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Stream water sourcing from high elevation snowpack inferred from stable isotopes of water: A novel application of *d-excess* values

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Abstract. About 80% of the precipitation in the Colorado River's headwaters is snow, and the resulting snowmelt-driven hydrograph is a crucial water source for about 40 million people. Snowmelt from alpine and subalpine snowpack contributes substantially to groundwater recharge and river flow. However, the dynamics of snowmelt progression are not well understood because observations of the high elevation snowpack are difficult due to challenging access in complex mountainous terrain as well as the cost- and labor-intensity of methods. We present a novel approach to infer the processes and dynamics of high elevation snowmelt contributions predicated upon stable hydrogen and oxygen isotope ratios observed in stream discharge. We show that *d-excess* values of stream water can serve as a comparatively cost-effective proxy for a catchment integrated signal of high elevation snow melt contributions to catchment runoff.

We sampled stable hydrogen and oxygen isotope ratios of the precipitation, snowpack, and stream water in the East River, a headwater catchment of the Colorado River and the stream water of larger catchments at sites on the Gunnison River and Colorado River.

The *d-excess* of snowpack increased with elevation; the upper subalpine and alpine snowpack (>3200 m) and had a substantially higher *d-excess* compared to lower elevations (<3200 m) in the study area. The *d-excess* values of stream water reflected this because *d-excess* values increased as the higher elevation snowpack contributed more to stream water generation later in the snowmelt/runoff season. Endmember mixing analyses based on the *d-excess* data showed that the share of high elevation snowmelt contributions within the snowmelt hydrograph was on average 44% and generally increased during melt period progression, up to 70%. The observed pattern was consistent during six years for the East River, and a similar relation was found for the larger catchments on the Gunnison and Colorado Rivers.

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High elevation snowpack contributions were found to be higher for years with lower snowpack and warmer spring temperatures. Thus, we conclude that the *d-excess* of stream water is a viable proxy to observe changes in high elevation snowmelt contributions in catchments at various scales. Inter-catchment comparisons and temporal trends of the *d-excess* of stream water could therefore serve as a catchment-integrated measure to monitor if mountain systems increasingly rely on high elevation water inputs during snow drought.

1 Introduction

The snowpack in mountainous regions provides a crucial water source for the ecosystems and human activities downstream (Immerzeel et al., 2020). In the alpine and subalpine headwaters of semi-arid regions where the summer precipitation contribution to streamflow is usually relatively low, as in the southwestern United States, snowmelt sustains streamflow during much of the growing season when water demands are higher. The Colorado River plays a special role in the hydrology of the southwestern United States because its headwaters in the Rocky Mountains support the water supply for about 40 million people, agriculture, industry and power generation (Bureau of Reclamation, 2012). The snowmelt from high elevation upper subalpine and alpine regions of the mountainous headwaters of the Colorado River was shown to be particularly important for the groundwater recharge and sustaining river flow (Carroll et al., 2019). However, observed (Faybishenko et al., 2022; Hoerling et al., 2019) and projected (Bennett and Talsma, 2021) increases in air temperatures in the headwaters of the Colorado River can lead to a decrease of the snow-to-rain ratio during the coming decades (Hammond et al., 2023). Therefore, if carbon emissions are not reduced, the mountainous catchments in the Colorado River could likely transition towards low-to-no snow conditions during the second half of this century (Siirila-Woodburn et al., 2021). Because we already observe a general trend towards lower snow packs and earlier snowmelt in the western United States (Musselman et al., 2021), it is crucial to better understand the role of high elevation snowpack in streamflow dynamics. However, the tools needed to observe high elevation snowmelt processes are either missing (e.g. point observations), too coarse a resolution (e.g. satellite), or expensive to obtain (e.g. airborne lidar techniques, numerical models), which is why we investigate the use of a stable isotope-based method that can help assess upper subalpine and alpine snowmelt contributions to streamflow.

Snowpack assessments and snowmelt dynamics are usually monitored with point observations like the U.S. Natural Resource Conservation Service's (NRCS) SNOw TELemetry (SNOTEL) network (Report Generator 2.0, 2023). However, the highest elevations in the western United States are not covered by this network (max. elevation 3543 m a.s.l.), despite this area harboring the largest snow water equivalent (SWE) and most surface water input volumes per square meter (Hammond et al., 2023). Therefore, while the measured snow pack at SNOTEL sites will indicate melt-out, there remains substantial snow cover in the alpine regions past the SNOTEL indicated melt-out dates (Dozier et al., 2016). To obtain a spatial representation of the SWE from the SNOTEL point measurements, regression analyses with physiographic variables (e.g., elevation, slope, aspect) are commonly used (Fassnacht et al., 2003). Heterogeneity of snowfall accumulation and redistribution of snow (Freudiger et al., 2017) in complex mountainous terrain makes such interpolation and extrapolation efforts difficult (Dozier et al., 2016). Adding information about the previous year's snow cover distribution from satellite data was shown to improve the reconstruction of SWE across the complex mountainous terrain of the Upper Colorado River Basin (Schneider and Molotch, 2016). However, maps of snowpack

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distribution from airborne snow observatory (ASO) based on airborne light-detection (Painter et al., 2016) are costly and therefore may not be applicable across multiple mountainous catchments and/or during several years.

In addition to the high costs and labor intensity of the currently available methods to study high elevation snowmelt dynamics, these approaches are generally limited to hydrometric data and do not include any tracer information. Beria et al. (2018) outlined multiple ways how stable hydrogen and oxygen isotopes of water (δ^2H and δ^{18}O) can provide valuable insights into snow hydrological processes. Because hydrogen and oxygen isotopes comprise the water molecule, δ^2H and δ^{18}O signatures are ideal tracers to track fluxes in the water cycle (Kendall and McDonnell, 1998). The relationship between the relative stable hydrogen and oxygen isotope ratios of water systems was identified by Craig (1961) as

$$\delta^2H = 8 \times \delta^{18}O + 10 \qquad (1)$$

who characterized this relationship as indicative of "waters which have not undergone excessive evapotranspiration." (Dansgaard, 1964) defined the concept of deuterium-excess, or *d-excess*, as

$$d\text{-}excess = \delta^2H - 8 \times \delta^{18}O \qquad (2)$$

which can be interpreted as an index of non-equilibrium in the simple condensation - evaporation of global precipitation. This formulation has been useful for screening isotopic results from water samples: values of *d-excess* between 10 and 11 are effectively the intercept in Craig's proposed relationship and indicate quasi-stable conditions at a relative humidity of ~85% (Dansgaard, 1964; Gat, 2000). Here, we test two hypotheses to examine how *d-excess* data from stream water samples are related to high elevation snowmelt contributions to the catchment runoff during the snowmelt periods. First, we hypothesize that *d-excess* values in stream water during the snowmelt hydrograph reflect the changing dominance of snowmelt contributions through time from lower to higher elevations. Second, we test if these patterns of *d-excess* of stream water are detectable across ranges in drainage area, thus increasing their broader applicability.

