



Stable isotope compositions of precipitation from Gunnison, Colorado 2007–2016: implications for the climatology of a high-elevation valley



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ABSTRACT

Stable isotope ratios of precipitation are useful tracers of climatic and hydrological processes. To better understand the isotope hydro-climatology of a high-elevation Rocky Mountain valley we collected meteoric water samples from Gunnison, Colorado, USA and determined stable isotope values for 239 individual precipitation events over a nine year period. Annual precipitation in Gunnison is moderately bi-modal with significant winter snowfall and convective summer thunderstorms associated with the North American Monsoon. Stable isotope values of precipitation span a large range, with summer rains as high as $\delta^2\text{H} = +19\text{‰}$ and $\delta^{18}\text{O} = +4.8\text{‰}$ (relative to V-SMOW) and winter snowfall as low as $\delta^2\text{H} = -286\text{‰}$ and $\delta^{18}\text{O} = -36.7\text{‰}$. These data define a local meteoric water line for Gunnison of $\delta^2\text{H} = 7.2 \delta^{18}\text{O} - 4.2$. Monthly meteoric water lines have slopes similar to the Global Meteoric Water Line (~ 8) for winter months and more evaporated slopes (~ 6) during the summer. Monthly mean temperature most strongly controls the monthly isotopic composition of precipitation ($m = 0.61\text{--}0.64 \text{‰}/^\circ\text{C}$); the slope of the isotope/temperature relationship is steeper in summer than winter.

1. Introduction

The stable isotopic composition (D/H and $^{18}\text{O}/^{16}\text{O}$) of meteoric water is a robust tracer of hydrologic and earth surface processes as hydrogen and oxygen are the sole components of the water molecule and are strongly fractionated during phase changes (Craig, 1961; Dansgaard, 1964). Therefore, meteoric waters have a stable isotopic signature that retains valuable information about the waters place of origin, travel history and state and place of deposition (Gat, 1996). The stable isotopic composition of natural waters have been used to study processes in a variety of environmental science fields including: regional climatology (e.g. Friedman et al., 2002; Vachon et al., 2010a, b; Qu et al., 2018), paleoecology/paleoclimatology (e.g. Jouzel et al., 2000; Levin et al., 2006; McLean and Emslie, 2012) and hydrology (e.g. Smith et al., 2002; Reddy et al., 2006; Good et al. 2015; Ala-aho et al., 2018).

Key to all of these applications is an empirical understanding of the annual and monthly stable isotopic composition of precipitation for the site under study. To that end, the International Atomic Energy Agency (IAEA) set up the Global Network of Isotopes in Precipitation (GNIP) monitoring network (IAEA/WMO, 2012) in the 1960's and more recently, a similar isotopes in precipitation network was set up for the

U.S. (United States Network for Isotopes in Precipitation; USNIP) (Welker, 2000; Harvey and Welker, 2000). Researchers have used derivatives of those datasets to produce models which predict stable isotopic values in precipitation and river water across the globe (e.g. Bowen and Wilkinson, 2002; Bowen and Revenaugh, 2003; Dutton et al., 2005; Lechler and Niemi, 2011; Bowen, 2017). The distributions of GNIP and USNIP sites are coarse in some regions which somewhat limits the utility of those data for interpolations to all locations, especially those that have differing climate or geography compared to the sites comprising the greater data set. Stable isotopic variation is often modelled by considering a few key variables: geographic location, elevation, distance inland ('continentality') and persistent relative humidity conditions. Thus, sites with an unusual source of stable isotopic variability could be missed and cause cascading uncertainty in the various applications that follow. More calibration sites (c.f. Lechler and Niemi, 2011) are needed to extend stable isotope datasets and test and improve stable isotope precipitation models.

Here we present a nine-year meteoric precipitation dataset from Gunnison, Colorado. We create a local meteoric water line and assess the relationship between our precipitation stable isotope data and geographic and climatological variables. Our extensive precipitation dataset will be of use to researchers refining stable isotope precipitation

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models, studying the climatology of the North American Monsoon, and investigating the hydrogeology of high-elevation valley systems in the Rocky Mountains and other mountainous regions.

2. Study area

2.1. Geography

Gunnison is located in northeastern quarter of southwestern Colorado

at 38.546 °N and 106.927 °W (Fig. 1). The town, at 2350 m (~7708 ft.), sits in a high valley nearly encircled by the Southern Rocky Mountains including (Fig. 1): the West Elk Mountains, Elk Mountains, Sawatch Range, Cochetopa Hills, La Garita Mountains and the greater San Juan Mountains. Most have peak elevations exceeding 4000 m (~13,000 ft.). The town also sits near the confluence of the Gunnison River, whose tributaries drain the mountains to the northwest through northeast, and Tomichi Creek which drains the southerly and easterly mountain ranges.

