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Influence of climate on alpine stream chemistry and water sources

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Abstract

The resilience of alpine/subalpine watersheds may be viewed as the resistance of streamflow or stream chemistry to change under varying climatic conditions, which is governed by the relative size (volume) and transit time of surface and subsurface water sources. Here, we use end-member mixing analysis in Andrews Creek, an alpine stream in Rocky Mountain National Park, Colorado, from water year 1994 to 2015, to explore how the partitioning of water sources and associated hydrologic resilience change in response to climate. Our results indicate that four water sources are significant contributors to Andrews Creek, including snow, rain, soil water, and talus groundwater. Seasonal patterns in source-water contributions reflected the seasonal hydrologic cycle, which is driven by the accumulation and melting of seasonal snowpack. Flushing of soil water had a large effect on stream chemistry during spring snowmelt, despite making only a small contribution to streamflow volume. Snow had a large influence on stream chemistry as well, contributing large amounts of water with low concentrations of weathering products. Interannual patterns in end-member contributions reflected responses to drought and wet periods. Moderate and significant correlations exist between annual end-member contributions and regional-scale climate indices (the Palmer Drought Severity Index, the Palmer Hydrologic Drought Index, and the Modified Palmer Drought Severity Index). From water year 1994 to 2015, the percent contribution from the talus-groundwater end member to Andrews Creek increased an average of 0.5% per year ($p < 0.0001$), whereas the percent contributions from snow plus rain decreased by a similar amount ($p = 0.001$). Our results show how water and solute sources in alpine environments shift in response to climate variability and highlight the role of talus groundwater and soil water in providing hydrologic resilience to the system.

KEYWORDS

alpine, climate, end-member mixing, groundwater, water sources

1 | INTRODUCTION

Alpine and subalpine headwater catchments in the Rocky Mountains are fragile ecosystems because of their short growing season, dependence upon snowfall for moisture, and weak hydrologic resilience, all of which reflect their susceptibility to changes in the climate (Beniston, 2003; Creed et al., 2014). Here, we define hydrologic resilience as the resistance of streamflow or stream chemistry to change under varying climatic conditions, which is governed by the relative size (volume) and transit time of surface and subsurface water sources. The ratio of rain/snow that falls within a catchment, evapotranspiration rates, and the early depletion of snowpack due to increasing air temperatures control the hydrologic resilience of a watershed and are variables that are critical to ecosystem function, are highly susceptible to climate change, and are impacted in the Rocky Mountains (Foster, Bearup, Molotch, Brooks, & Maxwell, 2016; Heath & Baron, 2014). Previous studies in alpine/subalpine watersheds have focused on seasonal changes in streamflow, geochemical processes, and solute exports (e.g., Clow & Mast, 2010), as well as the effects of episodic acidification and nitrogen deposition on stream chemistry and ecosystem integrity (e.g., Bachmann, 1994; Baron et al., 2000; Lepori, Barbieri, & Ormerod, 2003; Williams, Brown, & Melack, 1993). In our study, we build on previous work by examining how water sources and solute sources change in response to climate variability.

Defining current and past water source inputs to headwater streams is key to quantifying how flow paths, hydrologic storage, and transit times have changed and will change in the future. Over interannual time periods, the relative geochemical role and physical supply of groundwater, rain, snow, snowmelt, and soil water to streams within alpine to subalpine watersheds is relatively unknown and fundamental to quantifying how systems have and will respond to future stressors such as climate change and atmospheric pollution. Many hydrologic processes that buffer biogeochemical responses and acidity, and that lead to the assimilation of atmospherically deposited nitrogen, occur in the subsurface, soil, and hyporheic zones (Brooks, Williams, & Schmidt, 1998; Campbell, Baron, Tonnessen, Brooks, & Schuster, 2000; Sullivan, Cosby, Tonnessen, & Clow, 2005). If the relative importance of water sources or flow paths change (seasonally or interannually), then the system's ability to buffer climate change or atmospheric pollution will change too. Already, climate change has led to warmer temperatures, reduced snowpack cover, and less precipitation falling as snow (IPCC, 2014; Jepsen, Harmon, Meadows, & Hunsaker, 2016; Kapnick & Hall, 2012). These changes have led to shorter snow-cover duration from early melting of snowpack and thus decreased water retention within the watershed (Barnett, Adam, & Lettenmaier, 2005; Clow, 2010; Meixner et al., 2016). These water cycle changes have also altered ecosystems by lengthening growing seasons without increased plant production (Wheeler et al., 2014; Wipf, Stoeckli, & Bebi, 2009) or nutrient assimilation (Ernakovich et al., 2014), ultimately altering surface water chemistry and aquatic habitat health (Fuss, Driscoll, Green, & Groffman, 2016; Kampf & Lefsky, 2016).

