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Key Points:

- The most depleted isotopic water inputs occur in the upper subalpine where snow accumulation is high and rainfall is low.
- Deep snowpack and shading of conifer forests limit the influence of kinetic fractionation (sublimation) of snowpack in the subalpine.
- Effects of kinetic fractionation decreases in big snow years except in the lower montane where added snowfall reduces water-limitation.

Abstract

A coupled hydrologic and snowpack stable water isotope model assesses controls on isotopic inputs across a large, mountainous basin. The most depleted isotope conditions occur in the upper subalpine where snow accumulation is high and rainfall is low. Snowmelt evolution over time indicates isotopic enrichment is not dictated by melt fractionation but is determined by elevation which controls the amount, phase and isotopic mass of spring precipitation coincident with the ablation period. With respect to snowpack kinetic fractionation, its effect on snowmelt is a balance between energy and snow-availability. It is highest above treeline and in the shrub-dominated upper montane where vegetation shading is low, while deep snowpack and conifer forests limit the influence of kinetic fractionation in the subalpine. Wet years reduce the effects of snowpack fraction on snowmelt across the basin, except in the lower montane where added snowfall bolsters water-limited conditions.

Plain Language Summary

Stable water isotopes have been used for decades in hydrology to track vegetation water use, groundwater recharge and stream water source. Watersheds reliant on snow alter the timing of water inputs through snow storage and melt and may produce a different isotopic input signal due to evaporation of the snowpack prior to melt. We combine a hydrologic and snowpack isotope model to understand how landscape position and climate may affect isotopic water inputs in a large mountain basin with nearly 2 km in vertical relief. The heaviest isotopes occur in the upper subalpine where snow accumulation is highest and rain inputs are low. The temporal evolution of isotopes in snowmelt is controlled by elevation and its influence on the amount, phase (rain or snow) and isotopic mass of spring precipitation coincident with the snowmelt period. Changes to the snowpack isotopic signature by vapor loss are most important where vegetation does not

shade the snow, where moderate snowfall occurs and evaporation potential is relatively high. Changes are highest above treeline and in the shrub-dominated upper montane. Less change occurs in the deep snow found in the conifer forests of the subalpine, and in the snow-limited lower montane.

1 Introduction

Mountain snowpack is an important water resource globally (Barnett et al., 2005) and is especially vulnerable to climate change (Hock et al., 2019; Huning & AghaKouchak, 2020; Milly et al., 2008). Despite the importance of snow-dominated systems, uncertainty on how snow becomes streamflow remains (Jullander & Clayton, 2018). Stable isotopes of water ($^{18}\text{O}/^{16}\text{O}$, $^2\text{H}/^1\text{H}$) have long been used as tracers in hydrologic research to identify the partitioning of rain and snow to vegetation water use (Berkelhammer et al., 2020; Sprenger et al., 2016), groundwater recharge (Earman et al., 2006; Fiorella et al., 2018; Jasechko, 2019; Oiro et al., 2018), and stream water (Cowie et al., 2017; Zhang et al., 2018). Isotopic mass balance studies in watersheds reliant on snow water must adjust isotopic boundary influxes as a function of snow storage and snowmelt timing, and the potential for isotopic modification due to post-depositional fractionation in the snowpack. While isotopic fractionation processes in snow are fairly well defined (section 1.1), less work has addressed these processes at watershed-scales in mountain environments. Challenges are largely due to obtaining hydrologic and isotopic observations at the scales important to snow processes (Bales et al., 2006; Clark et al., 2011; Mott et al., 2018). Temporal scales are defined by meteorological inputs (hourly-daily) needed to quantify the energy balance of the snowpack, while the spatial resolution needed to capture non-uniform hydrologic processes in mountain systems is on the order of 100 to 250 m (Baba et al., 2019; Foster et al., 2020). An added complication arises given most of snow resides near treeline (Carroll et al., 2019) with regular and safe access for field samples often not possible. As a consequence, isotopic tracer studies in mountain environments tend to extrapolate limited plot-scale, snowpit data across an entire watershed (Bearup *et al.*, 2014; Carroll *et al.*, 2018; Fang *et al.*, 2019; Evans *et al.*, 2016) with the potential to introduce significant error in stream water source estimates dependent on isotopic inputs.