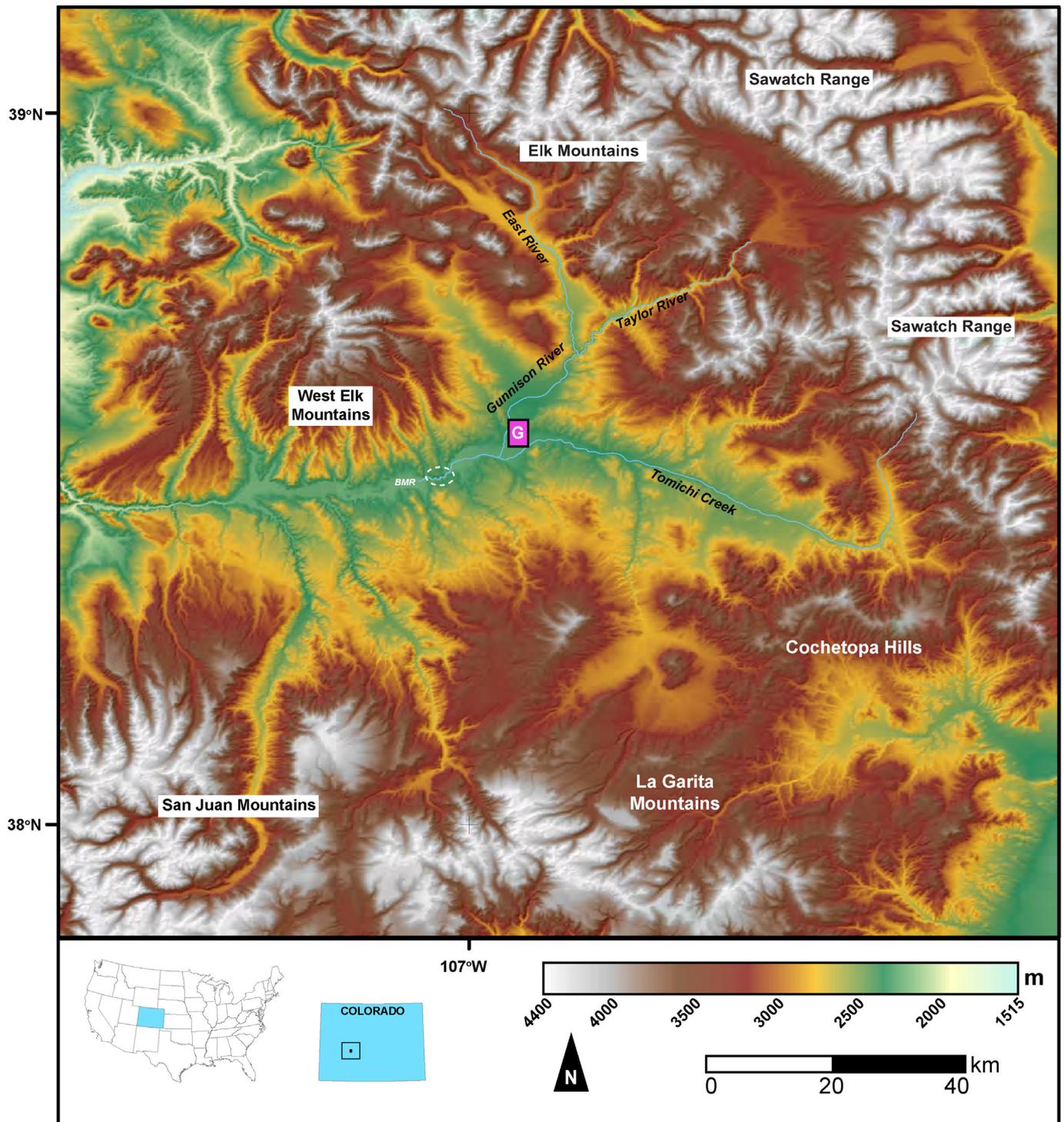


Fig. 1. DEM of the study area. The town of Gunnison is outlined with a pink rectangle filled with a “G”. The location we collected Gunnison River water samples (Supplementary Materials) from is on the west edge of that box near the USGS Gunnison River at Gunnison, CO gauging station. The location of the Gunnison River Canyon is shown with a dashed oval. BMR refers to Blue Mesa Reservoir.

2.2. Climatology

The 30-year climate data (1981–2010) for Gunnison are shown in Fig. 2 (WRCC, 2018). Gunnison's climate is most simply classified as “frigid” (MAT 0–8 °C) and “semi-arid” (MAP 25–50 cm), although with a MAP of ~26 cm, it is likely “arid” some years. Gunnison's climate is highly seasonal with respect to temperature and moderately seasonal with respect to precipitation (Bull, 2007). Three regional geographical and climatological phenomena strongly influence the climate of Gunnison. The first is temperature inversion and cold-air drainage. When significant snow persists in the mountains, cold air drains into the Gunnison valley from the surrounding ranges. This cold air gets trapped in the lower part of the valley because of a constriction in the narrow bedrock-walled Gunnison River Canyon located southwest of town (Fig. 1). If associated with a stable atmosphere aloft this can create temperature inversions where the atmosphere near the valley floors is colder than the atmosphere above the valley. The second phenomenon is the North American Monsoon (NAM) or the southwestern U.S. monsoon (Adams and Comrie, 1997; Higgins et al., 1997; Higgins and Shi, 2000; Vera et al., 2006; Steenburgh et al., 2013). The NAM is defined by a marked increase in warm season precipitation and a seasonal change in predominant wind direction. It most strongly affects the mountainous areas of central and northern Mexico and penetrates northward into the southwestern U.S./four-corners region (Higgins and Shi, 2000; Vera et al., 2006). The NAM affects Gunnison by creating spatially discontinuous convective thunderstorms with strong outflow winds that are carried on southerly winds, typically starting in late June to early July. The precipitation data for Gunnison (Fig. 2) clearly show an increase in warm season precipitation and the synoptic-scale meteorology of most summer rain events are indicative of NAM (Mock, 1996; Wise, 2012; Steenburgh et al., 2013). The third phenomenon influencing Gunnison climate is rain shadow (Fig. 1). The San Juan Mountains are to the south and southwest, West Elk Mountains to the west, and Elk Mountains to the northwest and north of Gunnison all create orographic precipitation on their windward sides. Gunnison lies on the leeward side of all these ranges relative to most prevailing storm tracks.

3. Methods

Rain samples were collected by hand using a clean, dry pan put in an open field away from buildings and trees during the onset of a discreet rain event. We kept the pan outside for the duration of the active rain event and collected the sample immediately after the rain had stopped.

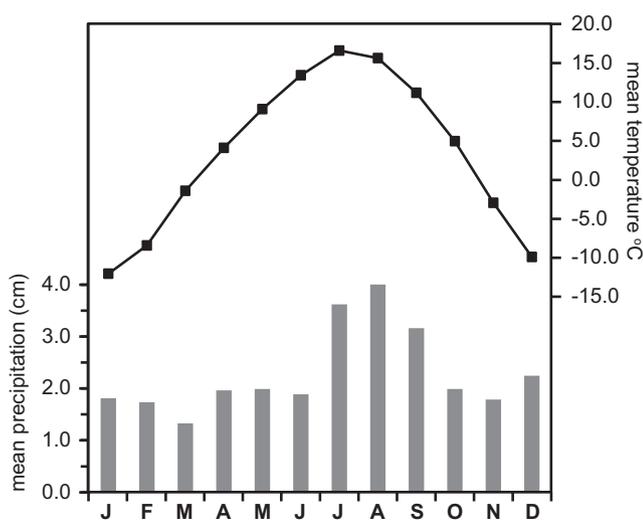


Fig. 2. Average monthly temperatures and precipitation for Gunnison, CO: 1981–2010 (data from WRCC).

