# Wilderness Water Isotopes

## Long-term mountain precipitation and stream water isotopes from New Hampshire wilderness; initial results

**Murray, Georgia.L.D.1, Bailey AdrianaR.2, Kelsey, E.P.3, Griffin, A.3, Gillies, S.1**
1Appalachian Mountain Club, Gorham NH, USA
2National Center for Atmospheric Research, Boulder CO, USA
3Plymouth State University, Plymouth NH, USA

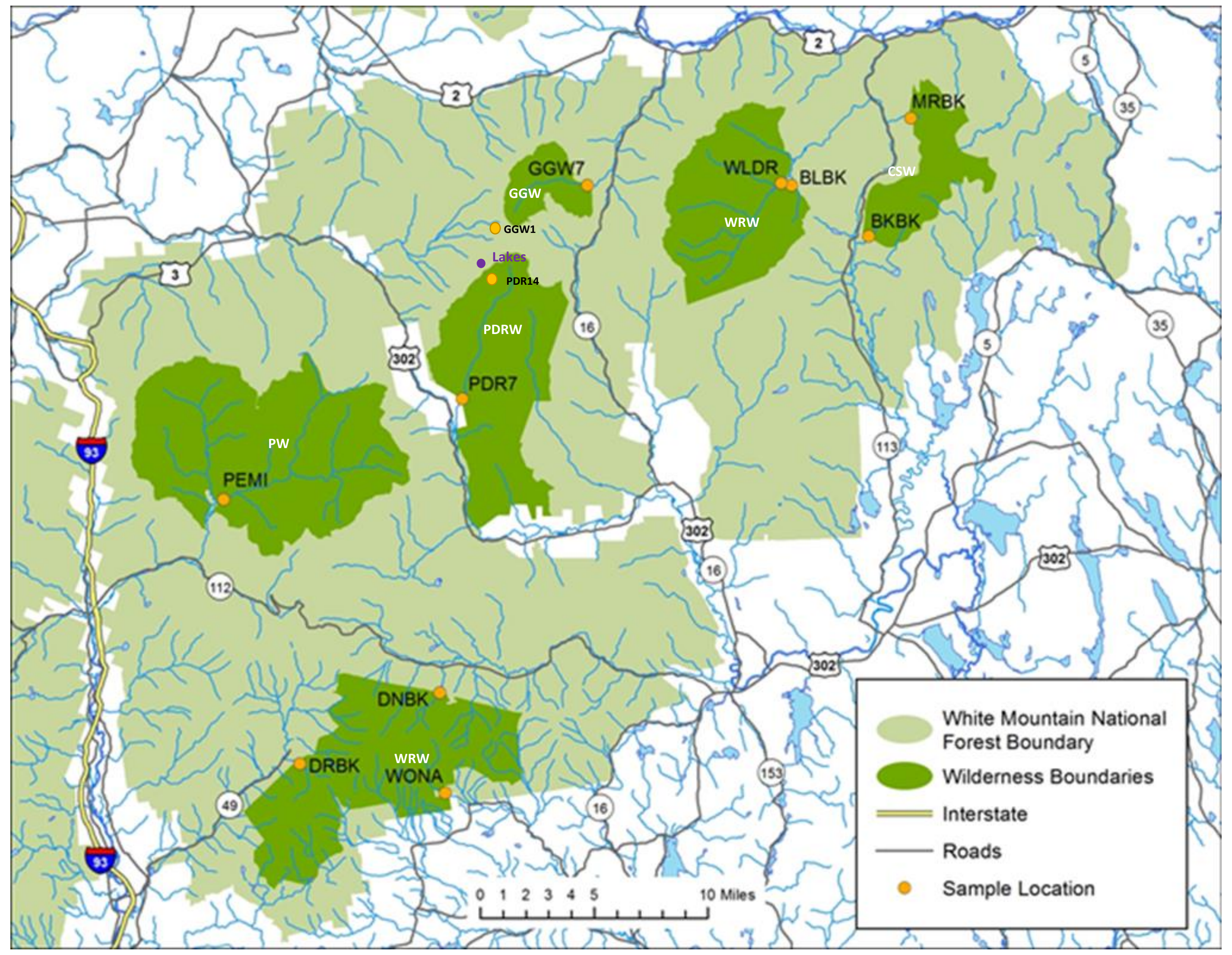

**Figure 1** Sampling sites at the boundaries or within Wilderness areas in the WMNF. Stream sample sites (black text with orange dot), Lakes rain and clouds site (purple) and Wilderness area codes (white text) are defined in Table1.