With respect to time-variable isotopic inputs from snowmelt, these have largely been confined to laboratory experiments (Feng et al., 2002; Taylor et al., 2002) or to field studies focused on snowpit (Friedman et al., 1991; Stichler et al., 1981; Taylor et al., 2001) or hillslope scales (Evans et al., 2016). More recently, Ala-aho et al. (2017) incorporated changes in snow isotopic values with a snow process model to estimate a spatially distributed snowmelt isotope signal into basins with contrasting snow conditions. We apply work by Ala-aho et al. (2017) across a much larger Colorado River headwater basin with greater relief. We constrain this model using a comprehensive isotopic dataset in precipitation, snowpack and snowmelt (Carroll et al., 2022). Through this data-modeling framework, we investigate water isotopic inputs at high spatial and temporal resolution over multiple years with reference to snow processes. Our objective

is to isolate key controls on isotopic water inputs and better constrain where and when post-depositional fractionation is important. Results will inform data needs for hydrologic tracer-based studies within mountain environments.

1.1 Stable Water Isotope Overview

Stable water isotopes are reported as the ratio of heavier to lighter isotopes in a sample ($R_{sample} = {}^{18}O/{}^{16}O$, or ${}^2H/{}^1H$) relative to the Vienna Standard Mean Ocean Water standard (R_{VSMOW}). Results are presented in units of per mil (‰) as $\delta = 1000 * (R_{sample} - R_{VSMOW})/R_{VSMOW}$. The second order isotope parameter, d-excess ($d\text{-excess} = {}^2H + 8\text{ }^{18}O$) expresses the deviation of local samples from the Global Meteoric Water Line (GMWL) as plotted in the dual-isotope space defined by 2H versus ${}^{18}O$. D-excess decrease is in response to kinetic processes resulting from the molecular mass differential between oxygen and hydrogen during vapor loss. Specifically, the lighter 2H molecule turns to vapor more readily than the heavier ${}^{18}O$ molecule. A lowering of d-excess from its initial isotopic state indicates either evaporation or sublimation (Clark & Fritz, 1997).

In this study, we define the initial state as the isotopic composition of precipitation. Precipitation inputs depend on temperature, relative humidity, origin of the air mass (Clark & Fritz, 1997). For the continental interior of the United States, snowfall originates from northwest frontal storms (Marchetti & Marchetti, 2019) and contains depleted isotopic values due to cold, high elevation conditions with a low vapor fraction (Dansgaard, 1964). In contrast to snow, rain tends to experience more recycling of moisture via evaporation than winter precipitation as storms move inland from the ocean. Consequently, rainfall contains more enriched isotopic conditions and is comparatively lower in d-excess. Precipitation isotopic inputs are also affected by elevation with ${}^{18}O$ lapse rates in North America ranging from -0.17 to -0.22‰ per 100 m in elevation (Friedman et al., 1992; Tappa et al., 2016). After deposition, the ratios of heavy to light isotopes in the snowpack can vary due to diffusional transport of water from the soil, temperature-gradient induced vapor diffusion within the snow column, lateral flow through the snowpack and fractionation processes associated with sublimation, evaporation, and melt-freeze cycles (Beria et al., 2018; Cooper, 1998; Evans et al., 2016; Friedman et al., 1991; Sinclair & Marshall, 2008; Stichler et al., 1981).