Rainwater samples were poured into a sample vial which was tightly closed, sealed with film and put into a refrigerator. This rain sampling technique is slightly different than methods described in the IAEA/GNIP precipitation sampling guide (IAEA/GNIP, 2014) where they provide sampling protocols for integrated monthly or daily rain sampling by suggesting modifications to rain gauges/collectors to reduce evaporation and isotopic fractionation as collected waters sit in the container awaiting sampling. By collecting samples by hand for each rain event we largely avoid the evaporation problem the IAEA/GNIP suggestions try to prevent as our samples were exposed to possible evaporation for much less time than in a fixed sampler. Additional benefits of our sampling scheme include: not needing a surface oil to reduce evaporation (surface oils can necessitate a significant correction when determining water isotopic ratios using laser spectrometric analytical techniques), avoiding bird feces contamination or attempted nesting in the sampler and avoiding deer and/or elk breaking our sampling device and post as they rub their antlers against it. Our rain sampling technique also allows us to sample multiple individual rain events that may occur during a single day (Supplemental Table 1) instead of integrating them into a ‘daily’ sample. Our sampling technique does have some negative aspects. Since we do not use a rain gauge we do not know the amount of rain that fell during an event. This means we cannot test relationships between precipitation isotopic values and precipitation amount (the ‘amount effect’, Eastoe and Dettman, 2016). Snow samples were collected by filling a sample tube with fresh snow from a flat, unobstructed surface that was wiped clean after every snow event, and then sealing and refrigerating the sample. Ultimately our rain and snow sampling methods allow us to determine the stable isotopic composition of individual precipitation events over our nine year sampling window. Our event samples should have less averaging than the IAEA/GNIP daily sampling techniques and less evaporation effects compared to both monthly and daily integrated samples. Therefore, we argue that our sampling technique provides precipitation stable isotope data as useful as daily-averaged fixed container methods.

Every 3–6 months samples were sent to the University of Utah Stable Isotope Ratio Facility for Environmental Research lab (SIRFER) for isotopic analysis. Early collected samples were measured for δD and $\delta^{18}O$ by Isotope Ratio Mass Spectrometry, later samples (starting about 2010) were analyzed using Cavity Ring-Down Spectroscopy. Results from both techniques were corrected for machine offset and drift with time using primary and secondary reference standards of known isotopic composition which were shown in the QA/QC portions of laboratory data reports. We evaluated the QA/QC portion of each report and checked to make sure any deviations between measured and accepted values for isotopic reference standards did not exceed the precision estimates given below. Stable isotope values are given in the standard delta notation: $\delta = (R_{\text{sample}}/R_{\text{standard}} - 1) * 1000$; where $R = {}^2H/{}^1H$ or ${}^{18}O/{}^{16}O$, units are in per mille ‰ and the standard is V-SMOW. Analytical precision for these analyses range from ± 0.5 – 1.5 ‰ for δ^2H and ± 0.1 – 0.2 ‰ for $\delta^{18}O$.

4. Results and discussion

4.1. Meteoric precipitation

A total of 239 meteoric water samples were collected between 11/30/2007 and 10/11/2016 (Supplemental Table 1; additional isotope data for local ground and river waters are also given in the Supplemental Materials). 124 (52%) of the samples were rain (liquid water) while 115 (48%) of the samples were snow, hail or graupel (all technically ice, but herein ‘snow’; vast majority was snow; Supplemental Table 1). For the entire dataset, $\delta^{18}O$ values range from +4.8 to -36.7‰ and δ^2H values range from +19 to -286‰. Thus, precipitation in Gunnison spans a large isotopic range: > 40‰ in $\delta^{18}O$ and 300‰ in δ^2H (compare to Bowen, 2008). Table 1 summarizes the statistics of the dataset in total, broken down by precipitation type and weighted by monthly precipitation amount.

Table 1
Descriptive statistics for the precipitation dataset.

| Precipitation samples | $\delta^{18}\text{O}$ | $\delta^2\text{H}$ | d-excess |
|--|-----------------------|--------------------|----------|
| mean all data | -12.8 | -97 | 5.6 |
| median all data | -12.7 | -90 | 8.9 |
| mean rain samples | -6.3 | -50 | 0.4 |
| median rain samples | -6.7 | -52 | 2.2 |
| max rain samples | 4.8 | 19 | 25.4 |
| min rain samples | -15.9 | -120 | -32.0 |
| mean snow samples | -19.9 | -147 | 11.8 |
| median snow samples | -20.1 | -146 | 11.6 |
| max snow samples | -7.4 | -32 | 38.8 |
| min snow samples | -36.7 | -286 | -6.7 |
| monthly precipitation-weighted isotope annual mean (30-yr 1981–2010 precipitation data) | -12.1 | -92 | 5.3 |
| monthly precipitation-weighted isotope annual mean (11/2007 to 10/2016 precipitation data) | -12.4 | -94 | 5.7 |

Using the entire dataset we determined a Local Meteoric Water Line (LMWL) for Gunnison (Fig. 3) of $\delta^2\text{H} = 7.2 \delta^{18}\text{O} - 4.2$ (all statistical tests done in KaleidaGraph v. 4.5.2). Gunnison's LMWL is similar to the Global Meteoric Water Line (GMWL) defined as $\delta^2\text{H} = 8 \delta^{18}\text{O} + 10$ (Craig, 1961), or $\delta^2\text{H} = 8.17 \delta^{18}\text{O} + 10.35$ (Rozanski et al., 1993) but with a lower slope. Breaking our data set down into rain and snow and comparing the corresponding water lines is illustrative of a fundamental meteorological difference of warm and cold season precipitation in Gunnison (Fig. 3). The 115 snow samples define a *snow* LMWL with a slope of 8.3 which is close to the IAEA–GNIP GMWL slope of 8.17 (Fig. 3) (Rozanski et al., 1993). The 124 rain samples define a *rain* LMWL with a slope of 6.4 indicating that deviation from the GMWL predominantly happens during rain events, likely with some significant amount of evaporation.

4.2. Monthly meteoric precipitation

Breaking our entire meteoric precipitation dataset down by month further demonstrates the isotopic difference between cold (snow) and warm (rain) season precipitation and allows us to study intra-annual isotope and climate relationships for Gunnison (e.g. Harvey and Welker, 2000; Bowen, 2008; Vachon et al., 2010a,b). Our precipitation dataset creates monthly meteoric water lines with strong statistical significance (Table 2) and has good temporal coverage with only one 7 day period without any samples (late May to early June) (Supplemental Table 1).