2 Methods

2.1 Study sites and data

Our study is situated in the headwaters region of the Upper Colorado River (Figure 1) with a focus on an East River subcatchment (85 km^2) as defined by the gaging and sampling station at the Pumphouse location (38.922447, -106.950828) near Mount Crested Butte, CO. The Pumphouse subcatchment has a large elevation gradient from 2700 to 4100 m (Figure 1) and is predominantly underlain by Paleozoic and Mesozoic sedimentary rocks, including Mancos Shale that covers 44% of the catchment area, and localized intrusive igneous rocks like granodiorite (Gaskill et al., 1991). The vegetation is dominated by shrubs, grasses, and forbs in the montane (<2800 m elevation, 2% of catchment area), aspen and conifers in the lower subalpine (2800 to 3200 m, 34% of the catchment area) and conifers in the upper subalpine (3200 to 3500 m, 32% of the catchment area) regions. In the alpine region (>3500 m, 31% of the catchment

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area), shrubs are dominant until 3800 m, above which land is mostly barren (Carroll, Deems, Sprenger, et al., 2022). Meadows are distributed across the catchment, but take up a relatively small share of the total area above the montane. The climate is dominated by cold winters with substantial snow cover and snowpack accumulation that constitutes about 80% of the total annual precipitation (Carroll, Deems, Sprenger, et al., 2022). Summers are relatively warm and dry with monsoonal rain that accounts for 20% of the annual precipitation. The snowpack depth is generally greater and snowmelt timing is later with increasing elevation across the catchment (Carroll et al., 2022a). The catchment hydrograph is dominated by the snowmelt pulse with an onset in April, a pronounced peak during June and a subsequent snowmelt recession interspersed with smaller peaks driven by monsoon rainfall events. Between September and March, the catchment streamflow is generally limited to base flow (Carroll et al., 2020). The East River has been intensely instrumented and studied since 2015; more details are provided in Hubbard et al. (2018).

In addition to the East River, we also sampled the Upper Gunnison River near Gunnison, CO, about 50 km downstream from Mount Crested Butte. This catchment is defined by the USGS streamgage #09114500 (38.54193567, -106.9497661) and has a drainage area of 2,618 km^2. A third basin was included, which is defined by the USGS streamgage # 09095500 (39.2391463 -108.2661946) of the main stem of the Colorado River near Cameo, CO. Its drainage area is of 20,683 km^2 (USGS Water Data for the Nation, 2023). Hereafter, these two basins locations are referred to as Gunnison and Cameo, respectively, and their catchment areas are shown in Figure 1.

Within the Gunnison River Basin, there are 15 SNOTEL sites located at elevations ranging between 2674 and 3523 m providing snow water equivalent (SWE) observations (Suppl. Table 1). Across these SNOTEL sites, elevation was not a good predictor for the maximum snowpack depth (Suppl. Fig. 1). For the Colorado River at Cameo, we chose the 31 SNOTEL sites in the Colorado Headwaters ranging between 2610 and 3452 m(Report Generator 2.0, 2023) (Figure 1).

We sampled snowpack between 2016 and 2019 across a gradient spanning 1324 m in elevation (from 2347 to 3671 m) in the Gunnison catchment (Figure 1a&b). A total of 53 snow pits were dug in flat areas with samples collected in duplicate at 10-cm depth increments to tabulate snow density, temperature, and stable isotope ratios. Bulk snowpack isotopic content represents the SWE-weighted composite value across the entire snow column (Carroll et al., 2022b). Precipitation was first sampled on an event basis via a collector from 2014 to 2017 in Mount Crested Butte at 2885 m, and the sampling procedure was outlined in Carroll et al. (2022b). Since 2020, we sampled the precipitation on an approximate event basis at the locations Estess (2513 m), Mount Crested Butte (2885 m), and Irwin Barn (3181 m). (Figure 1). We sampled stream water from the East River at the Pumphouse location from 2014 to 2022 on daily to fortnightly frequency. There was a gap of sampling in April 2018; and therefore, 2018 was excluded from the present analyses. Sampling at the Gunnison River was done between March 2020 and December 2021 on a weekly basis with occasional higher (3 days) or lower (15 days) frequency. At Cameo, stream water sampling occurred at weekly to fortnightly frequency in 2021 and 2022.

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All water samples were measured for stable hydrogen and oxygen isotopes using a Cavity Ring-Down Spectroscopy (Picarro L2130-i). We report isotope ratios as δ^{18}O and δ^{2}H values expressed relative to the Vienna Standard Mean Ocean Water.