2 Site Description and Modeling Strategy

The East River, Colorado (ER, 750 km², Figure 1a) is a headwater basin of the Colorado River in the southwestern United States with elevations ranging from 2440 to 4346 m. Climate for the area is continental subarctic with long, cold winters and short, cool summers. Annual precipitation $1,434 \pm 258$ mm/yr (years 1987-2020), with $25 \pm 7\%$ falling as rain. Most rain occurs during the summer monsoon (Carroll et al., 2020). Water year 2015 had the most annual rainfall to total precipitation (40%) and 2017 had the least (12%). June is typically very dry with little precipitation. Water years considered in this study

(2015-2020) are coincident with isotopic surveys in the ER (Carroll et al., 2022). Water year 2016 represents average snow conditions, and 2018 and 2019 represent dry and wet snow conditions, respectively. For the years studied, winter temperatures were highest in 2017 and 2018, while 2019 represents the coolest winter. Ecozones are broadly defined by elevation and dominant vegetation cover (Figure 1b). Montane conditions (<2800 m) are dominated by shrubs, grasses and forbs. The subalpine is divided into the lower subalpine with dense conifer forests mixed with aspen (2800-3200 m), and the upper subalpine which is a combination of low density conifer forests, shrubs and barren ground (3200-3500 m). The alpine (>3500 m) occurs above treeline.

The hydrologic model uses the semi-empirical, spatially distributed U.S. Geological Survey (USGS) numerical code Precipitation-Modelling Runoff System (PRMS, Markstrom et al., 2015). Water and energy are tracked daily through the atmosphere, canopy and subsurface at a 100 m grid resolution. Daily climate forcing assigns minimum and maximum temperature lapse rates based on two local snow-telemetry stations and adjusted for aspect. Potential evapotranspiration (PET) is calculated with a modified version of the Jensen-Haise formulation dependent on air temperature and solar radiation (Jensen et al., 1969). Solar radiation is based on a modified degree-day method developed in the Rocky Mountain region and applicable for sites with clear skies on days that lack precipitation (Leavesley et al., 1983). Following methods presented in previous work (Carroll et al., 2019), the spatial distribution of snow water equivalent (SWE), based on airborne light-detection and ranging (LiDAR) (Painter et al., 2016). The approach implicitly allows redistribution by wind and avalanche to move snow off mountain ridges and into high elevation cirque valleys to produce the deepest snowpack near treeline. Rain was distributed using the Parameter-elevation Relationships on Independent Slopes Model (PRISM, 800 m) 30-year monthly averages for 1981-2010 (OSU, 2012). Figure 1c illustrates predicted SWE near peak accumulation in a wet water year. Vegetation cover at the 1 m resolution (Breckheimer, 2021) was overlain with the USGS Landfire (2015) 30 m resolution meadow and then resampled to the 100 m grid. PRMS parameters for summer and winter cover density, canopy interception characteristics for snow and rain, and transmission coefficients for short wave solar radiation follow (Gardner et al., 2018).

Precipitation phase (rain, snow) for a given location is controlled by a user-defined temperature threshold. Precipitation contributes water to the snowpack and adds/subtracts energy content based on its phase and temperature. Shortwave radiation at the snowpack surface is limited by the winter vegetation transmission coefficient and reduced by the estimated albedo. Trees and shrubs are assumed to diminish wind, and the energy applied to the snowpack in these areas is diminished by half. Sublimation is calculated with a user-defined fraction of PET adjusted for heat deficit in the snowpack and snow-covered area. Refer to Carroll *et al.*, (2022) for model calibration.

Snowpack isotopic samples were collected years 2016 to 2020 to span gradients in

topography, vegetation and seasonal climate. Overlapping isotopic campaigns for precipitation and snowmelt were conducted across elevation. Refer to Carroll et al. (2022) for detailed analysis of data. Observed isotopic values in snowfall are defined by air temperature and occur along the GMWL. More enriched snowfall occurs when temperatures are warmer meaning snowfall in the spring has higher ^{18}O than in the middle of winter. Observed isotopic values in rainfall are also dependent on air temperature but are modified by wind speed and barometric pressure. Rain is more enriched than snowfall for an equal temperature and falls below the GMWL (d-excess is lower). The observed isotopic elevational lapse rate is -0.16‰ ^{18}O per 100-m. The isotope mass balance model is a parsimonious approach that follows Ala-aho et al. (2017) to track ^{18}O entering the soil system as snowmelt or rain. The approach was expanded to include ^2H and kinetic fractionation. Water stores and fluxes needed for the isotope model use hydrologic model output for each timestep and model grid location. Similar to Ala-aho et al. (2017), isotopic parameters related to fractionation are estimated using a Monte Carlo approach with uniform input distributions and 1000 realizations. Modeled fit is based on a relative root mean squared error (rRMSE) for each isotope parameter (e.g. ^2H , ^{18}O , d-excess) and type of observation (e.g. snowpack, snowmelt). The final parameter suite for melt, evaporative and kinetic fractionation is determined from the average of the 10-best realizations with the lowest composite rRMSE. A full description of the snowpack isotopic model and its calibration is provided in the Supporting Information (SI).