Monthly meteoric water line slopes for Nov–Apr range from 8.0 to 8.6 which is very similar to the GMWL (Table 2). May–Sept have much lower slopes, ranging from 5.8 to 6.8. Precipitation water line slopes that low indicate considerable evaporation of precipitation during descent. Indeed, the slope of 5.8 for June is approaching the slopes of water lines determined from highly evaporated lakes (e.g. Henderson and Shuman, 2009; Anderson et al., 2016). October has a slope transitional between the GMWL-like slopes and the summer evaporated slopes. However, if

Table 2
Monthly precipitation isotope data and meteoric water line (MWL) slopes and statistics.

| Month | n | Mean $\delta^{18}\text{O}$ | Mean $\delta^2\text{H}$ | Mean d-excess | Monthly MWL slope | r^2 † | % snow |
|-------|----|----------------------------|-------------------------|---------------|-------------------|---------|--------|
| Jan | 18 | -22.2 | -171 | 9.7* | 7.98 | 0.963 | 100 |
| Feb | 24 | -20.9 | -157 | 10.4 | 8.18 | 0.974 | 100 |
| Mar | 15 | -16.7 | -123 | 10.6 | 8.61 | 0.981 | 93 |
| Apr | 21 | -16.5 | -119 | 13.1 | 8.19 | 0.986 | 81 |
| May | 23 | -10.9 | -84 | 3.2 | 6.34 | 0.931 | 22 |
| June | 14 | -6.4 | -56 | -5.0 | 5.80 | 0.922 | 0 |
| July | 33 | -3.2 | -29 | -4.2 | 6.31 | 0.958 | 0 |
| Aug | 25 | -4.8 | -38 | 0.5 | 6.14 | 0.922 | 0 |
| Sept | 20 | -8.5 | -60 | 8.0 | 6.77 | 0.888 | 5 |
| Oct | 12 | -13.8 | -104 | 6.7 | 7.23 | 0.982 | 42 |
| Nov | 13 | -16.6 | -119 | 14.1 | 8.13 | 0.971 | 77 |
| Dec | 21 | -21.7 | -161 | 12.8 | 8.10 | 0.987 | 100 |

* Jan data has high skew so we use median d-excess for that month.

† Regressions for all months have high significance ($p < 0.0001$).

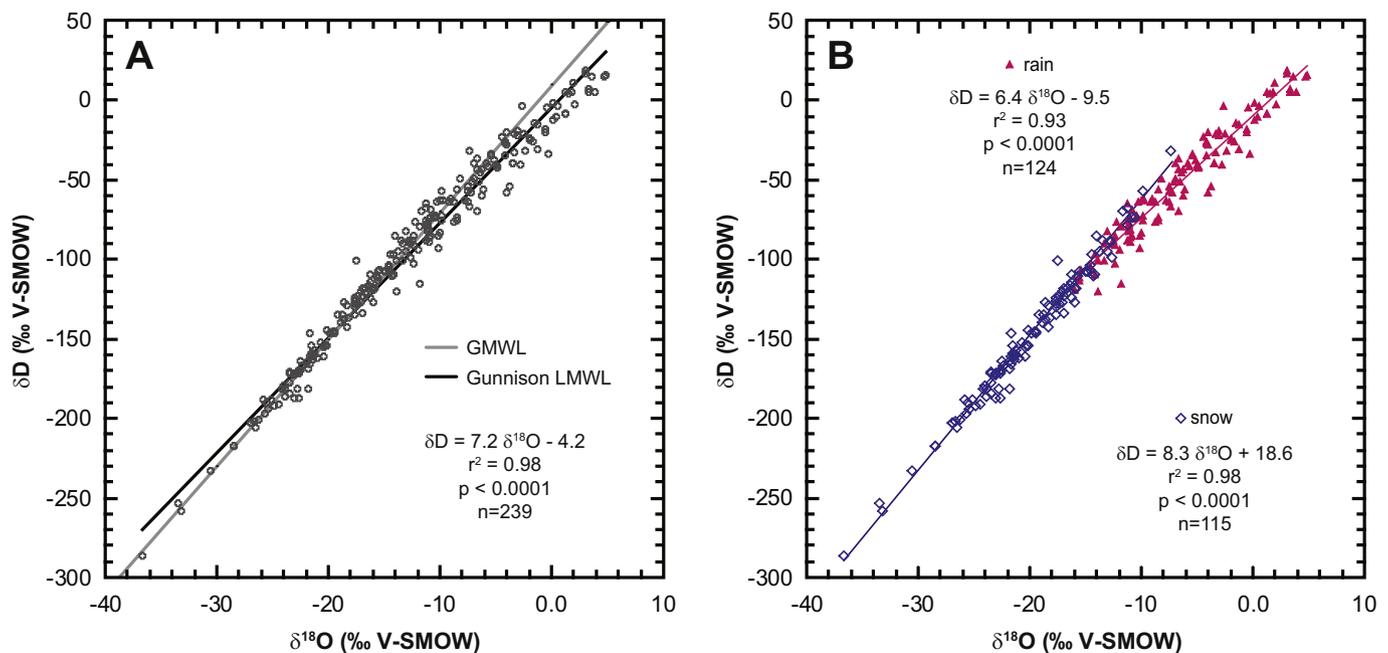


Fig. 3. A: Precipitation isotope data and the local meteoric water line for Gunnison, CO; GMWL = global meteoric water line. B: Precipitation isotope data separated into 'snow' and 'rain' meteoric water lines.

the Oct dataset is split into a first and second half of the month, the first half has a slope of 6.5 ($n = 6$) and the second half has a slope of 7.8 ($n = 6$). May also appears to be a transitional month with a first half slope of 7.3 ($n = 15$) and a second half slope of 5.9 ($n = 8$) (Supplemental Table 1).

The snow dominated monthly isotopic values are indicative of the geographic location of Gunnison: a continental interior, high-elevation valley site receiving often long-traveled winter storms commonly originating in the near northeastern Pacific Ocean region. Fig. 4A and B show the 500 mbar (mb) geopotential surface and 500 mb vector wind means for Nov–Apr of 2007–2016 (monthly MWL slopes of ~ 8 and $>75\%$ snow; Table 2) (NCEP-NARR, 2018). These climate reanalyses indicate mean ridging near the U.S. west coast and broad mean trough in the mid-western U.S with predominantly zonal upper level winds. Short to long wavelength troughs occasionally breakdown the western U.S. ridging (Schafer and Steenburgh, 2008; Wise, 2012; Steenburgh et al., 2013), and bring cold frontal storms with associated precipitation from the northwest, as seen by the mean vector wind directions (Fig. 4B). Orographic enhancement likely increases snowfall relative to lower sites. Climate reanalyses indicate no near surface temperature or relative humidity anomalies for western Colorado over Nov–Apr of 2007–2016 (NCEP-NARR, 2018).

