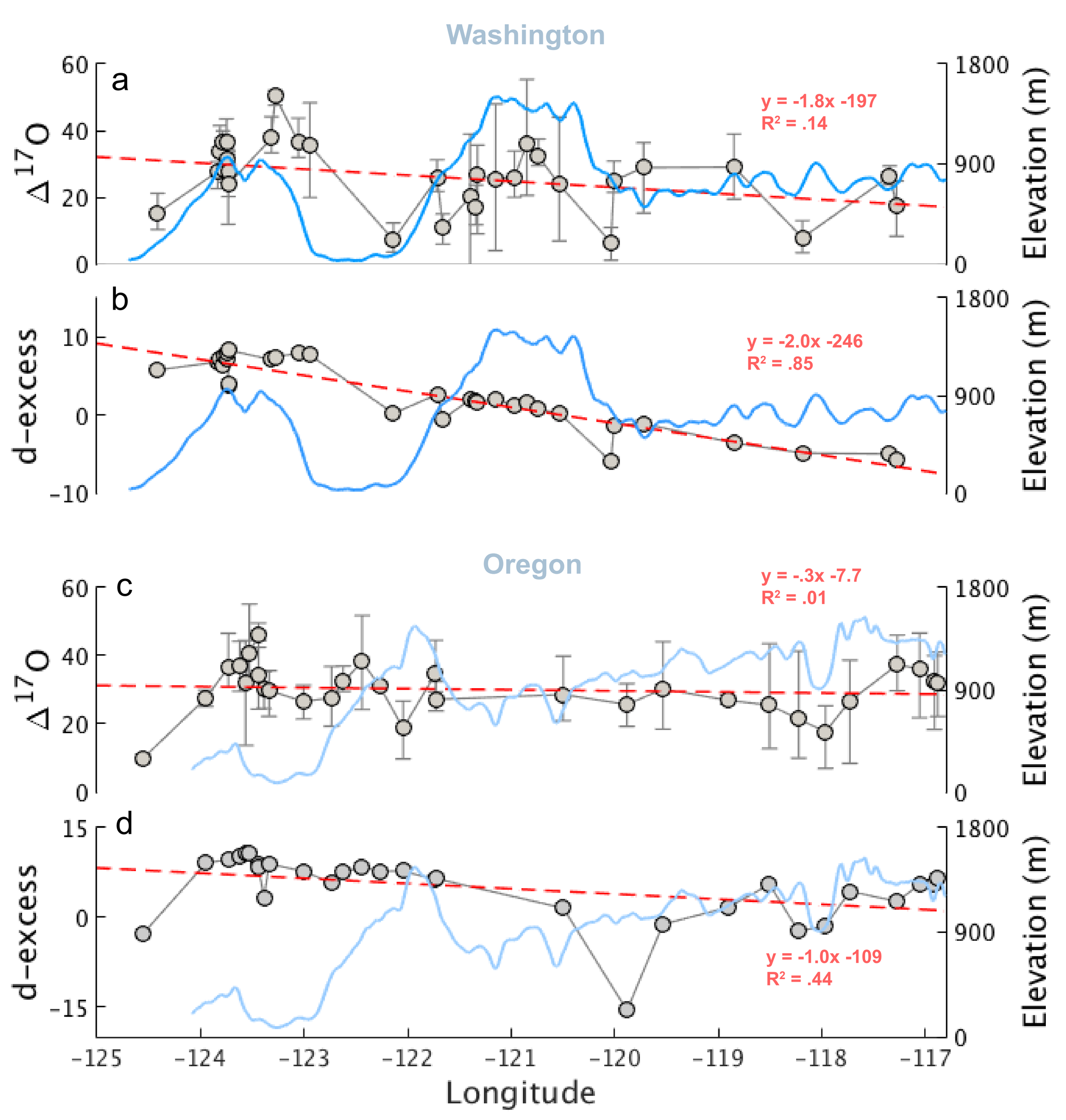


Figure 2. Longitudinal profiles of Δ^{17}O and d-excess across Oregon (a & b) and Washington (c & d). Circles represent the mean value for each sample. For plots (a) and (c), bars depict the range of Δ^{17}O measured for each sample. For plots (b) and (d), bars are omitted since the range in d-excess mostly lies within the boundaries of the circle. Blue lines represent the average elevation of a 50 km swath taken along each transect. Red dashed lines show linear regressions through the data points. For the linear fit in plot (d), two samples were omitted from the regression, one of which was ocean water and the other a highly evaporated outlier.