4 Results

The spatial distribution of annual ^{18}O influxes from snowmelt and rain for average water year conditions is given in Figure 1d. Excluding 2015, the most depleted values ($-17.8\pm0.4\text{‰}$) occur in the transition between the upper sub-alpine and alpine (3500 m) where the snow fraction (0.90 ± 0.04) and spring snow water inputs are largest. Relative enrichment in heavy isotopes occurs in the alpine ($-15.6\pm1.2\text{‰}$) and montane ($-12.5\pm1.1\text{‰}$). Some enrichment also occurs along the west-to-east trajectory largely related to estimated summer rainfall. Water year 2015 was extremely warm, received much of its snow in May and experienced twice the annual average of its moisture as rain. This shifts ^{18}O to more enriched conditions ($+3.8\pm0.5\text{‰}$). Canopy interception losses are tracked and account for significant water loss back to the atmosphere (annually= $4\pm3\%$; Oct-May= $8\pm3\%$). The modeled effect is to bias toward more depleted snowmelt with the effect greatest in the lower subalpine and montane. Annually the bias of canopy loss on isotopic water influx to the soil is -1.6‰ and for winter only is -0.8‰ .

Melt fractionation is estimated a small effect in the ER. However, snowmelt evolution over time indicates the enrichment rate is largely associated with the amount and timing of spring precipitation coincident with the amount of SWE over the ablation period. To illustrate, daily SWE, snowmelt and snowmelt ^{18}O are provided for two locations (Figure 2). The higher elevation site is in

a conifer forest of the upper subalpine with a north aspect (3361 m). This site experiences deep and persistent snowpack with snowmelt delayed until mid-April and lasting into early July. The highest melt rates occur during the dry month of June. Initial ^{18}O in snowmelt is -20.4‰ and enriches by 2.5‰ at snowpack disappearance on 1 July. Prior to 26 June snowmelt ^{18}O exhibits a non-linear, direct relationship to snowmelt ($r^2=0.58$, $p\ll 0.01$). Initial snowmelt enriches quickly as a function of snowmelt rate but plateaus at -19.3‰ when snowmelt exceeds 5 mm/d. On average, the enrichment rate is 0.017‰ per day. Snowfall occurs on 25 June adding enriched late spring snow to a diminished snowpack (SWE=40 mm). This forces a jump in the remaining snowmelt by $+1\text{‰}$. With no added snowfall, snowpack and snowmelt rates decline with snowmelt enriching 0.06‰ per day with this very enriched snowmelt only 6% of the snowmelt mass from initial melt onset. The second, and lower elevation, site is located in a montane meadow (2620 m). Maximum SWE is half the subalpine example. Snowmelt begins on 18 February (-20.6‰) and enriches 3.9‰ when seasonal snowpack is gone on 25 April. SWE declines despite significant snowfall in March and April, with increased snowmelt rate describing 42% of the enrichment rate ($p\ll 0.01$) prior to 17 April, and snowmelt enrichment 0.038‰ per day. Significant late-April snowfall occurs under warm conditions (snow ^{18}O inputs $-14.1\pm 6.0\text{‰}$). Enriched snowfall contributes significantly to the snowpack when SWE is low, generates a substantial jump in snowmelt ^{18}O ($+2\text{‰}$) and maintains the same direct relationship to snowmelt rate and ^{18}O influx. Once SWE=0, ephemeral snow ^{18}O contributions are variable based on seasonal temperature with rain ^{18}O much more enriched than snow.