The rain-dominated monthly isotopic values are indicative of significant post-precipitation evaporation, predominantly convective rather than frontal precipitation, and possibly different storm track trajectories and oceanic water vapor sources. Fig. 4C and D show the 500 mb geopotential surface mean and 500 mb vector wind means for Jun–Sept of 2008–2016 (monthly MWL slopes of ~ 6 and $<5\%$ snow; Table 2) (NCEP-NARR, 2018). These reanalyses show a mean broad subtropical

upper level ridge centered over the U.S.–Mexico border. This large zone of hot air is often associated with high pressure aloft and a nearby surface ‘thermal’ low pressure (‘monsoon low’) located to the west of the upper level high (Adams and Comrie, 1997; Higgins and Shi, 2000). The associated mean vector winds show upper level anti-cyclonic flow around the upper level high, which combined with near surface cyclonic flow around the low, brings moisture from the Gulf of Mexico westward and from the Gulf of California/E. Pacific to the north and northeast (Fig. 4D) (Wright et al., 2001). This monsoonal flow often occurs in pulses and increases the dew point temperature of the surface through upper atmosphere in the southwestern U.S. for discrete periods (Adams and Comrie, 1997). Convective daytime heating and orographic lift in mountainous areas produce spatially discontinuous thunderstorms, usually in the afternoon. Climate reanalyses for Jun–Sept 2008 to 2016 indicate near surface temperature anomalies for western Colorado on the order of $+0.6$ °C and a mean relative humidity anomaly of -0.5% (NCEP-NARR, 2018).

Taken together, the climate reanalyses indicate that winter precipitation in Gunnison (months with $>75\%$ snow; Table 2) predominantly comes from northwestern frontal storms (with orographic enhancement) with moisture sources of the northeastern Pacific, although a variety of individual storm tracks are possible. These storms produce snow with isotopic ratios that fall along the GMWL because they experience little evaporation during descent. They produce low isotopic values (Table 1) because they occur during winter at a cold, high-elevation site and have a low fraction of vapor remaining (Dansgaard, 1964). Summer precipitation in Gunnison (months with $<5\%$ snow; Table 2) predominantly comes from monsoonal surges of tropical atmospheric moisture from the Gulf of California/E. Pacific region. Summer daytime heating and

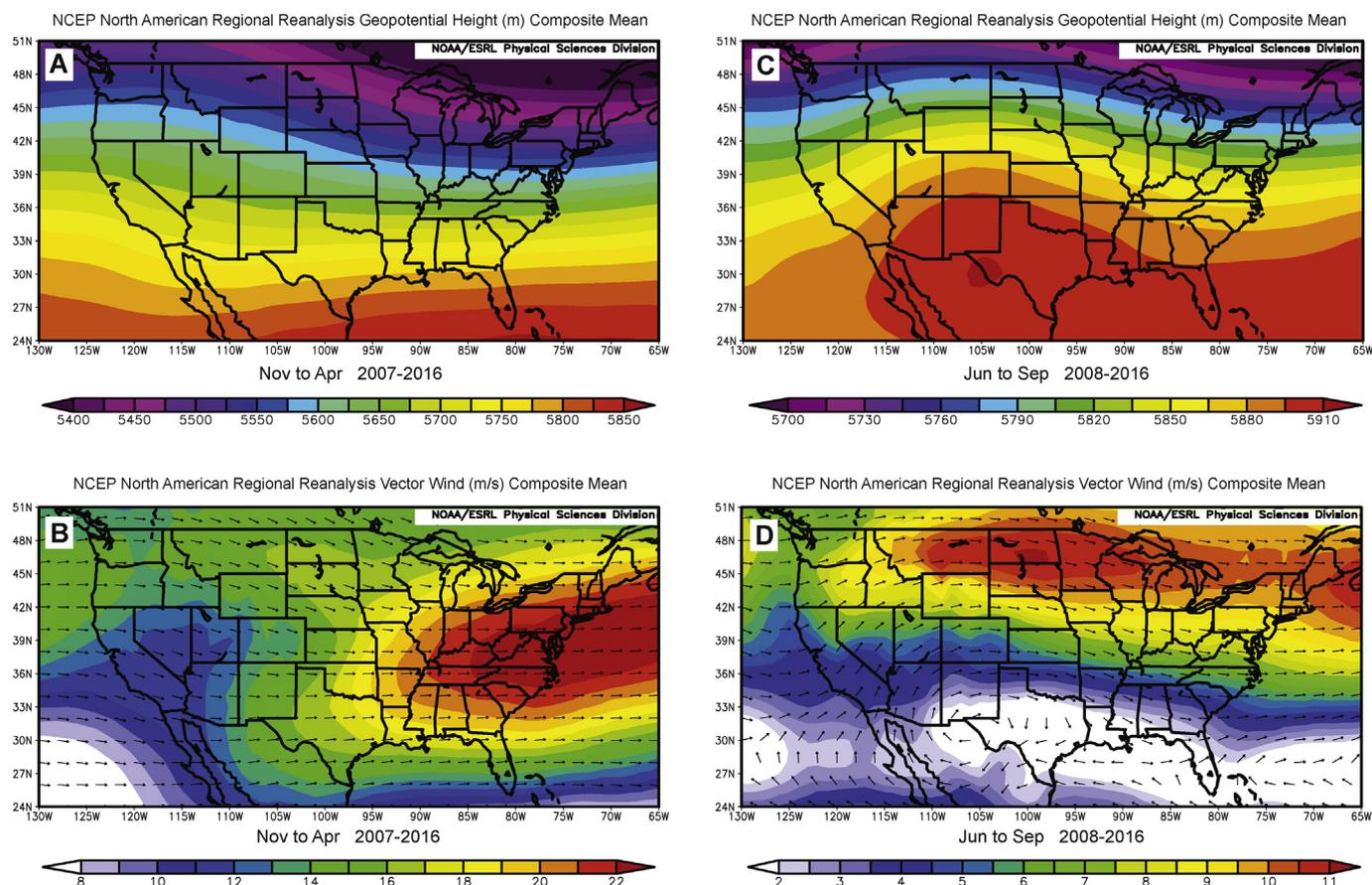


Fig. 4. A: 500 mb geopotential height (m) composite mean for Nov–Apr of 2007–2016. B vector wind (m/s) composite mean for Nov–Apr of 2007–2016. C: 500 mb geopotential height (m) composite mean for Jun–Sep of 2007–2016. D: vector wind (m/s) composite mean for Jun–Sep of 2007–2016. All data from (NCEP NARR, 2018).