Variation of Δ^{17}O and d-excess with Relative Humidity

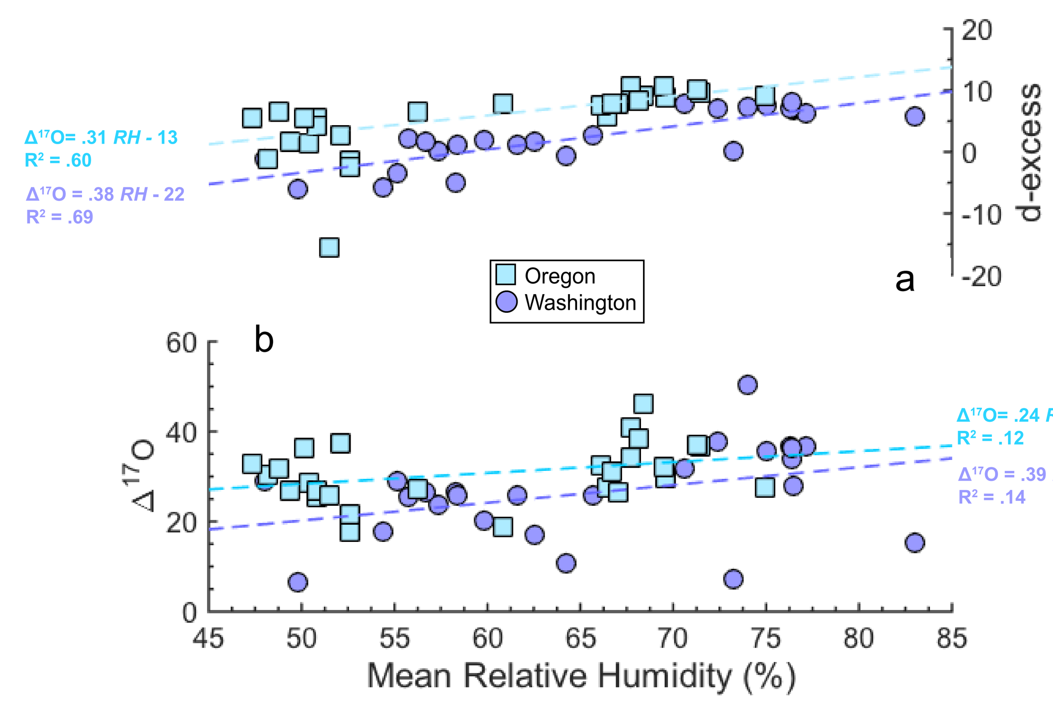


Figure 3 Relationship between d-excess (a) and Δ^{17}O (b) and relative humidity for Washington (purple) and Oregon (blue) stream waters. The relative humidity represents a one year average estimated for each watershed, using the approximation $RH_m = 100 - 5\,(T_m - T_{md})$, where RH_m is the mean relative humidity, T_m is mean temperature at ground surface and T_{md} is the mean dew point temperature. Monthy temperature data was obtained from the PRISM Climate dataset and averaged over the spatial extent of each watershed.