## INTRODUCTION

Since 1995, The Appalachian Mountain Club (AMC) has collected cloud, rain, and stream samples at mountain sites in the White Mountain National Forest (WMNF) in New Hampshire, USA. Samples are collected during the growing season and used to track air pollution. The WMNF Management Plan has identified the tracking of baseline air quality-related values as a key management objective for assessing the effects of new or modified emission sources of air pollution on Class I Airsheds. Our efforts work in collaboration with the WMNF Clean Air Act and their monitoring of wilderness air quality. In recognition of the potential insights into water and pollution cycles from rain and cloud inputs to stream water, the water isotopic composition of AMC's sample archive was recently analyzed. Here, we report preliminary results from this exploratory analysis.

## METHODS

Growing season stream samples have been collected since 1995 in Wilderness areas across the White Mountain National Forest, NH (Figure 1 map and Table 1). These sites include a climatic gradient from mid-elevation mix deciduous forest sites to those at treeline. Two alpine ponds near the Lakes site and GGW1 site (see map) are also included in the dataset. Rain and cloud water was collected at a high elevation site near Lakes of the Clouds hut during the growing season (see Murray et al. 2013). Soon after collection, sample pH was measured. Precipitation and stream samples were then analyzed for major anions, cations, and silica. Acid neutralizing capacity (ANC) in stream water is calculated as: (sum of cations) - (sum of anions)

Samples are stored in the original HDPE collection bottles and kept at approximately 13-18 degrees C. Water isotopic analysis was conducted on growing season precipitation samples (1996-2016) using a Picarro laser analyzer. A set of the stream and lake water sample archive (1995-1997;2001-2019) were analyzed at Plymouth State University using a Los Gatos Cavity Research analyzer.

No sample evaporation signal was apparent when examining $\delta^{18}O$ over time in either precipitation or stream samples. d-excess was calculated as defined by Dansgaard (1964) to evaluate its use as a tracer of water pathways and residence time.