orographic effects produce convective precipitation in the afternoons where relative humidity near the ground surface can be low enough for significant evaporation (2008–2016 May–Sept mean 2-m relative humidity range from 36–48%; mid-day values often <10%; NCEP-NARR, 2018), even with low cloud base and free convection levels. These storms produce rain with isotopic ratios that fall significantly off of the GMWL because they experience strong evaporation during descent. They produce high isotopic values (Table 1) because they occur in the summer and are strongly evaporated. The summer climate reanalysis indicate a significant positive summer temperature anomaly and a slight decrease in relative humidity over our collecting period, perhaps causing our summer isotope dataset to be more enriched and evaporated relative to climatology.

Deuterium excess (d-excess) is defined as $d = \delta^2\text{H} - 8 \delta^{18}\text{O}$ and is a measure of deviation ($d = < \text{or} > 10\text{‰}$) from the original GMWL of $\delta^2\text{H} = 8 \delta^{18}\text{O} + 10$ (Craig, 1961; Fröhlich et al., 2002, 2008). Considering the analytical uncertainty associated with the $\delta^2\text{H}$ and $\delta^{18}\text{O}$ measurements yields about a $\pm 1\text{‰}$ standard deviation uncertainty for any d-excess determination. Globally, d-excess is well correlated with the temperature (air and ocean) and relative humidity conditions at the site(s), usually oceanic, where most air mass evaporation occurred (Fröhlich et al., 2002; Pfahl and Sodemann, 2014). Lower d-excess values ($d \sim < 10\text{‰}$) for an air mass are caused by strong evaporation as the lighter $^1\text{H}^2\text{H}^{16}\text{O}$ molecule is evaporated into the vapor phase and the heavier $^1\text{H}^1\text{H}^{18}\text{O}$ molecule is preferentially retained in the liquid phase (Pfahl and Sodemann, 2014). Post-cloud evaporation of precipitation, which occurs as water droplets are falling through a low relative humidity atmosphere will also lower $\delta^2\text{H}$ values relative to $\delta^{18}\text{O}$, thus lowering the d-excess of the resulting precipitation (Stewart, 1975). The Gunnison dataset shows a strong seasonal relationship of d-excess (Tables 1 and 2). Months with >75% snow have a mean d-excess indicative of the GMWL (~10–13‰) while rain dominated months have a much lower mean d-excess (~–5 to 3‰) with a considerably larger variance. The low d-excess values in rainfall support the hypothesis of post-precipitation evaporation during summer rain events. During the NAM, the oceanic water source of atmospheric moisture reaching Gunnison is likely from the Gulf of California/E. Pacific with some possible contribution from the Gulf of Mexico during stronger monsoonal pulses (Adams and Comrie, 1997). This is a different ocean water vapor source than winter storms (Fig. 4C and D) and may affect resulting summer d-excess values (Fröhlich et al., 2002; Pfahl and Sodemann, 2014).

4.3. Intra-annual isotopic and climatic variations

Although the type (state) and season of precipitation appears related to the monthly water line slopes and d-excess (Table 2), and bounds the isotopic composition of precipitation (Fig. 3), we follow previous researchers (e.g. Gat, 1996; Bowen, 2008; Vachon et al. 2010a,b) and investigate the relationship between monthly isotope data and climatological variables (Table 3). We use both 30-yr climate normal (30-yr) (1981–2010) and climate means over the collection period of 11/2007 to 10/2016 (07–16) for each month (WRCC, 2018). The 07–16 data match the 30-yr data very well for temperature but are different for precipitation as several months in the 07–16 precipitation data have 1 to 5 or more missing days. Our temperature data is surface temperature, which is different from some previous work where they used condensation level temperature estimates derived from surface data by subtracting a consistent value by assuming an adiabatic or environmental lapse rate (Vachon et al., 2010a,b). This will not affect the slopes or statistics of the resulting linear regression tests but will change the y-intercepts. We only show the results for $\delta^{18}\text{O}$ as $\delta^2\text{H}$ follows very closely (Table 3).

The only relationship with significance and high coefficient of determination is between $\delta^{18}\text{O}$ and T, both for the 30 yr and 07–16 T data (Table 3). Regression slopes of 0.61–0.64 (‰/°C) are quite steep and approach the higher values presented in Bowen (2008) and Vachon et al. (2010a,b) and indicate that temperature is a strongly controlling variable

Table 3

Linear regression statistics of monthly mean isotope versus monthly mean climate data. Slopes (m) are either: (‰ / °C) or (‰ / cm H₂O).

| Regression | m | r ² | p |
|-------------------------------------|--------|----------------|----------|
| $\delta^{18}\text{O}$ vs. T (30 yr) | 0.643 | 0.956 | <0.00001 |
| $\delta^{18}\text{O}$ vs. T (07–16) | 0.613 | 0.954 | <0.00001 |
| dxs vs. T (30 yr) | -0.510 | 0.616 | 0.002 |
| dxs vs. T (07–16) | -0.478 | 0.594 | 0.003 |
| $\delta^{18}\text{O}$ vs. P (30 yr) | 5.73 | 0.509 | 0.009 |
| $\delta^{18}\text{O}$ vs. P (07–16) | 3.04 | 0.175 | 0.176 |
| dxs vs. P (30 yr) | -4.14 | 0.272 | 0.082 |
| dxs vs. P (07–16) | -2.25 | 0.098 | 0.321 |

of isotopes in precipitation for Gunnison. This is similar to Vachon et al. (2010b) where they find the steepest $\delta^{18}\text{O}$ vs. T slopes in the upper midwest and the Rocky Mountains. If the monthly $\delta^{18}\text{O}$ vs. T data is divided into cold (mean monthly T < 0 °C; Nov–Mar) and warm (mean monthly T > 0 °C; Apr–Oct) months, the resulting regressions are significant and well determined (cold: p = 0.002; r² = 0.97; warm: p < 0.0001; r² = 0.98–0.99) with slopes of 0.53–0.59 (‰/°C) for cold months and 0.96–0.98 (‰/°C) for warm months.