Local Mean Water Line

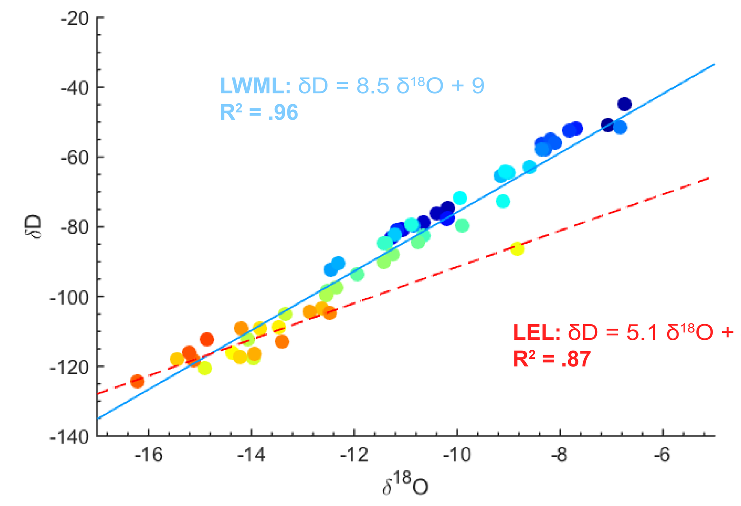


Figure 4. δD-δ^{18}O relationship for Oregon and Washington surface waters. Data points are color-coded by longitude, where blue corresponds to the westernmost samples and red to the easternmost. A regression through the entire dataset (solid blue line) gives the Local Mean Water Line (LMWL). The red dashed line shows a regression for data points east of the Cascade range, giving a Local Evaporation Line (LEL). Both the δ^{18}O/δD and the δD-δ^{18}O slopes concur with previously published values for the region (Coplin, 2001). Similar regressions in δ'^{17}O-δ'^{18}O space give slopes of .5276 and .569 for the entire dataset and for eastern samples respectively.