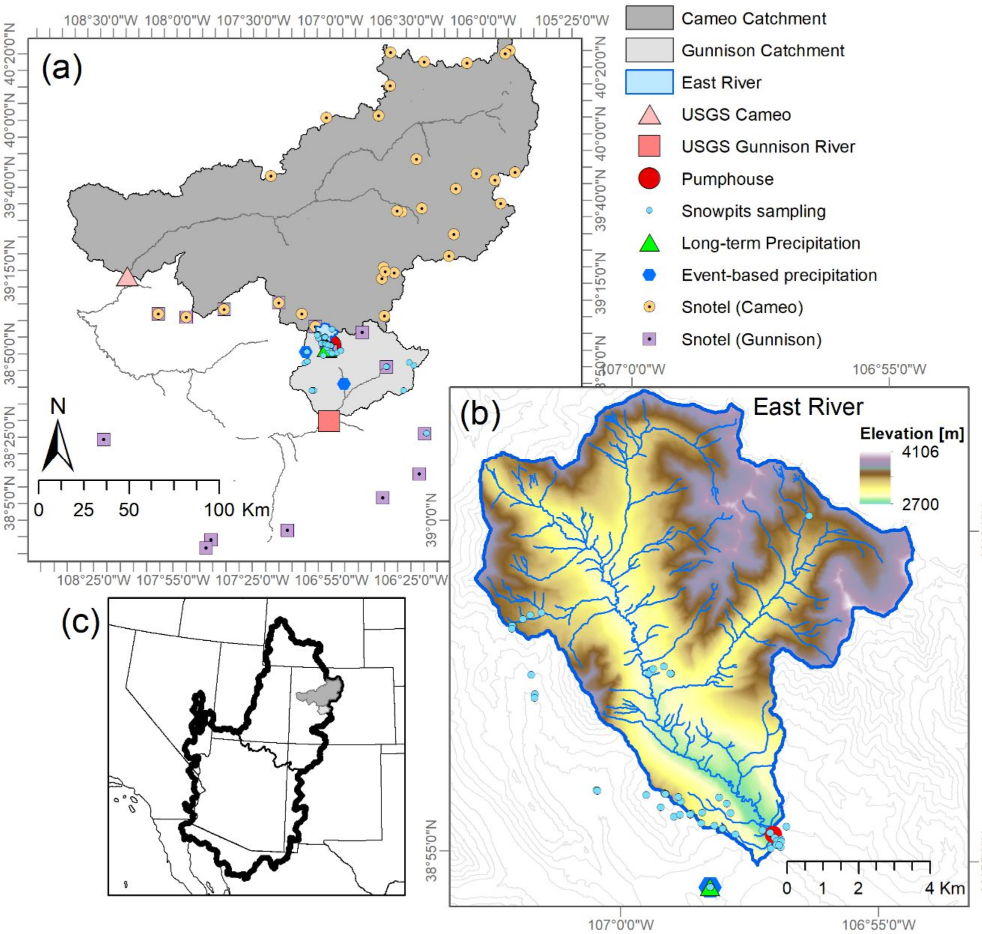

Figure 1 (a) Locations of streamgages and water sampling of the Colorado River near Cameo and the Gunnison River in Gunnison (black markers) and the river's catchment area (grey). Locations of event-based precipitation sampling (blue markers), SNOTEL stations in the Colorado (light blue) and Gunnison (light purple) areas. East River catchment area (blue outline) as defined by Pumphouse gaging and sampling location (red circle) located within the Gunnison river catchment also shown. (b) Area and elevation of the East River catchment with the streamgage and water sampling location at Pumphouse (red marker) and long-term precipitation sampling site (cyan triangle). (c) Locations of the catchments defined by the stream gages near Cameo and Gunnison (light grey) in the Colorado River Basin (thick black line).

2.2 Data analyses

We calculated the deuterium excess value (short "*d-excess*") for all water samples as defined by equation (2).

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While it was shown that the *d-excess* of precipitation is on average about 11.27 ‰ on a global scale (Rozanski et al., 1993), for snowpacks, the *d-excess* values were found to increase with elevation (Froehlich et al., 2008; Tappa et al., 2016) due to increased evaporative fractionation from lower elevation snowpacks which are re-condensed at higher elevations (Lambán et al., 2015). Because the slope of the local meteorologic water line, observed to be 7.4 (Carroll et al., 2022b) near Mt Crested Butte and 7.2 at the lower elevation Gunnison site (Marchetti and Marchetti, 2019), does not deviate much from the slope of 8 of the global meteorologic water line that defines the *d-excess* (see Suppl. Fig. 2), we decided to use the *d-excess* rather than lc-excess (Landwehr and Coplen, 2006). We used linear correlation analyses to describe various relation and provide Pearson (r) coefficients. For significant correlations ($p<0.05$), we added linear regression lines to the plots.

We used the SNOTEL data to compute the fraction of peak SWE through time for each water year (a value of one equals maximum SWE and zero indicates the snowpack is melted). Because SNOTEL SWE data only reflects conditions at the stations, we used spatially explicit snowmelt simulations, as published by Carroll et al. (2022a), that were informed by the airborne snow observatory (ASO). For each water year with snowmelt simulations available, we calculated the cumulative difference through time between the simulated snowmelt for the montane and alpine elevation bands in the East River, given as millimeter (mm) SWE. In this case, a value of zero indicated equal snowmelt volumes from the montane and alpine snowpack, whereas positive values show that alpine snowmelt exceeded montane snowmelt.

We applied for each day with a stream water sample the Bayesian mixing framework HydroMix by Beria et al. (2020) to estimate the temporal dynamics of the share of high elevation snowmelt in the streamflow during the snowmelt period, which occurred between day 200 to 300 of the water year (water year starts on October 1st). The two end members were defined as the *d-excess* of the snowpack from the upper subalpine and alpine snowpack (>3200 m, n=31, defined as "high elevation") and lower subalpine and montane area (<3200 m, n=60), respectively. We report the mean fraction of high elevation snowmelt in each water sample with standard deviations based on the distribution of the two endmembers as described in Beria et al. (2020). We further report the seasonal average and maximum share of high elevation snowpack in the stream samples. We compared the HydroMix results with MixSIAR (Stock et al., 2018) calculations and found with both methods very similar results. A multiple linear regression was used to explore the predictability of the maximum share of high elevation snowmelt during the different years as a function of the maximum SWE and the mean air temperature measured at the Gunnison SNOTEL sites during the snowmelt period.