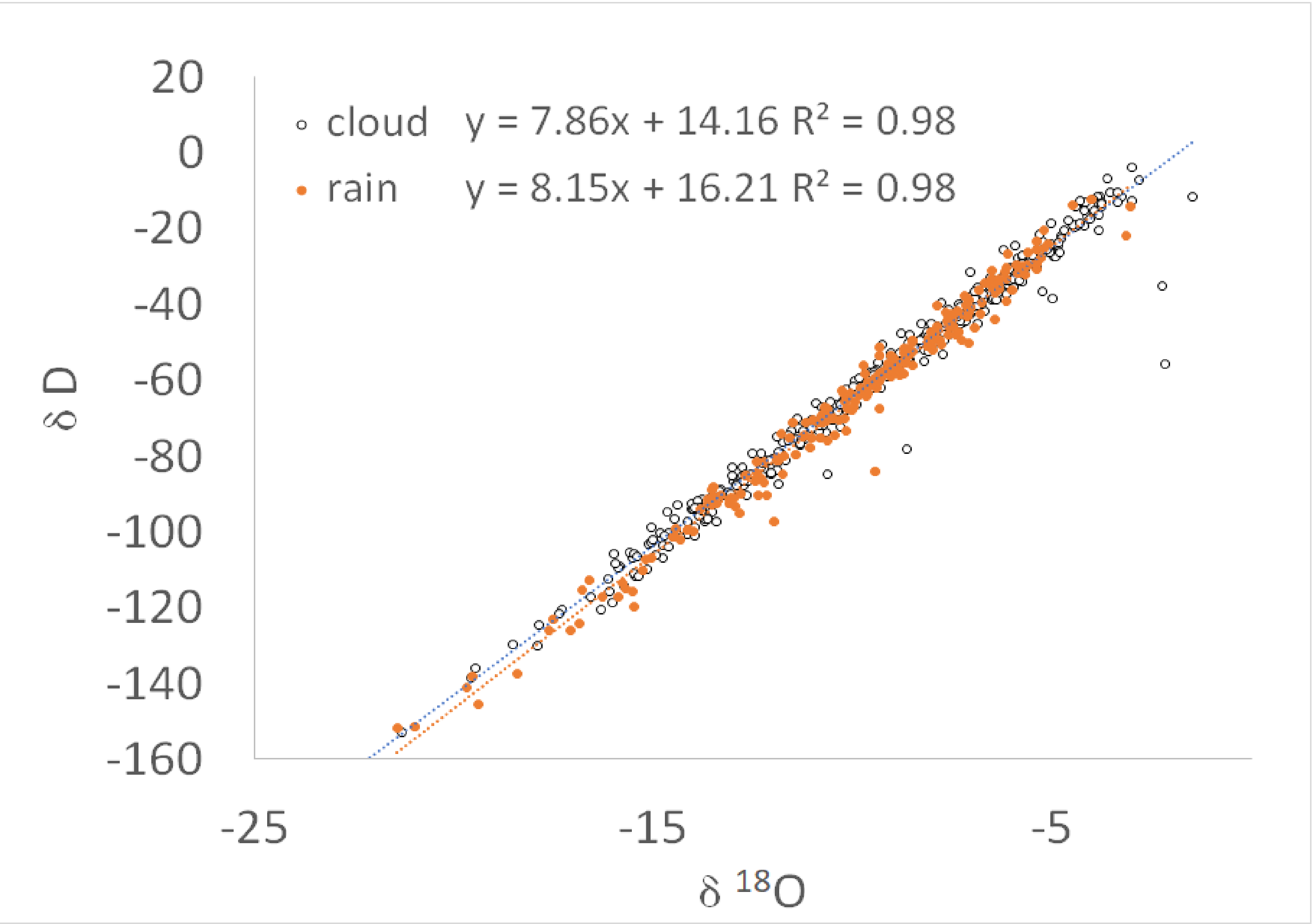

**Figure 2** del 18O vs. del D Lakes Rain and Cloud.

## RESULTS

Using the high elevation (1539 m) rainwater, a local meteoric water line (LMWL) was established ($\delta D = 16.21 + 8.15\,\delta^{18}O$), see Figure 2. This LMWL was similar to that reported at nearby USFS Hubbard Brook Experimental Forest, Thornton, NH for the 2006-2010 growing season but with a slightly steeper slope; Hubbard Brook LMWL slope: 7.56 (Green et al 2015). More isotopic variability occurred in rain and cloud precipitation than in stream waters (Fig. 2 and Fig 3. and Table 2), as has been observed elsewhere (McGuire and McDonnell, 2008, Green et al., 2015). AMC's surface water samples to date had a d-excess inter-quartile range from 11.00-17.25 (values more variable than, but comparable to, stream samples from Hubbard Brook 12.57-16.56) with overall isotopic signatures indicating more of an upper elevation precipitation input signal. Surface water d-excess from our high elevation site was higher than rainwaters, which indicates some evaporation.