Variation of Δ^{17}O with δ^{18}O and d-excess

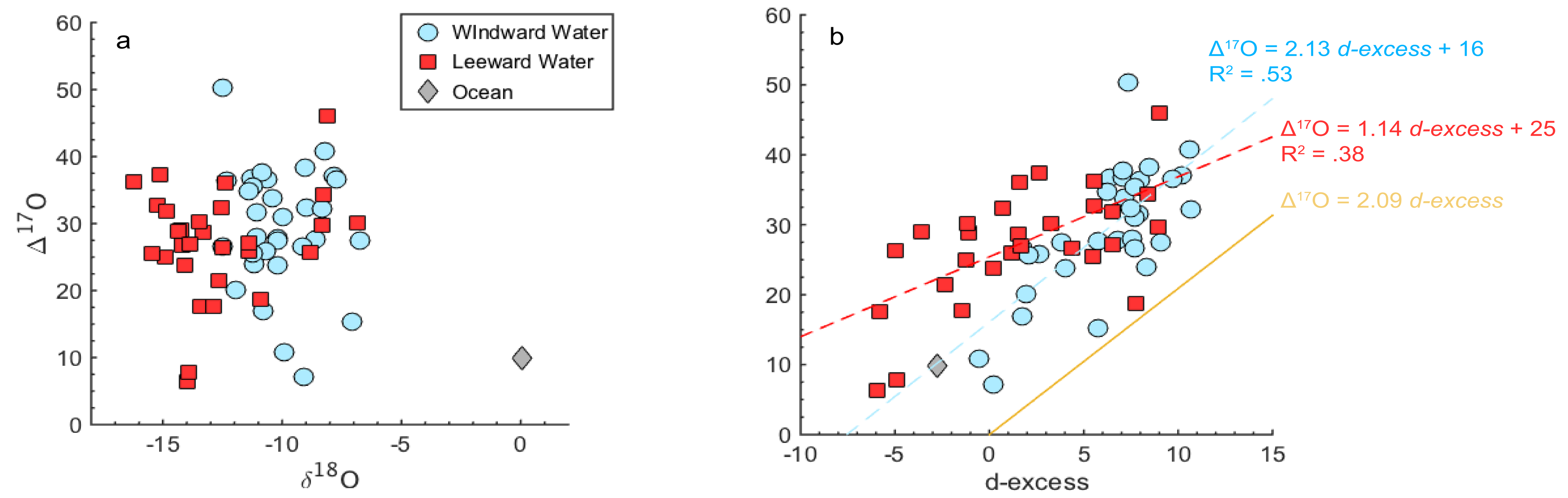


Figure 6a: Variation of Δ^{17}O with δ^{18}O for windward samples (blue) and leeward samples (red). No statistically significant correlation between Δ^{17}O-δ^{18}O is observed for windward or leeward stream waters. **4b:** Variation of Δ^{17}O with d-excess.The yellow line represents the slope of Δ^{17}O-d-excess relationship predicted by a simple one box subcloud evaporation mixing model, which has been utilized extensively to study the effect reevaporation on d-excess (Stewart, 1975; Froelich, 2008, Wang et al., 2016; Salamalikis et. al. 2016). Subcloud evaporation was modeled for select watersheds with site-specific climate conditions obtained through PRISM that were averaged over a ten year span.