This study focuses on water and solute sources, flow paths, and processes governing stream water chemistry in Andrews Creek, an alpine–subalpine headwater stream in the well-studied Loch Vale watershed in Rocky Mountain National Park, Colorado, USA (Figure 1). This study aims to address three related questions: (a) What are the water and solute sources that contribute to Andrews Creek? (b) How do the contributions of these sources vary seasonally? And (c) how have the relative contributions of water sources changed in response to climate variability on an interannual timescale? To characterize alpine–subalpine water source contributions and processes, we examine source-water contributions to Andrews Creek at seasonal and interannual time scales from 1994 through 2015 using end-member mixing analysis (EMMA; Christophersen & Hooper, 1992; Christophersen, Neal, Hooper, Vogt, & Andersen, 1990). The percent and discharge-weighted contributions of each water source to the stream during a given sample collection is identified for this 22-year

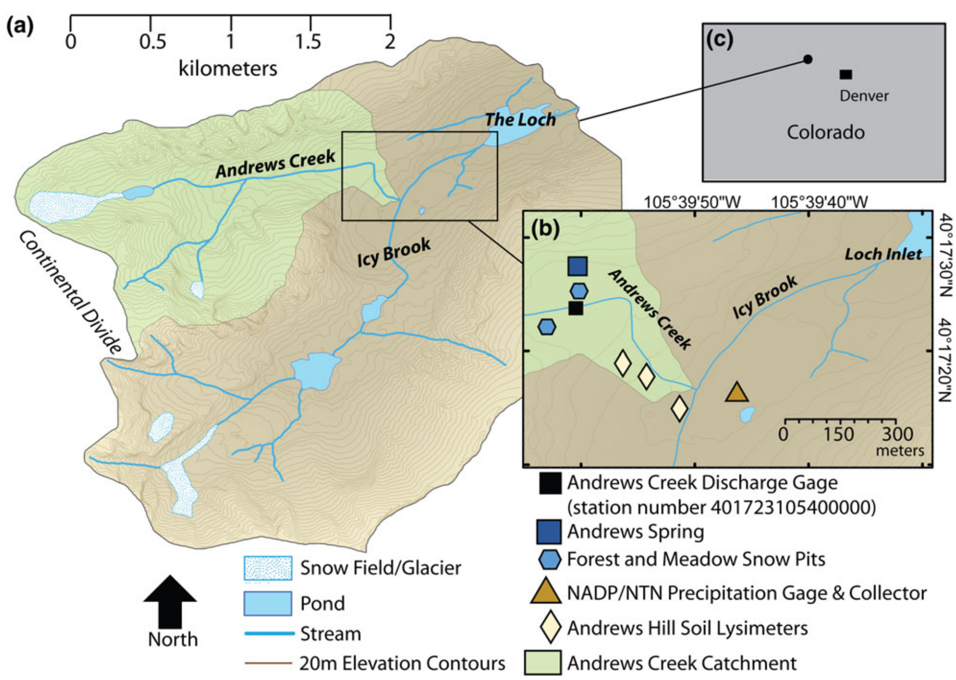

FIGURE 1 Overview map of the Loch Vale watershed (a), which borders the continental divide in Colorado, USA (c), and an inset map of sampling locations within the Loch Vale watershed (b). The Andrews Creek catchment is delineated from where Andrews Creek intersects with Icy Brook. Catchment hydrography provided by the U.S. Geological Survey National Hydrography Dataset (USGS NGP, 2016) and contours derived from the U.S. Geological Survey National Elevation Dataset (USGS, 2015)

period using hydro-geochemical signatures of each end member. We also present correlations between water source contributions and climate indices. The goal of this research is to develop a conceptual framework for how water source contributions have changed over time so that the influence of future change on streamflow and water quality can be evaluated.