**Table 1** Sampling sites in WMNF Wilderness areas, including elevation, latitude and longitude.

| Wilderness Area (codes) | Location ID | Elevation (ft) | LAT DMS | LONG DMS |
|---|---|---|---|---|
| Lakes rain and cloud | Lakes | 5050 | 44° 15' 31" | -71° 19' 6" |
| Great Gulf Wilderness (GGW) | GGW-1 | 4300 | 44° 17’ 05” | -71° 18’ 30” |
| | GGW-7 | 1810 | 44° 18’ 06” | -71° 14’ 58” |
| Presidential Dry River Wilderness (PDRW) | PDR-7 | 1300 | 44° 11’ 31” | -71° 20’ 38” |
| | PDR-14 | 4613 | 44° 15’ 12” | -71° 18’ 53” |
| Pemigewasset (PW) | PEMI | 1460 | 44° 06’ 09” | -71° 33’ 59” |
| Sandwich Range (SRW) | DRBK | 1583 | 43° 56’ 03” | -71° 29’ 58” |
| | WONA | 1290.1 | 43° 54’ 56” | -71° 22’ 16” |
| | DNBK | 1585.9 | 43° 58’ 45” | -71° 22’ 33” |
| Caribou-Speckled (CSW) | MRBK | 1294.4 | 44° 20’ 34” | -70° 57’ 21” |
| | BKBK | 797.5 | 44° 16’ 04” | -70° 59’ 39” |
| Wild River (WRW) | BLBK | 1181.3 | 44° 18’ 02” | -71° 3’ 44” |
| | WLDR | 1171.6 | 44° 18’ 07” | -71° 4’ 17” |