Variation of Δ^{17}O and d-excess with Mean Basin Hypsometry for Windward Steams

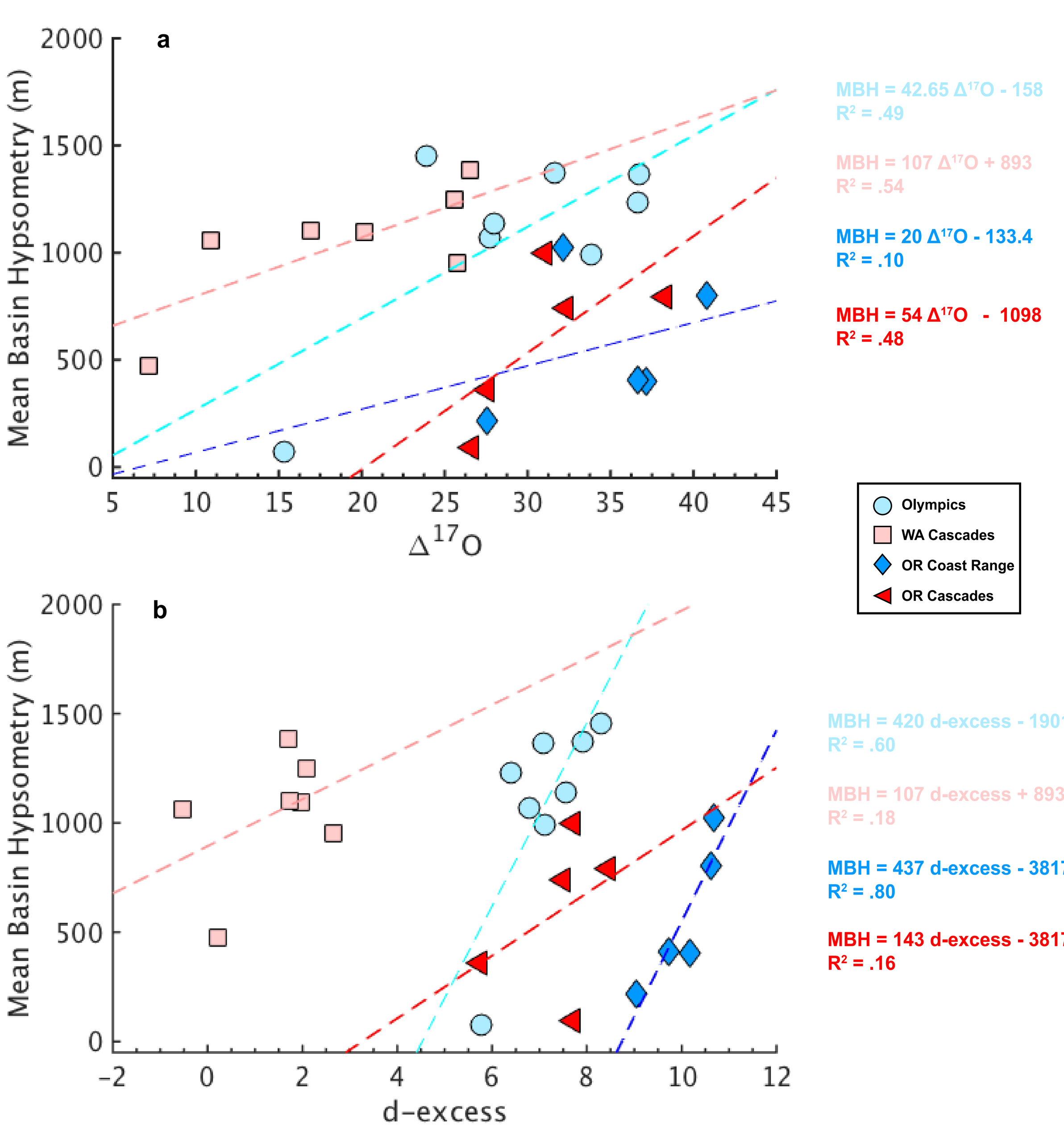


Figure 5. Relationship between Δ^{17}O and d-excess and Mean Basin Hypsometry (MBH) for windward streams. **5b.** Linear regressions a show strong correlation for d-excess and MBH for coastal mountains (R^2 = .6 and .8 for Oregon and Washington respectively). This relationship is substantially weaker for the inland Cascade range (R^2 = .1 and .8)., which coupled with the decrease in slope indicates that evaporation at the surface becomes the dominant signal. This behavior is less pronounced for Δ^{17}O **(5a)**.

Discussion and Takeaways

- The LEL east of the Cascades indicates evaporative enrichment significantly influences the isotopic composition of water in this region. This signal is less apparent for δ'^{17}O-δ'^{18}O, however, as the corresponding λ= .569 for the same samples mostly points to equilibrium fractionation (λ_{eq} = 0.529) with relatively a small proportion of kinetic fractionation (λ_{diff} = 0.518) (Barkan and Luz , 2007).
- Δ^{17}O and d-excess are positively correlated; however, the degree to which these parameters covary differs for windward and leeward samples, indicating that different mechanisms are contributing to Δ^{17}O evolution.
- The Δ^{17}O-d-excess slope of ~2.13 per meg ‰$^{-1}$ (R^2= .53) for windward stream waters is very close to the slope (~2.09) predicted by the simple subcloud evaporation model we employed in this study and slightly above the upper bound (1.6-2.0 per meg ‰$^{-1}$) given by Landais et al. (2010) using a different reevaporation model (Bony, 2008).
- Both the magnitude of the slope (~1.1 per meg ‰$^{-1}$) and the strength of the correlation (R^2= .44) decrease for leeward waters. This observation is consistent with the ~1.2 per meg ‰$^{-1}$ slope Li et al. (2014) recorded for summer precipitation in the western United States. One possible explanation for the decreased slope is that reevaporation in the lee of mountain ranges increasingly drives up Δ^{17}O in water vapor (Landais et al., 2010).
- Elevation appears to influence the spatial distribution of Δ^{17}O (and d-excess to a lesser degree) in mountainous terrain, where the highest values are found at the highest elevation and vice versa. Subcloud evaporation likely contributes to this phenomena, at least in part, as the distance from ground to cloud base for a site increases the evaporated fraction of a raindrop and thereby decreases Δ^{17}O and d-excess in precipitation.
- Overall, Δ^{17}O in the Pacific Northwest appears to bemuch less sensitive to changes in relative humidity than d-excess and lacks a clear relationship with δ^{18}O, thus complicating its use as a proxy for aridity in similar environments.

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