2 | METHODS

2.1 | Site description

This study focuses on Andrews Creek, a perennial stream draining a 174-ha alpine and subalpine basin in the Loch Vale Watershed (Figure 1; 40°17′24″, −105°40′00″). The U.S. Geological Survey (USGS) operates a streamgage (USGS station number 401723105400000) on Andrews Creek at Andrews Meadow, a small wetland at 3,211-m elevation bordered by talus slopes and subalpine forest (Baron & Mast, 1992). Andrews Creek discharge at the streamgage shows strong seasonal variability; it is lowest in March, at around 0.001 m^3/s, and greatest in July, with an average discharge of 0.2 m^3/s (USGS National Water Information System: https://doi.org/10.5066/F7P55KJN). This pattern reflects low-flow conditions during winter, when precipitation falling as snow accumulates in deep snowpacks, and high-flow conditions during the summer snowmelt period.

Water storage within the Loch Vale watershed occurs in snowpack, snowfields, glaciers, rock glaciers, wetlands, lakes, permafrost, shallow alluvial aquifers, and talus-slope groundwater reservoirs (Clow, Schrott, et al., 2003). Talus slopes, which are abundant in Loch Vale and throughout the Colorado Front Range, help sustain base flow, contribute substantially to total annual solute export (Clow & Mast, 2010; Clow & Sueker, 2000), and have the largest groundwater storage capacity in this watershed, although only a portion of that capacity is ever full (Clow, Schrott, et al., 2003). Previous hydrograph separation analyses indicate that subsurface water, including soil water and talus-slope groundwater, contributes nearly 70% to 100% of the Andrews Creek streamflow during the winter and early spring but only 20% to 32% of the total annual streamflow and as little as 15% during peak snowmelt (Clow & Mast, 2010; Clow, Schrott, et al., 2003; Webb & Parkhurst, 2017). In the summer, snowmelt that is routed to the stream via surface run-off and shallow, subsurface flow paths is the dominant source of water to Andrews Creek (Mast, Kendall, Campbell, Clow, & Back, 1995). Although groundwater within the Loch Vale watershed makes a smaller contribution to annual run-off than snow, concentrations of base cations are greater resulting in a relatively large influence on stream chemistry (Campbell et al., 1995). It is unknown what proportion of groundwater is from talus slope reservoirs versus shallow soil reservoirs on a seasonal and inter-annual basis, or how these inputs vary with summer rainfall.

For this work, we define four possible water sources that are likely to contribute to Andrews Creek. We define a water source as a temporary reservoir in which water is or becomes chemically distinct before entering the stream and a flow path as the route water will take before reaching the stream. The chemical characteristics of each water source differ depending upon the transit time, flow paths, influence from evapotranspiration, and chemical reactions to which the water is subjected. Most of the water entering Loch Vale does so as snow, but the chemical composition of that water varies depending on the path that water takes to reach the stream. The four chosen water sources, or end members, were rain, snow, talus groundwater, and soil water. Snow and talus groundwater are recognized generators of streamflow and modifiers of stream chemistry in alpine environments, whereas rain contributes to wet deposition in the catchment during the late summer and fall (Campbell et al., 1995; Clow & Mast, 2010; Clow, Schrott, et al., 2003; Mast et al., 1995). Soil water was included because of its previously recognized role in seasonally modifying stream chemistry in this environment (Liu, Williams, & Caine, 2004; Mast et al., 1995).

2.2 | Data collection and preprocessing

Rain, snow, stream water, talus groundwater, and soil water were analysed for alkalinity, Ca^{2+}, Mg^{2+}, Na^+, K^+, Si, Cl^-, and $\delta^{18}O$. These analytes were chosen because their behaviour and fate has been previously studied (Clow & Mast, 2010; Clow, Schrott, et al., 2003; Mast et al., 1995), and there was a comprehensive dataset of these analytes collected from water year (WY) 1994 to 2015. Samples were also analysed for dissolved organic carbon (DOC), but this analyte was not used in the EMMA because it did not behave conservatively. All references to "year" throughout the manuscript refers to the WY; WY 1994 begins on October 1, 1993, and ends on September 30, 1994. USGS data generated in this study are available in National Water Information System at https://doi.org/10.5066/F7P55KJN; other data used for calculations in the study can be found at http://nadp.sws.uiuc.edu/data/NTN/.