Kinetic fractionation in snowpack is tracked by decreases in d-excess compared to incoming precipitation. The largest decreases in d-excess in comparison to precipitation inputs occur where there is a moderately high amount of available energy (PET) compared to precipitation (P) ($\text{PET}/\text{P} = 1.5$, Figure 3d). This occurs in upper portions of the montane. At higher elevations, where energy is limited ($\text{PET}/\text{P} < 1$), changes in d-excess are dictated by vegetation type ($r^2=0.62$, $p\ll 0.01$) with the ranking of highest-to-lowest d-excess declines occurring at locations containing meadow, bare rock, aspen, shrub and conifer. An indirect relationship to snow fraction acts as a secondary control but its predictive power is weak ($r^2=0.08$, $p\ll 0.01$). For locations in the ER where water is more limited ($\text{PET}/\text{P} > 1.5$), lower snowfall fraction reduces the influence of snowpack kinetic fractionation ($r^2=0.15$, $p\ll 0.01$). Cover type ($r^2=0.06$) and increased solar radiation ($r^2=0.06$) add only modest descriptive ability.

Interannually, the relative amount of kinetic fractionation in snowpack increases when total precipitation is low but snow fraction is high and solar radiation is high ($r^2=0.89$). A comparison of d-excess declines is provided in Figure 3 for a dry/warm water year (2018) and a wet/cool water year (2019). The influence of kinetic fractionation in snowpack decreases across most of the basin in 2019 with the largest reductions in kinetic fractionation occurring in the shrub-dominated upper montane. Very little change occurs in the subalpine. Increases in kinetic fractionation occur only in the lower montane. Hydrologically, water year 2019

snowfall is 183% greater than 2018, with snow covered area larger and more persistent, lasting two additional months. Daily sublimation losses are similar for both winters, based on energy limited conditions, until late April when sublimation losses in 2019 exceed those in 2018 as a function of snow persistence. By years-end sublimation loss in 2019 is 23% larger than 2018 but the basin average sublimation to snowfall in 2019 is half that computed for 2018.

5 Discussion

The spatial variability in simulated annual ^{18}O water inputs from snowmelt and rain is dominated by the isotopic composition of precipitation (Dahlke & Lyon, 2013; Stichler et al., 1981) which is based on air temperature, altitude and precipitation phase (Carroll et al., 2022; Clark & Fritz, 1997; Dansgaard, 1964; Otte et al., 2017). Cold season snowfall is isotopically depleted in comparison to rainfall to produce large seasonal isotopic swings. Therefore the timing of precipitation matters, and water years like 2015, that received a significant amount of snow in May and an exceptional amount of rainfall is estimated to produce a much lighter annual isotopic input signal to the soil compared to other years simulated. Elevation is another critical control producing a 2.9‰ variation in ^{18}O across the ER based on the observed lapse rate. Elevation also determines precipitation phase and associated snow fraction of annual water inputs. The largest volumes of snowmelt occur in the upper subalpine, where deep and persistent snowpack accumulates over the cold winter months to produce a large pulse of the most depleted water entering the basin. At higher elevations in the alpine environment, snow redistribution moves snow off ridges toward treeline. The diminished snowpack is combined with large quantities of enriched summer rain from orographically-driven monsoon events to reduce the annual snow fraction and promote more enriched isotopic inputs compared to the conifer regions. Isotopically light water inputs to the montane from more enriched snowfall is further enriched by a much lower snow fraction due to temperature-driven phase shifts producing more rain in the fall and spring. Quantifying the isotopic lapse rate, the amount of precipitation and where and when precipitation is rain or snow are critically important to estimating the annual mass flux of ^{18}O into the terrestrial system.