In summary, our precipitation isotope data suggests highly predictable isotope ratios for most winter snowfall events with almost all snow data plotting along the GMWL (Tables 1 and 2; Fig. 3). Snow in Gunnison is largely from frontal storms coming from the northwest to west with a northeastern Pacific Ocean moisture source (Fig. 4A & B). Snow isotopic ratios are well determined by mean monthly temperature with a slope of around 0.5–0.6 (‰/°C). Summer precipitation isotope ratios are probably less predictable as summer months show considerable evaporative effects creating monthly MWL slopes of ~6 with associated low d-excess values (Table 2). Climate reanalyses (Fig. 4C & D) indicates that rains associated with the precipitation peak in summer (Fig. 2) are related to the NAM with moisture sources of the Gulf of California/E. Pacific and possibly the Gulf of Mexico. Rain isotopic ratios are well determined by mean monthly temperature with an incredibly steep slope of 0.9–1.0 (‰/°C). Given the spatially heterogeneous nature of summer NAM rains, the mild-to-extreme possible effects of evaporation on post-cloud rain isotopic values, and the steep isotope and temperature relationship for warm months, we suggest that predicting summer rain isotopic ratios for Gunnison will have a higher uncertainty than for winter. The greater dataset may bear that out as most rain dominated months have larger standard deviations in both isotopic ratios and d-excess than snow dominated ones (Supplemental Table 1). The months of May and October appear transitional between winter and summer, and vice-versa, respectively. Much of the rain data that overlaps with the snow data along the GMWL (Fig. 3) occurs during those two months, apparently before, or after, the strong evaporation of summer can affect the precipitation.

5. Conclusions

The City of Gunnison sits in a frigid, semi-arid, high-elevation valley. The climatology of Gunnison is affected by the North American Monsoon which increases the summer component of precipitation relative to other months. 239 precipitation samples collected from 11/2007 to 10/2016 have a large range of stable isotopic compositions: >40 ‰ in $\delta^{18}\text{O}$ and >300 ‰ in $\delta^2\text{H}$. The precipitation data define a local meteoric water line that is similar to the GMWL but with a slightly lower slope. Rain and snow precipitation data are different, not only in terms of stable isotopic composition but also in deuterium excess and determined water line slopes. This suggests strong evaporation of summer rains and possibly a different air-mass trajectory and oceanic water vapor source between warm and cold season precipitation. There is a strong relationship between monthly isotopic values and temperature, especially for summer months.

Declarations

Author contribution statement

David W. Marchetti: Conceived and designed the experiments; Performed the experiments; Analyzed and interpreted the data; Contributed reagents, materials, analysis tools or data; Wrote the paper.

Suzanne B. Marchetti: Performed the experiments; Analyzed and interpreted the data; Wrote the paper.

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Competing interest statement

The authors declare no conflict of interest.