3 Results

3.1 The *d-excess* of stream water increased with high elevation snowmelt contributions

Our snowpack sampling campaigns along a 1324 m elevation gradient showed that the average (±SD) *d-excess* value of the high elevation (>3200 m) snowpack was 13.8 (±1.6) ‰ and thus significantly higher than for the lower elevation snowpack 10.7 (±1.8) ‰ (Suppl. Fig. 3). The *d-excess* of the lower elevation snowpack was not significantly different from groundwater (10.5±1.0 ‰, Suppl. Fig. 3) nor from the *d-excess* of summer rainfall (Suppl. Fig. 4). We further observed a strong and temporally consistent (generally $r > 0.63$ and $p<0.05$ for the four individual years) increase in *d-excess* of the snowpack with elevation (Figure 2b). The *d-excess* lapse rate of the snowpack +0.52 ‰/100 m, leading to 12.9 ‰ to 14.4 ‰ and 14.4 ‰ to 17.6 ‰ for the *d-excess* of the snowpack in the upper subalpine and alpine region, respectively. Lapse rates for the snowpack were not seen in δ^{18}O (Figure 2b) or δ^2H (data not shown). The precipitation sampled via collectors across the 667 m elevation gradient from the event-based sampler also showed a relation between average *d-excess* and elevation for the samples collected weekly to fortnightly between November and April during water years 2021 and 2022 (Suppl. Fig. 5). These samples reflect a *d-excess* lapse rate for winter precipitation of +0.7 ‰/100 m, which was slightly higher than snowpack, though the elevation range for the precipitation sampler was lower. There was generally a large variability of SWE dynamics across the SNOTEL sites in the Gunnison catchment (Figure 3a), and this variation among the sites did not result from elevation differences (Suppl. Fig. 1).

The hydrograph of the snowmelt period had peak streamflow during May and June, a recession towards August and lowest flows between September and March (Figure 3a). This pattern was consistent during the seven water years, but years with lower SWE resulted in lower peak flows, as expected (Suppl. Fig. 6).

The stream water δ^{18}O dynamics reflected the seasonality of precipitation inputs, from having lower values (depleted in 18O) during peak flow and trending towards higher values (enriched in 18O) during summer and early fall due to greater fractional contributions from base flow and rainfall contributions that had higher δ^{18}O values compared to the snowfall. Due to the strong difference in δ^{18}O values of rain and snowfall (see discussion in Sprenger et al., 2022), the δ^{18}O of stream water decreased during the low flows in winter due to a higher fraction of groundwater sourced from snowmelt vs. rain in the catchment runoff (orange points and line in Figure 3b). The δ^{18}O of snowmelt stream water reached a minimum in June during maximum snowmelt contribution, after which the snowpack ceased to exist and δ^{18}O of stream water increased throughout the summer with recession to base flow and monsoonal rainfall.

The *d-excess* values of stream water did not show a strong seasonal dynamic, but in general, *d-excess* values mainly increased during the snowmelt season and subsequently dropped again during the summer (red points and line in Figure 3b). The increase of *d-excess* of stream water was not due to the rainfall input because there was no seasonal trend in *d-excess* of rainfall (Suppl. Fig. 4). Instead, *d-excess* of stream water resulted from melting snowpack at higher elevations due to snowmelt progression, as evidenced by the SNOTEL SWE data, that resulted in increases in *d-excess* of stream water consistently for each of the investigated years (Figure 4a). The hypothesis that this increase in *d-excess* of stream water resulted from high elevation snowmelt contributions is supported by its relation with simulated snowmelt differences between alpine and montane snowmelt volumes through time (Figure 4b). When the high elevation snowmelt volumes became increasingly larger than the low elevation snowmelt, *d-excess* of stream water increased consistently. Notably, Figure 4b also shows that stream water *d-excess* values of stream water were highest for years with largest differences between alpine and montane snowpack (2017 and 2019).

Our *d-excess*-based endmember mixing analyses revealed that 41 to 57% of the flow in the East River during the snowmelt period stemmed from high elevation snowpack (Figure 5 left). Periods when there were an increase in the fraction of high elevation snowmelt contributions tend to be later in the snowmelt hydrograph and coincided with periods of runoff intensification (Figure 5, right). During peak alpine snowmelt contributions, about two-third of the East River flow stemmed from the high elevation snowpack. There was a general trend that the maximum high

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elevation snowpack contributions were higher in water years with lower SWE (Suppl. Fig. 7a, r=-0.51, p=0.24). However, the relatively warm snowmelt period of 2017, following a winter with deep snowpack, resulted in relatively large high elevation snowmelt contributions and thus did not follow that trend. Because of this observation, we included the average air temperature measured at the SNOTEL sites during the snowmelt period as a second variable in a multiple regression analysis. This regression explained 66% of the interannual variation of the maximum high elevation snowmelt contribution, and all variables had significance levels of <0.1. Our results therefore indicate that the snowpack at the highest elevation can be more important for runoff generation in low-snow years and when the air temperature is higher (Figure 6). We also tested the streamflow volumes during the snowmelt period as a variable, but did not include it, because of its strong correlation with SWE_{max} (r=0.84, p=0.018).

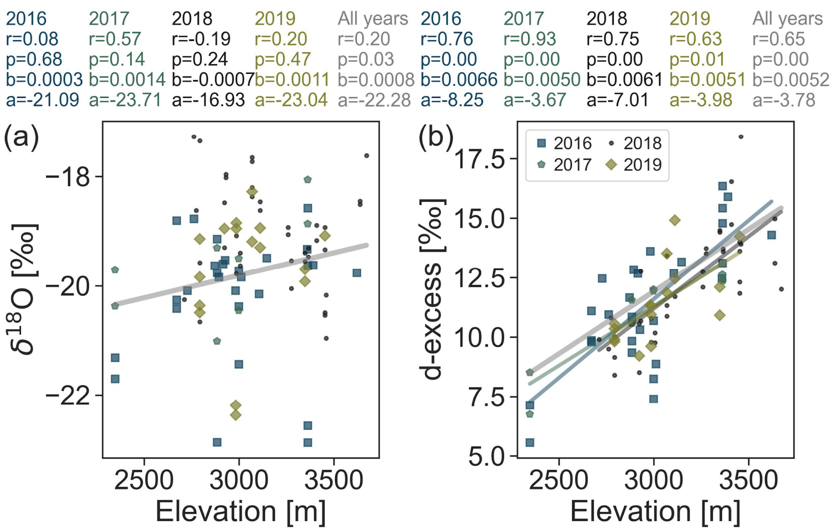

Figure 2 The δ^{18}O of snowpack (a) and *d-excess* (b) values sampled in the Upper Colorado River Basin during four different winters along an elevation gradient. Regression lines are plotted for correlations with p<0.05. For each year and for the bulk isotope data, Pearson correlation coefficients (r), significant levels (p), as well as slope (b), and intercept (a) of the regression are given.