Precipitation chemistry data were collected weekly in Loch Vale from WY 1994 to 2015 through the National Acid Deposition Program/National Trends Network (NADP/NTN) (NADP, 2015). NADP/NTN precipitation samples collected from June to September (WY 1994–2015) were assumed to be representative of a rain end member; the other months consisted of snow or mixed rain–snow conditions (NADP/NTN, 2016). Alkalinity and Si were not measured by the NADP/NTN, as concentrations in rain are negligible; thus, these concentrations were assumed to be zero within all rain end-member samples (Granat, 1972; Hofmann, Roussy, & Filella, 2002).

Snowpack chemistry data were collected through the USGS's Rocky Mountain Regional Snowpack Chemistry Monitoring Study (USGS, 2016). Samples were collected in accordance with methods stated in Ingersoll et al. (2005). Snow-pit chemistry, representing the snow end member in our study, was collected every April from snow pits just before snowmelt from WY 1994 to 2015 in two different locations within the Andrew Creek catchment (Figure 1).

Stream water from Andrews Creek and talus-groundwater samples were collected by the USGS's Water, Energy, and Biogeochemical Budgets Program (WEBB, 2016). Water chemistry samples from Andrews Creek and Andrews Spring, a talus-fed spring, were collected weekly to biweekly from April to November from WY 1994 to 2015 and on a monthly basis during winter (Figure S1). The talus-groundwater chemical signature was restricted to samples collected from Andrews Spring from November to March because of the below-freezing air temperatures during this time that mark snow and rain contributions to this end member as negligible.

Soil-water chemistry samples were collected in Loch Vale by the water, energy, and biogeochemical budgets program as part of a special, short-term study during May to September of WY 1994 and 1995. Although having additional data would more thoroughly constrain a chemical signature for this end member, assumptions of EMMA are that end members are static over time and that is assumed here from the two years of available data. Soil-water samples were collected from hillslope porous cup tension lysimeters following methods outlined in Denning, Baron, Mast, and Arthur (1991), except the lysimeters were not leached with hydrochloric acid to avoid altering the measured chloride concentrations. The soil-water chemistry data were limited to samples collected only during September in order to represent soil-water compositions just before winter snowfall. We selected this timeframe because we hypothesized that flushing of soil-water that had undergone evapoconcentration, retained heavier $\delta^{18}O$ within pore waters, and/or that had accumulated dry-deposited aerosols might be an important source of solutes to stream water during spring snowmelt (Campbell et al., 1995; Clow & Mast, 2010; Denning et al., 1991; Mast et al., 1995).

2.3 | Principal component and end-member mixing analyses

Contributing water sources, or end members, to Andrews Creek were identified using principal components analysis and EMMA (Christophersen et al., 1990; Christophersen & Hooper, 1992; Hooper, 2003). We assumed that each chemical solute was conservative and hence had no biogeochemical reactions within the stream that would nonlinearly influence its concentration over time (Hooper, 2003; Hooper, Christophersen, & Peters, 1990). We also assumed that the set of chemical solutes that were chosen to represent an end-member signature did not vary temporally (Christophersen & Hooper, 1992). Our final assumption was that the fractional contribution from all of the significant end members equates to one, and that the solutes from these end members mixed to create the observed stream chemistry (Christophersen et al., 1990; Christophersen & Hooper, 1992). Percent contributions were calculated for each end member for each day that water chemistry was sampled by solving a linear system via a non-negative least squares algorithm (Lawson & Hanson, 1974), which allowed for a quick direct calculation of fractional contributions for four end members without having to project samples back into the end-member-bounded **U** space (eigenvector-projected space). Discharge-weighted contributions from end members were calculated by multiplying the daily stream discharge at the Andrews Creek streamgage (USGS station number 401723105400000) by the percent contribution. This was to distinguish between average percent contributions on the basis of solute composition versus volumetric (discharge-weighted) contributions to Andrews Creek. A detailed explanation of the method, including principal equations, are provided in section 2 of the Supplementary Information.

2.4 | Trends in end-member contribution to Andrews Creek and correlation to climate indices

To address if end-member contributions have changed monotonically over the study period, a partial seasonal Kendall test (pSKT) was implemented using the R package *rkt*, with a correction for serial correlation (Darken, Zipper, Holtzman, & Smith, 2002; Marchetto, 2015). A pSKT differs from a traditional seasonal Kendall test by incorporating and correcting for a covariate that may also explain some of the observed trend (Libiseller & Grimvall, 2002). In our case, we were interested if end-member contributions were changing independently of short-term variations in precipitation. A pSKT was performed on streamflow and end-member contributions for the months of May through October during 1994 to 2015, using total monthly precipitation as a covariate. End-member contributions for each month during each year were averaged, whereas the precipitation for each month during each year was summed. Contributions from May through October were used when discharge and chemistry data sets are more complete and when sample collection and discharge measurements are minimally affected by ice in the stream. All tests for statistical significance were evaluated at a significance level α of 0.05, unless otherwise noted.