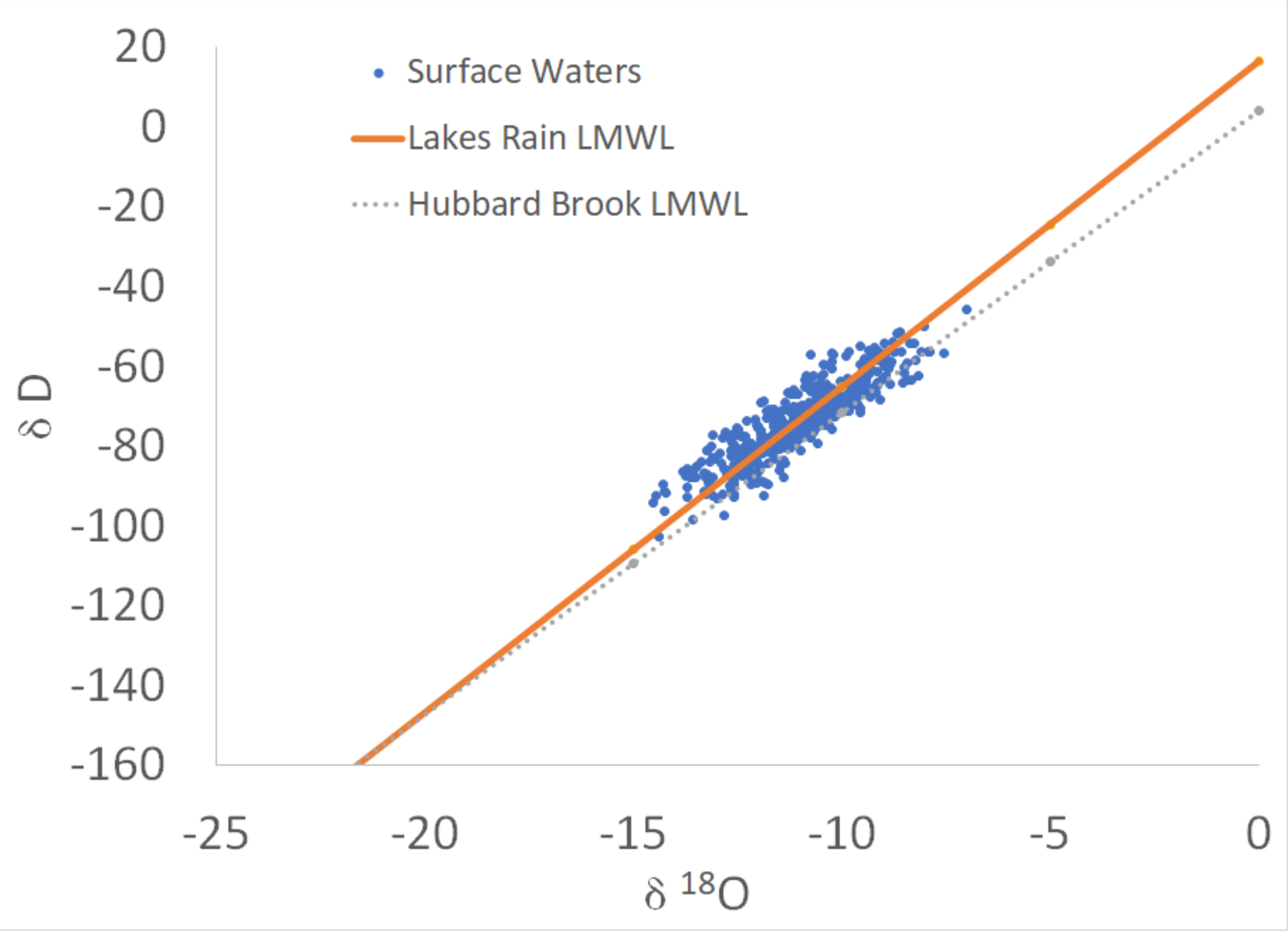

**Figure 3** Stream and alpine pond del 18O vs. del D with Lakes Rain and Hubbard Brook LMWL.

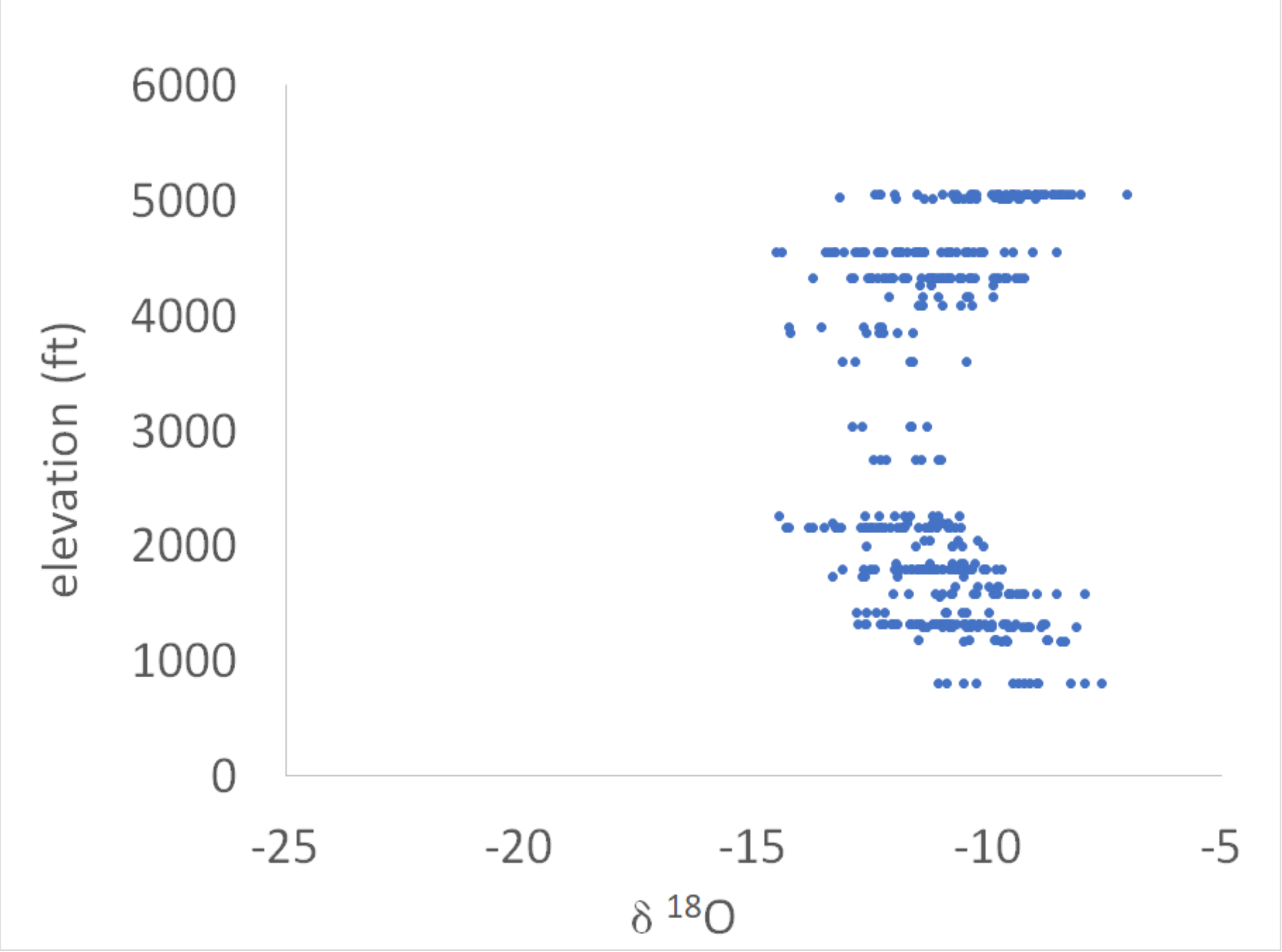

**Figure 4** δ 18O vs. elevation for all stream and alpine pond sites.

Data also suggest depletion in $\delta^{18}O$ in surface waters along an elevational gradient up to about 2500 feet. Sites above 2500 ft showed greater variability including some of the most enriched values (Figure 4) and includes both alpine ponds and headwater streams with the signal in the former potentially explained by evaporation. Enrichment in headwater streams may indicate that fresh precipitation contributions are being measured, which is plausible considering the lack of tree cover and the steep terrain accommodating expedited runoff.

**Table 2** Median and interquartile range of del D, del 18O, an dd-excess for high (>2700), and mid (<2700) elevation surface water sites and high’) rain water. elevation (5050

| | Median (Interquartile range) | | |
|---|---|---|---|
| | δ D | $\delta\ ^{18}O$ | d-excess |
| High elevation surface waters | -74.50<br>(-80.32 -67.47) | -11.00<br>(-11.99 -9.88) | 13.75<br>(11.31 17.03) |
| Mid-elevation surface waters | -73.31<br>(-78.94 to -67.76) | -10.94<br>(-11.83 to -10.22) | 13.74<br>(10.71 to 17.63) |
| High elevation Rain water | -59.20<br>(-81.05 -45.90) | -9.34<br>(-11.86 -7.53) | 15.10<br>(13.10 16.90) |