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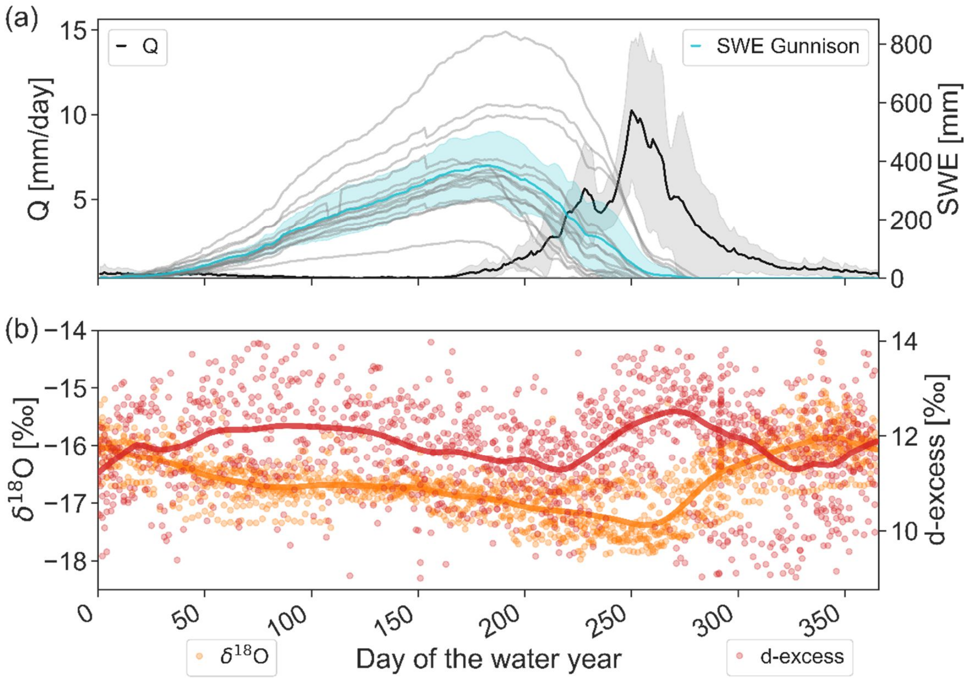

Figure 3 (a) Median annual dynamics of East River streamflow (Q, black) and snow water equivalent (SWE) at the individual SNOTEL sites within the Gunnison River catchment (grey) and the average of all sites (cyan) from water year 2015 to 2022 with semitransparent grey and cyan area representing the standard deviation of Q and SWE, respectively. (b) The $\delta^{18}O$ (orange) and *d-excess* (red) of all stream water samples collected between water year 2015 and 2022 from the East River at the Pumphouse location. The orange and red lines are a LOWESS fit to the data points. See Suppl. Fig. 6 for a time series plot of the same data.

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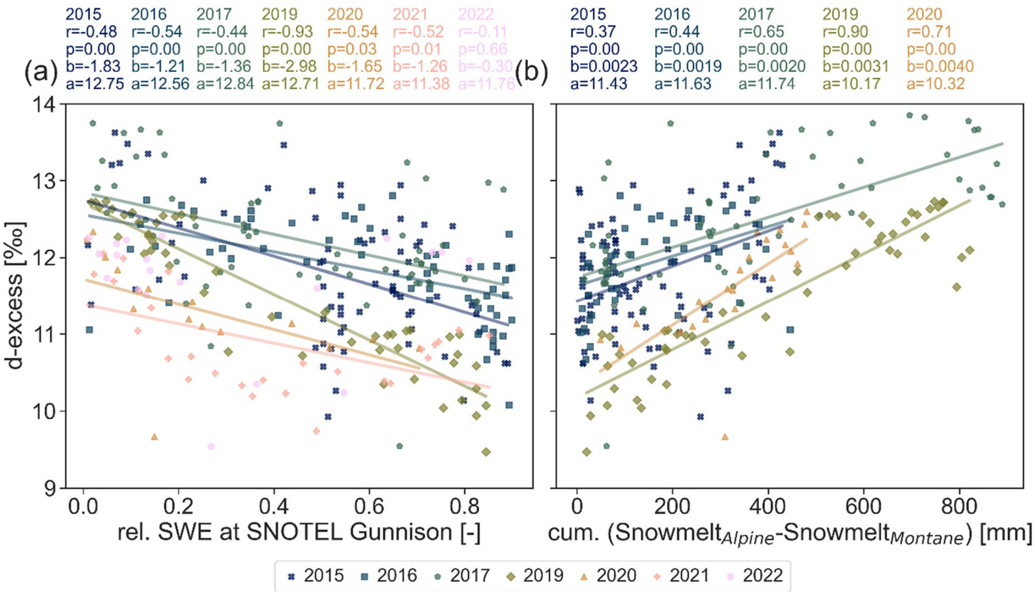

Figure 4 (a) The d-excess of stream water values during snowmelt for seven individual years, shown as a function of relative snow water equivalent (SWE) measured at the SNOTEL stations across the Gunnison River catchment at the time of sampling. For each year, the Pearson correlation (r) and the associated significance level (p) are given as well as the intercept (a) and slope (b) of the regression. (b) The *d-excess* of stream water as a function of the cumulative differences between the simulated snowmelt at alpine (=highest elevation in the East River) and montane (lowest elevation in the East River) region at the time of each stream water collection. Regression lines are shown for p≤0.05.