Pearson correlations were also calculated between WY average end-member percent and discharge-weighted contributions and the following climate indices and teleconnection patterns: North Atlantic Oscillation (NAO), Pacific/North American Index (PNA), Colorado Modified Palmer Index (COMPI) for Region 14 and 25 (COMPI-14; COMPI-25), Palmer Drought Severity Index (PDSI), Palmer Hydrologic Drought Index (PHDI), and the Modified Palmer Drought Severity Index (PMDI; CCC, 2016; NCDC, 2016; NWSCPC, 2016a; NWSCPC, 2016b). These climate indices were chosen because of their gradient in coverage, from continental to river-basin scale, and because these indices provided slightly different ways of indicating climate variability. The NAO and PNA, although correlated, are defined by different teleconnection patterns that are spatial and temporal patterns of pressure and circulation anomaly heights that drive temperature and precipitation variations. A positive NAO index is associated with above-average temperatures in the eastern United States, whereas a positive PNA index is strongly associated with El Niño–Southern Oscillation, which tends to result in above-average temperatures in the western United States. The Palmer drought indices (PDSI, PMDI, and PHDI) are derived from inputs of temperature and precipitation into physical water balance models to determine the extent and intensity of long-term drought and to calculate the hydrologic effects of drought within moderately sized basins (such as the Platte River and the Colorado River used within this study). The COMPI are more localized versions of the PMDI, using fewer stations to average temperature and precipitation inputs than the moderate scale Palmer indices. The climate indices (PDSI, PHDI, PMDI, and COMPI) are standardized for each location, and dry periods are indicated by negative index values, whereas positive values represent wetter time periods.

3 | RESULTS

3.1 | Number of significant water sources to Andrews Creek

We tested for the appropriate number of end members (water sources) in stepwise fashion, to find the minimum number of end members that could adequately describe stream chemistry variations.