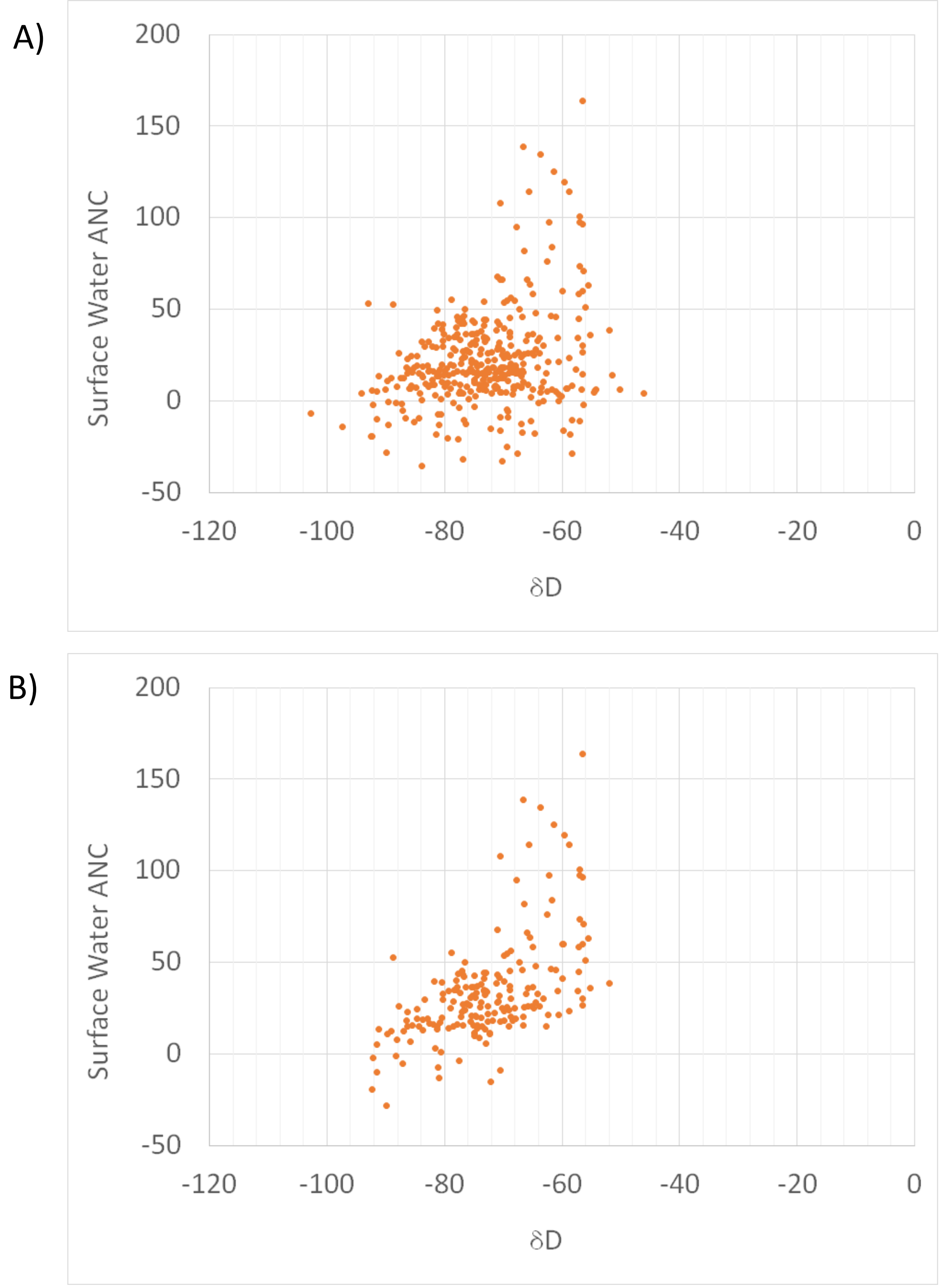

**Figure 5** A) All surface waters. B) Surface waters below 2750 feet in elevation.

Surface water ANC vs. δD (Figure 5A) indicates waters with higher ANCs are often more enriched while the low and negative ANC’s, that are damaging to biota, were not differentiated. However, when only mid-elevation sites were included, waters with negative ANC’s do appear to be more often depleted (Fig. 5B). No relationships between isotopic variables and sulfate were observed, nor were there relationships between chemistry and d-excess. We hypothesize that well buffered waters are more influenced by groundwater while less buffered, low ANC, samples may be more influenced by snowmelt or direct precipitation runoff.

## CONCLUSIONS

This preliminary analysis of water isotopes for a historical surface water archive shows overall consistency in its isotopic signatures to a nearby USFS research site, Hubbard Brook. The decrease in d-excess, from precipitation to surface waters, indicates evaporative processes. Relationships between isotopic variables and ANC are emerging, however additional data, including snow and groundwater samples, are needed before their utility can be fully evaluated. As more data from this historical archive becomes available, we will re-examine these watershed patterns with more detailed mountain topography.

## ACKNOWLEDGMENTS

Thanks to the Research Interns who have collected Wilderness stream waters over the years including Patrick Lynch, AJK Lodge, Rachel Goland, Annie Colgan and so many more! Sampling has been in part funded by the WMNF grant 19-CS-11092200-016 . Thanks also to the USFS Durham Laboratory staff.

## REFERENCES

Dansgaard, W. 1964. Stable isotopes in precipitation, Tellus 16: 436-468.
Green, M. B., Laursen, B. K., Campbell, J. L., McGuire, K. J., and Kelsey, E. P. (2015) Stable water isotopes suggest sub-canopy water recycling in a northern forested catchment. Hydrol. Process., 29: 5193– 5202. doi: 10.1002/hyp.10706.
McGuire, Kevin & McDonnell, Jeffrey. (2008). Stable Isotope Tracers in Watershed Hydrology. 10.1002/9780470691854. Ch. 11.
Murray, G.L.D., Kimball, K.D., Hill, L.B., Hislop, J.E. and Weathers, K.C. Long-Term Trends in Cloud and Rain Chemistry on Mount Washington, New Hampshire. *Water Air Soil Pollut*. **224,** 1653 (2013). https://doi.org/10.1007/s11270-013-1653-7