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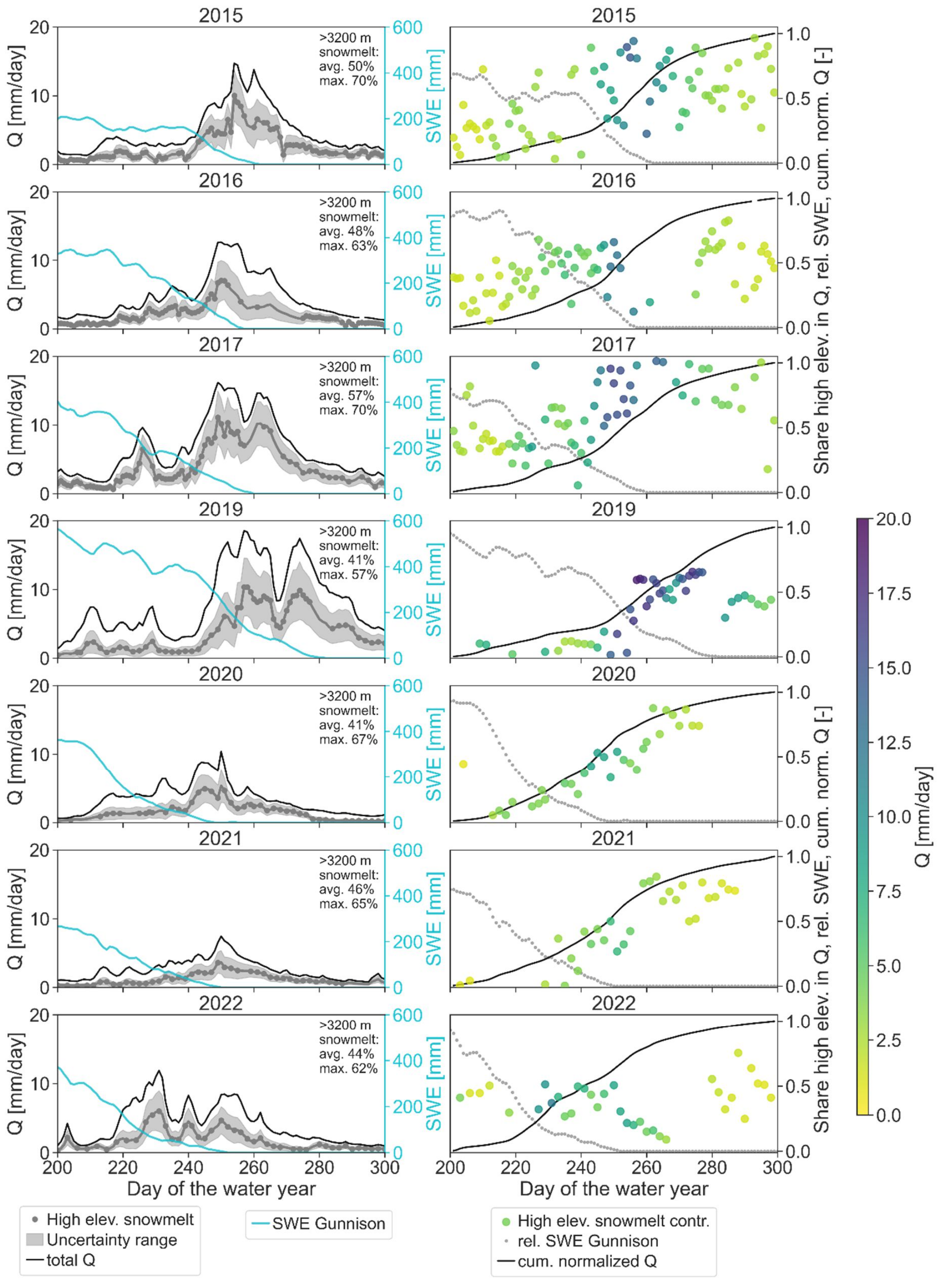

Figure 5 (left) Endmember mixing analyses based on *d-excess* of stream water inferring the share of high elevation snowmelt (grey dots and lines) in the streamflow during the snowmelt-induced peak flow of the East River. The uncertainty range is

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shown as grey bands and it represents the standard deviation (22% on average). Additionally, we show the total streamflow (Q, black line) as well as the snow water equivalent (SWE, cyan) for the SNOTEL sites in the Gunnison catchment. (right) Share of high elevation snowmelt in the streamflow (points, color coded by Q), relative SWE in Gunnison (1= peak SWE), and cumulative streamflow between day 200 and 300 of the water year. Note that the y-axis for the graphs on the right is plotted on the right-hand side.

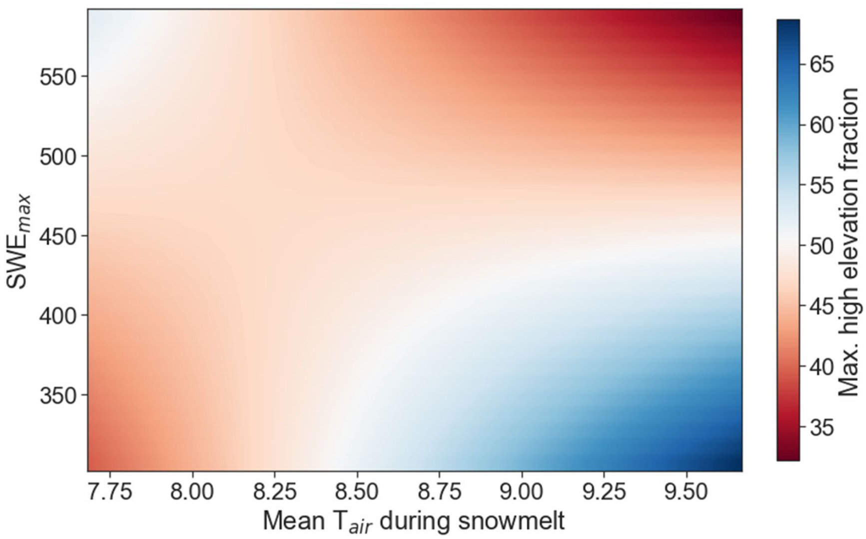

Figure 6 Result of the multiple regression analyses to assess predictability of the maximum contribution of high elevation snowmelt to stream water as a function of the maximum snow water equivalent (SWE_{max}) and the air temperature (T_{air}) during the snowmelt period measured at the SNOTEL sites in Gunnison. Note that the regression includes interaction between SWE_{max} and T_{air}.as follows: $-37.03*T_{air} -0.73*SWE_{max} + 0.089*T_{air}*SWE_{Max} + 350.74$

3.2 The *d-excess* dynamics of stream water beyond headwaters

Downstream from the East River, the Gunnison River stream water samples showed similar increase in *d-excess* as streamflow during the snowmelt season increased. This pattern was observed for both years in which stream water sampling in Gunnison was done. In 2020, the snowpack was deeper, and the runoff was higher than in 2021. Additionally, the *d-excess* values of stream water were different for the different years with generally higher values for 2020 than in 2021 (Figure 7a,c). Despite 30 times larger drainage area of the Gunnison River compared to the East River, the effect of the high elevation snowmelt on the *d-excess* measurements of stream water was detectable, albeit dampened given the greater fraction of lower elevations contributing to its flow.