Studies focused on intercepted snow by canopy in the intermountain western United States indicate ^{18}O enrichment of stored snow is approximately 2.1‰ with rates of enrichment increasing for smaller snow particles, denser canopy, longer residence times and under clear-sky conditions (Claassen & Downey, 1995; Koeniger et al., 2008). Exchange of enriched snow from the canopy to the ground could have an influence on water inputs to the soil. For example, Ala-aho *et al.* (2017) simulated 0.7‰ enrichment in ^{18}O in ground snowpack with a three-fold increase in leaf-area index. We find canopy interception loss is consequential on the annual water balance of the ER ($16\pm4\%$) and comparable to other estimates in north-central Colorado (Sexstone et al., 2018). We do not simulate the exchange of enriched snow stored in the canopy to the underlying snowpack, but we do account for the isotopic mass balance of underlying snowpack based

on canopy evaporation. When atmospheric demand is high, canopy storage is continually freed-up for more interception. This occurs in the lower subalpine and montane where either denser conifer forests or high PET occur, and rate of possible vapor loss is higher in the summer than winter. The emphasis on summer canopy capture of rain is to bias annual ground influxes of ^{18}O toward more depleted winter values. This is not necessarily incorrect, but future work will need to assess if enrichment of snowpack by throughfall is important or if forest shading (discussed below) is a more important control on snowpack isotopic content.

The temporal evolution of simulated ^{18}O in snowmelt for the ER follows well established trends that reflect mass conservation in the snowpack during ablation with initial melt water isotopically depleted in ^{18}O in comparison to snowpack and enriching over time (Ala-aho et al., 2017; Beria et al., 2018; Taylor et al., 2002; Taylor et al., 2001). Total enrichment in snowmelt is similar to observed trends in other studies (Lee et al., 2010; Unnikrishna et al., 2002) with total snowmelt enrichment and faster rates of enrichment occurring at lower elevations (Carroll et al., 2022). However, model results suggest ER snowmelt enrichment rates are not dictated by melt fractionation. Ala-aho et al. (2017) found a similar result for Bogus Creek in Idaho and suggested this may reflect preferential meltwater flow and limited interaction with the bulk snowpack (Evans et al., 2016; Unnikrishna et al., 2002).

We propose, the timing of snow accumulation and melt across mountain gradients is more consequential on snowmelt isotopic evolution than melt fractionation. From empirical evidence, Carroll *et al.*, (2022) suggests initially depleted snowmelt at low elevations is related to delayed snowpack accumulation when seasonal precipitation is more depleted. Model results suggest this depleted initial melt signature is also a consequence of earlier melt onset when the snowpack is still fairly depleted. Melt enrichment is faster at lower elevation as a consequence of the precipitation lapse rate contributing a larger mass of ^{18}O over the spring compared to higher elevations and doing so when melt has begun. The result is a direct relationship between snowmelt enrichment and melt rate. At high elevations, the largest melt rates occur in June when there is no added spring snow or rain. As a result, snowmelt enrichment tracks bulk ^{18}O mass accrued over the entire snow season and appears rate-limited with respect to melt. At both locations, very shallow snowpack (<100 mm) is influenced by spring/summer snowfall to dramatically enrich snowmelt. Volumetrically, the effect is more significant to the overall water influx from seasonal snowpack at lower elevations.

D-excess reductions in snowpack are explored as functions of landscape position and climate to provide guidance to where and when isotopic sampling of snowpack needs to consider kinetic fractionation in its calculation of isotopic inputs to the soil. D-excess delines are also an indicator of where sublimation is a critical component of the water balance. Sublimation is affected by energy and snow availability and is highest where both are maximized (PET/P~1). Model

results find d-excess reductions in snowpack described by decreased precipitation, increased snow fraction and increased solar radiation. The combination of all three variables minimizes the snowpack such that sublimation is a larger proportion of the snow budget, but maximizes snow persistence and energy. The winters in the ER are energy-limited and while increased sublimation may occur in a big snow year due to increased snow persistence, it is not globally sufficient to increase the effect of post-depositional kinetic fractionation over large increases in SWE. Model results find the spatial distribution of post-depositional fractionation is highest where snow fraction is moderate and vegetation shading is low, with secondary controls at lower elevations related to PET and solar radiation. Consequently the largest effect of snowpack fractionation occurs in the upper montane, and to a slightly lower degree in the alpine.