Additional information

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References

- Adams, D.K., Comrie, A.C., 1997. The North American Monsoon. *Bull. Am. Meteorol. Soc.* 78, 2197–2213.
- Ala-aho, P., Soulsby, C., Pokrovsky, O.S., Kirpotin, S.N., Karlsson, J., Serikova, S., Vorobyev, S.N., Manasypov, R.M., Loiko, S., Tetzlaff, D., 2018. Using stable isotopes to assess surface water source dynamics and hydrological connectivity in a high-latitude wetland and permafrost influenced landscape. *J. Hydrol.* 556, 279–293.
- Anderson, L., Berkelhammer, M., Barron, J.A., Steinman, B.A., Finney, B.P., Abbott, M.B., 2016. Lake oxygen isotopes as recorders of North American Rocky Mountain hydroclimate: holocene patterns and variability at multi-decadal to millennial time scales. *Glob. Planet. Chang.* 137, 131–148.
- Bowen, G.J., 2008. Spatial analysis of the intra-annual variation of precipitation isotope ratios and its climatological corollaries. *J. Geophys. Res.* 113.
- Bowen, G.J., 2017. The Online Isotopes in Precipitation Calculator version 3.1. <http://www.waterisotopes.org>.
- Bowen, G.J., Revenaugh, J., 2003. Interpolating the isotopic composition of modern meteoric precipitation. *Water Resour. Res.* 39, 1299.
- Bowen, G.J., Wilkinson, B., 2002. Spatial distribution of $\delta^{18}\text{O}$ in meteoric precipitation. *Geology* 30, 315–318.
- Bull, W.B., 2007. *Tectonic Geomorphology of Mountains*. Blackwell, Singapore.
- Craig, H., 1961. Isotopic variations in meteoric waters. *Science* 133, 1702–1703.
- Dansgaard, W., 1964. Stable isotopes in precipitation. *Tellus* 16, 436–468.
- Dutton, A., Wilkinson, B.H., Welker, J.M., Bowen, G.J., Lohmann, K.C., 2005. Spatial distribution and seasonal variation in $^{18}\text{O}/^{16}\text{O}$ of modern precipitation and river water across the conterminous USA. *Hydrol. Process.* 19, 4121–4146.
- Eastoe, C.J., Dettman, D.L., 2016. Isotope amount effects in hydrology and climate reconstructions of monsoon climates: implications of some long-term data sets for precipitation. *Chem. Geol.* 430, 78–89.
- Friedman, I., Smith, G.I., Johnson, C.A., Moscati, R.J., 2002. Stable isotope compositions of waters in the Great Basin, United States, 2, Modern precipitation. *J. Geophys. Res.* 107, 4401.
- Fröhlich, K., Gibson, J.J., Aggarwal, P., 2002. Deuterium excess in precipitation and its climatological significance. In: *Study of Environmental Change Using Isotope Techniques*. Proc. Int. Conf., pp. 54–66.
- Fröhlich, K., Kralik, M., Papesch, W., Scheifinger, H., Stiehler, W., 2008. Deuterium excess in precipitation of Alpine regions – moisture recycling. *Isot. Environ. Health Stud.* 44, 61–70.
- Gat, J.R., 1996. Oxygen and hydrogen isotopes in the hydrologic cycle. *Annu. Rev. Earth Planet Sci.* 24, 225–262.
- Good, S.P., Noone, D., Bowen, G.J., 2015. Hydrologic connectivity constrains partitioning of global terrestrial water fluxes. *Science* 349, 175–177.
- Harvey, F.E., Welker, J.M., 2000. Stable isotopic composition of precipitation in the semi-arid north-central portion of the U.S. Great Plains. *J. Hydrol.* 238 (1–2), 90–109.
- Henderson, A.K., Shuman, B.N., 2009. Hydrogen and oxygen isotopic compositions of lake water in the western United States. *Geol. Soc. Am. Bull.* 121, 1179–1189.
- Higgins, R.W., Yao, Y., Wang, X.L., 1997. Influence of the north American monsoon system on the U.S. Summer precipitation regime. *J. Clim.* 13, 759–776.
- Higgins, R.W., Shi, W., 2000. Dominant factors responsible for interannual variability of the summer monsoon in the southwestern United States. *J. Clim.* 10, 2600–2622.
- IAEA/WMO, 2012. *Global Network of Isotopes in Precipitation*. Global Network of Isotopes. http://www-naweb.iaea.org/naweb/ih/IHS_resources_gnip.html.
- IAEA/GNIP, 2014. *Precipitation Sampling Guide, v.2.02 September 2014*. http://www-naweb.iaea.org/naweb/ih/documents/other/gnip_manual_v2.02_en_hq.pdf.
- Jouzel, J., et al., 2000. Water isotopes in precipitation: data/model comparison for present-day and past climates. *Quat. Sci. Rev.* 19, 363–379.
- Lechler, A.R., Niemi, N.A., 2011. Controls on the spatial variability of modern meteoric $\delta^{18}\text{O}$: empirical constraints from the western US and east Asia and implications for stable isotope studies. *Am. J. Sci.* 311, 664–700.
- Levin, N.E., Cerling, T.E., Passey, B.H., Harris, J.M., Ehleringer, J.R., 2006. A stable isotope aridity index for terrestrial environments. *Proc. Natl. Acad. Sci.* 103, 11201–11205.
- McLean, B.S., Emslie, S.D., 2012. Stable isotopes reflect the ecological stability of two high-elevation mammals from the late Quaternary of Colorado. *Quat. Res.* 77, 408–417.
- Mock, C.L., 1996. Climatic controls and spatial variations of precipitation in the western United States. *J. Clim.* 9, 1111–1125.
- NCEP-NARR, 2018. *NCEP Reanalysis Data Provided by the NOAA/OAR/ESRL PSD, Boulder, Colorado, USA from*. <https://www.esrl.noaa.gov/psd/last>. (Accessed 26 June 2018). see also: Mesinger, F. et al. 2006. North American regional reanalysis. *Bull. Am. Meteorol. Soc.* 87:343–360.
- Pfahl, S., Sodemann, H., 2014. What controls deuterium excess in global precipitation? *Clim. Past* 10, 771–781.
- Qu, S., Chen, X., Wang, Y., Shi, P., Shan, S., Gou, J., Jiang, P., 2018. Isotopic characteristics of precipitation and origin of moisture sources in Hemuqiao catchment, a small watershed in the lower reach of the Yangtze River. *Water* 10, 1170.
- Reddy, M.M., et al., 2006. Characterization of surface and ground water $\delta^{18}\text{O}$ seasonal variation and its use for estimating groundwater residence times. *Hydrol. Process.* 20, 1753–1772.
- Rozanski, K., Araguas-Araguas, L., Gonfiantini, R., 1993. Isotopic patterns in modern global precipitation. In: Swart, P.K., Lohmann, K.C., McKenzie, J., Savin, S. (Eds.), *Climate Change in continental Isotopic Records*. American Geophysical Union, Washington, DC, pp. 1–36.
- Schafer, J.C., Steenburgh, W.J., 2008. Climatology of strong Intermountain cold fronts. *Mon. Weather Rev.* 136, 784–807.
- Smith, G.I., Friedman, I., Veronda, G., Johnson, C.A., 2002. Stable isotope compositions of waters in the Great Basin, United States, 3, Comparison of groundwaters with modern precipitation. *J. Geophys. Res.* 107, 4402.
- Steenburgh, W.J., Redmond, K.T., Kunkel, K.E., Doesken, N., Gillies, R.R., Horel, J.D., Hoerling, M.P., Painter, T.H., 2013. Present weather and climate: average conditions. In: Garfin, G., Jardine, A., Merideth, R., Black, M., LeRoy, S. (Eds.), *Assessment of Climate Change in the Southwest United States: A Report Prepared for the National Climate Assessment*. Island Press, Washington, DC, pp. 56–73. A report by the Southwest Climate Alliance.
- Stewart, M., 1975. Stable isotope fractionation due to evaporation and isotopic exchange of falling waterdrops: applications to atmospheric processes and evaporation of lakes. *J. Geophys. Res.* 80, 1133–1146.
- Vera, C., et al., 2006. Toward a unified view of the American monsoon systems. *J. Clim.* 19, 4977–5000.
- Vachon, R.W., Welker, J.M., White, J.W.C., Vaughn, B.H., 2010a. Moisture source temperatures and precipitation $\delta^{18}\text{O}$ -temperature relationships across the United States. *Water Resour. Res.* 46, W07523.
- Vachon, R.W., Welker, J.M., White, J.W.C., Vaughn, B.H., 2010b. Monthly precipitation isoscapes ($\delta^{18}\text{O}$) of the United States: connections with surface temperatures, moisture source conditions, and air mass trajectories. *J. Geophys. Res.* 115, D21126.
- Wise, E.K., 2012. Hydroclimatology of the US intermountain west. *Prog. Phys. Geogr.* 36, 458–479.
- Welker, J.M., 2000. Isotopic ($\delta^{18}\text{O}$) characteristics of weekly precipitation collected across the USA: an initial analysis with application to water source studies. *Hydrol. Process.* 14, 1449–1464.
- WRCC, 2018. *Western Regional Climate Center, Cooperative Climatological Data Summaries last accessed 2 July 2018*. <http://wrcc.dri.edu/climatedata/climsum/>.
- Wright, W.E., Long, A., Comrie, A.C., Leavitt, S.W., Cavazos, T., Eastoe, C., 2001. Monsoonal moisture sources revealed using temperature, precipitation, and precipitation stable isotope timeseries. *Geophys. Res. Lett.* 28 (5), 787–790.