The drainage area of the Colorado River near Cameo is eight times the drainage area of the Gunnison River, but the difference between the *d-excess* of stream water at the beginning and end of the snowmelt period was greater than3 ‰ in 2021 and 2022. Thus, despite the large catchment area of the Colorado River near Cameo, and greater mixing of runoff in reservoirs within that catchment, the snowmelt contribution from high elevation regions was substantial during the snowmelt peak flow (Figure 7b,d).

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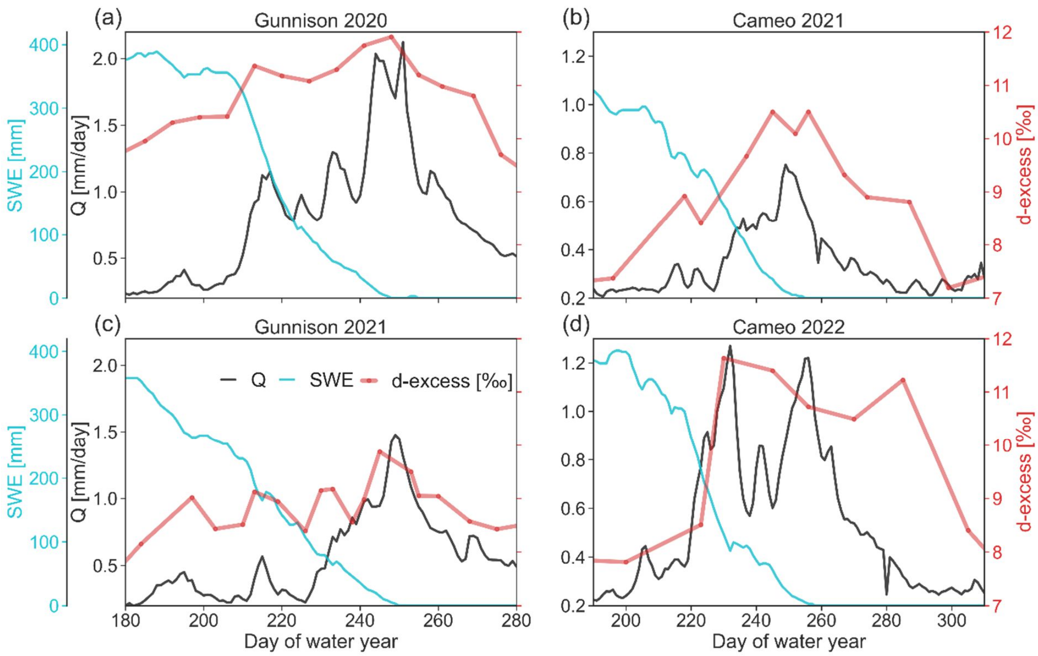

Figure 7 Streamflow (Q, black) and *d-excess* (red dots and line) of the stream water before and during snowmelt for the Gunnison River near Gunnison, Colorado in 2020 (a) and 2021 (c) and for the Colorado River near Cameo, Colorado for 2021 (b) and 2022 (d). Further shown is the average snow water equivalent (SWE, cyan line) of all the SNOTEL sites located in the Gunnison catchment and in the Colorado River ehadwaters for the Cameo site, respectively. Note that the y-axes have different scales for each subplot.

4 Discussion

4.1 The *d-excess* of stream water reflects high elevation snowmelt

We find that *d-excess* of stream water can be used to differentiate the effects of snowmelt from low vs. high elevations using three independent approaches: First, the comparisons of *d-excess* dynamics of stream water with the observed snowpack reduction at SNOTEL sites in the region showed a strong relation that was consistent during six of the seven investigated snowmelt periods (Figure 4a). The SNOTEL data do not show an increased snowpack with elevation (Suppl. Fig. 1), but ASO flight data indicate that snowpack depth generally increases with elevation (Carroll, Deems, Sprenger, et al., 2022). Thus, with decreasing SWE during the snowmelt period, the ratio of high elevation snowmelt can increase. Such a trend of relative increase of the high elevation snowpack during low snow years was observed. Second, simulated differences based on spatially explicit hydrological modeling of snowmelt timing and volumes between the montane and alpine regions within the East River catchment correlated significantly with *d-excess* of stream water for every simulated snowmelt period (Figure 4b). Third, the increase in *d-excess* of stream water coincided with the peak streamflow during each snowmelt period (with exception for 2022, Figure 5). Thus, elevated *d-excess* values cannot stem from low elevation snowmelt but most likely result from higher elevation snowmelt as the snowmelt generally progresses from lower to higher elevations due to the temperature gradients across the catchment.

Because we observed consistent lapse rates of *d-excess* values in the snowpack during several years (Figure 2b), significant differences between the *d-excess* at lower and higher elevation snowpack (Suppl. Fig. 3), and also a *d-excess* lapse rate in the winter precipitation (Suppl. Fig. 5), we see a great potential for *d-excess* measurements to serve as a tracer for endmember-mixing analyses to derive high elevation snowmelt contributions to the catchment's streamflow during snowmelt periods.

Other studies have also shown that snowpack at highest elevations had the highest *d-excess* values; data by Froehlich et al. (2008) indicate a lapse rate for *d-excess* values of +0.2 ‰/100 m across an elevation range between 469 and 2245 m across the Alps, and data published by Tappa et al. (2016) indicate a lapse rate of +0.38 ‰/100 m in the Rocky Mountains in Idaho. Our lapse rate of +0.52 ‰/100 m was slightly higher than those reported by others. However, the sampling strategies for the different studies are different, and importantly, the general trend of increased *d-excess* values with elevation was the same for all three studies in mountainous systems.

A potential explanation for how *d-excess* lapse rates in the snowpack develop is sublimation of snow at lower elevation and the subsequent condensation of the water vapor at colder higher elevation (Beria et al., 2018; Lambán et al., 2015). Our long-term sampling of the precipitation in the East River can further rule out a potential precipitation *d-excess* seasonality to influence the *d-excess* of stream water during the snowmelt period (Suppl. Fig. 4). Therefore, there are several independent data sources that all point towards high elevation snowmelt contributions to the catchment streamflow driving the observed *d-excess* of stream water variation during the snowmelt period.