Effects of snowpack fractionation are estimated very low in the deep snowpack and conifer forests of the subalpine across all climate conditions. Conifer forests greatly reduce wind scour (Elder et al., 1991) to promote deeper snowpack to buffer d-excess declines via mass balance. Conifer forests also reduce solar radiation on the snowpack surface (Musselman, Molotch and Brooks, 2008; Molotch et al., 2009; Varhola et al., 2010) to limit evaporative losses. Snow water-limitation in the lower montane also reduces the potential for fractionation, except on wet and cool years when snow persistence is sufficient that sublimation increases and d-excess declines are more significant. Globally, post-depositional metamorphism in the energy-limited ER is not a major consideration given the bulk of snow water entering the system resides in the subalpine, but detailed hydrologic analysis above treeline or in the montane needs to consider snowpack fractionation in isotopic tracer-based analyses to reduce error.

6 Conclusions

We combined a hydrologic and snowpack isotopic fractionation model with a previously published comprehensive isotopic data set to assess stable water isotope influxes into a large mountainous watershed of large relief. Modeled inputs are assessed at the temporal and spatial scales pertinent to quantifying energy and water balance of snowpack in complex terrain. Influxes of ^{18}O from snowmelt and rain are dominated by the seasonal variability in precipitation amount, phase and isotopic value with the most depleted inputs occurring in the upper subalpine where snow accumulation is highest and rain inputs minimal. Total enrichment and rate of enrichment in ^{18}O is higher at lower elevations based on higher mass of ^{18}O in precipitation, earlier onset of melt and ongoing spring snowfall coincident with the melt of seasonal snowpack. Post-depositional kinetic fractionation by vapor loss is most important where and when persistent but low snowpack can sustain sufficient sublimation. It is most important in the barren alpine environment (above treeline) and the shrub-dominated upper montane. It is least important in the subalpine where snowpack is deep and is shaded by conifer forests. Given the ER is largely energy-limited, wet water years reduce the effect of snowpack kinetic fractionation across the basin.

The exception is in the the lower montane where snow-limited conditions are moderated by the added snowfall.

Acknowledgments and Data

The snowpack isotope model is provided in the Supporting Information. Refer to Carroll et al. (2020) for details on the hydrologic model. Isotope data files are available to the public (<https://data.ess-dive.lbl.gov/view/doi:10.15485/1824223>). Funding from the US Department of Energy, Office of Science under contract DE-AC02-05CH11231 through Lawrence Berkeley National Laboratory.

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Figure Captions.

Figure 1. The East River (ER) watershed, Colorado (a) elevation with inset showing the ER in the context of the Colorado River Basin in the southwestern United States. (b) spatial distribution of ecozones based on elevation and dominant vegetation type. (c) Simulated snow water equivalent (SWE) near peak accumulation for an average water year (d) Spatial distribution of volume-weighted ^{18}O annual inputs from snowmelt and rain for an average water year (2016).

Figure 2. Subalpine (3361 m) daily (a) snow water equivalent (SWE), snow and rain, (b) snowmelt and ^{18}O influx, (c) ^{18}O influx as a function of snowmelt from initial melt to SWE=0. Montane daily (2620 m) (d) SWE, (e) snowmelt and ^{18}O influx, (f) ^{18}O influx as a function of snowmelt from initial melt to

SWE=0 Influx is defined as snowmelt or rain.

Figure 3. Percent change in d-excess snowmelt due to snowpack kinetic fractionation (a) dry/warm year, 2018, (b) wet/cool year, 2019, and (c) difference between 2019 and 2018, with negative percentages indicating a reduction in kinetic fractionation and positive percentages an increase. (d) The average annual ratio of potential evapotranspiration to precipitation (PET/P).