Our findings, based on endmember-mixing analyses via *d-excess* values highlight the importance of high elevation snowpack for runoff generation. The interannual variation in *d-excess* of stream water and the derived high elevation snowmelt contributions indicate that the snowpack of the upper subalpine and alpine region could be most important in years of relatively low snowpack accumulation and comparably high spring air temperatures. Thus, with the projection of a reduced snowpack in the western United States (Siirila-Woodburn et al., 2021), understanding the high elevation snowpack dynamics could most likely become more important, and *d-excess* observations are a tool to investigate the timing (e.g., trend towards earlier melt) and fate (e.g., streamflow contribution vs. sublimation or groundwater recharge) of the snowpack throughout the melting period.

4.2 Limitations and opportunities of *d-excess* of stream water with scale

Our results show that the *d-excess* patterns of stream water observed in a headwater stream can be upscaled because we see a similar *d-excess* pattern of stream water at larger scales from stream water sampling in Gunnison and Cameo. The latter sampling site is an entirely different catchment to the north of East River and Gunnison River in which the snowpack was not sampled for its *d-excess* values. However, the *d-excess* signal of stream water for Coal Creek, a smaller headwater catchment to the west of the East River catchment, did not show a similar pattern (Suppl. Fig. 8, Suppl. Fig. 9), likely because of a lower representation of high elevation bands within in the catchment (Suppl. Fig. 10). Twenty nine percent of the Coal Creek catchment area is the upper subalpine region, but only 6% of the catchment is alpine (>3500 m). Thus, high elevation snowpack with the highest *d-excess* values is essentially missing in Coal Creek, which presumably dampened *d-excess* response of stream water. We therefore hypothesize that the

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applicability of the *d-excess* of stream water as a signal for high elevation snowmelt is dependent on a sufficient area with high elevation (>3200 m) and sufficient elevation gradient in the catchment of the sampled stream. Lastly, although we see *d-excess* dynamics of stream water in response to high elevation snowmelt at relatively large scales, the isotope dynamics may likely not be detectable downstream from large reservoirs. Initial sampling of the Colorado River near the Colorado-Utah state line with a drainage area of 46,230 km^2 that includes several large reservoirs indicates that stream water *d-excess* changes are rather dampened and might not hold sufficient information to infer high elevation snowmelt contributions (not shown).

Because snowpack volumes are getting lower, and snowmelt is starting earlier in mountainous regions due to climate change (Musselman et al., 2021), we need to find ways to assess the effect of these both at sub-annual to decadal time scales. Short term identification of a snow drought could allow for adaptive water management measures on the sub-annual time scale, whereas long-term trends might show the trajectory of mountain snow dynamics. With 0.2 ‰ measurement uncertainty of the *d-excess* values due to 0.025 ‰ and 0.1 ‰ precision (1σ) in δ^{18}O and δ^2H, respectively, the observed variation of *d-excess* in snowpack and stream water are at least ten times larger. Our results and the discussion in the previous section show that measurements of *d-excess* of stream water is a relatively cost-effective way to obtain catchment integrated information about the high elevation snowpack.

Although SNOTEL sites are point measurements and therefore do not represent integrated patterns across heterogeneous mountainous regions, *d-excess* of stream water does integrate throughout catchment areas. The lidar based ASO data provide spatially explicit snowpack observations on catchment scales, but such data collection is costly and represents only snapshots in time, although time series changes of snowpack during the snowmelt period might be more informative. The costs of large-scale flight-based data collection may also make monitoring of interannual SWE changes difficult to conduct over every basin where trends induced by climate change need to be identified. The *d-excess* application introduced in this study is cost effective, applicable across scales that vary by orders of magnitude, and needs limited labor and instrumental investments for the water sampling (e.g., autosampler) and standardized laboratory analyses (e.g., laser spectrometer).

We suggest that *d-excess* of stream water could serve as an complementary information source in addition to the currently applied streamflow shape and flashiness at low and high flows to derive relations between snow persistence effects on the hydrograph across different climates (Le et al., 2022).

Measurements of *d-excess* of stream water can further help disentangling rapid high elevation snowmelt contributions to the streamflow versus groundwater inflow to the stream. This is important because mountainous catchments with lower groundwater influence were found to be more sensitive to snowpack changes due to warming (Tague and Grant, 2009).

5 Conclusion

Our snowpack and stream water stable hydrogen and oxygen isotope sampling program during several years links *d-excess* of stream water at the catchment outlet to high elevation snowmelt contributions during the snowmelt period. The relation between *d-excess* of stream water and snowmelt dynamics at high elevations was consistent during several years. End member mixing analyses based on *d-excess* values quantified the temporal dynamics of high elevation snowmelt contributions and its importance for the runoff generation from mountainous catchments. As compared to

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other approaches, such catchment integrated information is a cost-effective way to better quantify the role of upper subalpine and alpine snowpack for streamflow contributions in snow-dominated mountainous systems. Our findings indicate that high elevation snowpack contributions to the streamflow tend to be more important during years with lower snowpack and warmer spring temperatures. Thus, the high elevation snowpack could likely play a bigger role in the coming decades as snowpack reduces and air temperature rise.

We hypothesize that transferability of this approach could depend on the share of high elevation regions of the catchment area to contribute to streamflow, the presence of a *d-excess* lapse rate in the snowpack, and the absence of large reservoirs upstream from the isotope sampling location. With increasing availability of stable isotope data of mountainous catchments across the globe, future synthesis work could investigate the role of high elevation snowmelt contributions in headwater regions worldwide.

Data availability

The data on East River streamflow (Newcomer et al., 2022), snowpack (Carroll et al., 2021) precipitation and stable isotopes of stream water (Williams et al., 2020) are available online as cited. Snow water equivalent data from the SNOTEL sites are available at https://wcc.sc.egov.usda.gov/reportGenerator/, streamflow and water stable hydrogen and oxygen isotope data from the Gunnison and Cameo sites are available from USGS National Water Information System (NWIS; https://doi.org/10.5066/F7P55KJN) database.

Code availability

The HydroMix code by Beria et al. (2019) is available on GitHub at https://github.com/harshberia93/HydroMix/tree/20191007_GMD (last access: 20 August 2023).

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Author contributions

MS conducted the data analysis and wrote the initial draft of the manuscript. All co-authors contributed either to the analyses, the database, and the interpretation of both as well as improving the manuscript.

Competing interests

The authors declare that they have no conflict of interest.

Competing interests

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