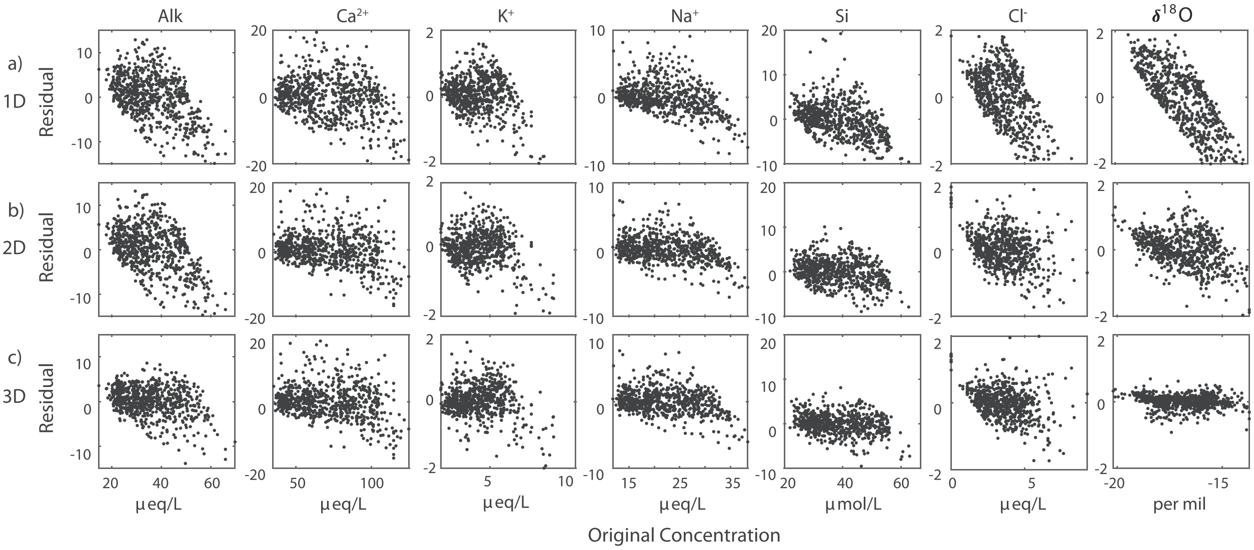

FIGURE 2 Residual analysis of (a) 1D, (b) 2D, and (c) 3D end-member mixing analysis systems. The residual structure and magnitude dissipate as more dimensions are added to the system. A three-dimensional, four end-member analysis was accepted because the residual magnitude lessens and the structure dissipates within the following parameters: alkalinity, K^+, Si, Cl^-, and $\delta^{18}O$. Ca^{2+} and Mg^{2+} (not displayed) behave similarly and do not noticeably change with the addition of a fourth end member. There are minor changes in Na^+ residuals when adding more dimensions

With the two end-member case (i.e., one dimensional), residuals from all of the parameters had a linear structure (Figure 2a), implying that substantial variance in the data remained unexplained. The three end-member case (i.e., two dimensional) met the Guttman–Kaiser criterion (the eigenvalue for each component was greater than one) and improved residual structure for most of the parameter distributions except alkalinity, K^+, and $\delta^{18}O$ (Figure 2b; Guttman, 1954; Kaiser, 1960; Kaiser, 1961). However, residual analysis strongly supported the inclusion of a fourth end member. Introduction of a fourth end member (i.e., three-dimensional case) reduced all of the parameter residual magnitudes and eliminated most of the structure in the alkalinity, K^+, and $\delta^{18}O$ residual distributions (Figure 2c). Thus, a four end-member mixing case was most successful at reproducing all of the solutes used in the analysis, especially the alkalinity, K^+, and $\delta^{18}O$ concentrations within the stream. In the four end-member analysis, the first three principal components explained 91.9% of the variance (73.8%, 13.0%, and 5.1%; Figures S2 and S3).

3.2 | Comparing viable end members with steam chemistry patterns in U space

An examination of the seasonal stream chemistry patterns and the projections of all the possible end members in **U** space indicated that talus groundwater, soil water, rain, and snow are likely end members contributing to Andrews Creek (Figures 3 and 4), as indicated by the fact that stream samples fell within and near the bounds of these end members (Figure 3). The concentrations of most solutes were greatest during the fall and winter and lowest in June and July, which is partially explained by dilution from melting snow (Clow & Mast, 2010; Figures 4 and S5). Cl^-, K^+, and DOC concentrations were an exception, with peak concentrations during April–May, likely due to an increase in contribution from soil water reservoirs and inputs from the ionic pulse (Figures 4 and S5; Campbell et al., 1995; Johannessen & Henriksen, 1978). Stream water $\delta^{18}O$ was lightest in June and July, reflecting the influence of snowmelt, and heaviest during the winter, due to increasing importance of talus groundwater after peak discharge (Figure 4b).

3.3 | Mixing analysis fit with chosen end members

Comparison of observed stream-solute concentrations with predicted stream-solute concentrations from the four end-member analysis (Figure 5) indicated that the chosen system accounted well for most of the observed solute ranges, with coefficients of determination (R^2) that ranged from 0.79 to 0.94. Despite this good agreement, notable deviations occurred between predicted and observed solute concentrations; K^+ at >7 µeq/L, Cl^- < 2 µeq/L and > 5 µeq/L, and $\delta^{18}O$ values of −19 to −16 per mil (‰; Figure 5). The $\delta^{18}O$ values between April and May were lighter than predicted due to preferential elution of light $\delta^{18}O$ during early snowmelt (Taylor et al., 2001). Observed Cl^- stream concentrations were greater than predicted during April and May, suggesting that the median soil-water end-member values may underestimate true soil-water Cl^- concentrations in some samples. The under-predicted concentrations of K^+ in the stream during October to March also implies we are missing a high-concentration source of K^+ during the winter with our current end-member datasets. This is likely due to absent winter soil-water end-member chemistry and the uncertainty in this end-member's chemical designation with regards to soil weathering products and reactions during this time. Winter soil-water chemistry likely consists of greater K^+ concentrations from the weathering of biotite, heavier isotopic concentrations, and potentially greater Cl^- concentrations (Webb & Parkhurst, 2017).

3.4 | Seasonal and interannual behaviour of end-member percent contributions

The talus-groundwater, snow, rain, and soil end-member percent contributions to Andrews Creek showed strong seasonal variation throughout the 22-year study period, which reflected the importance

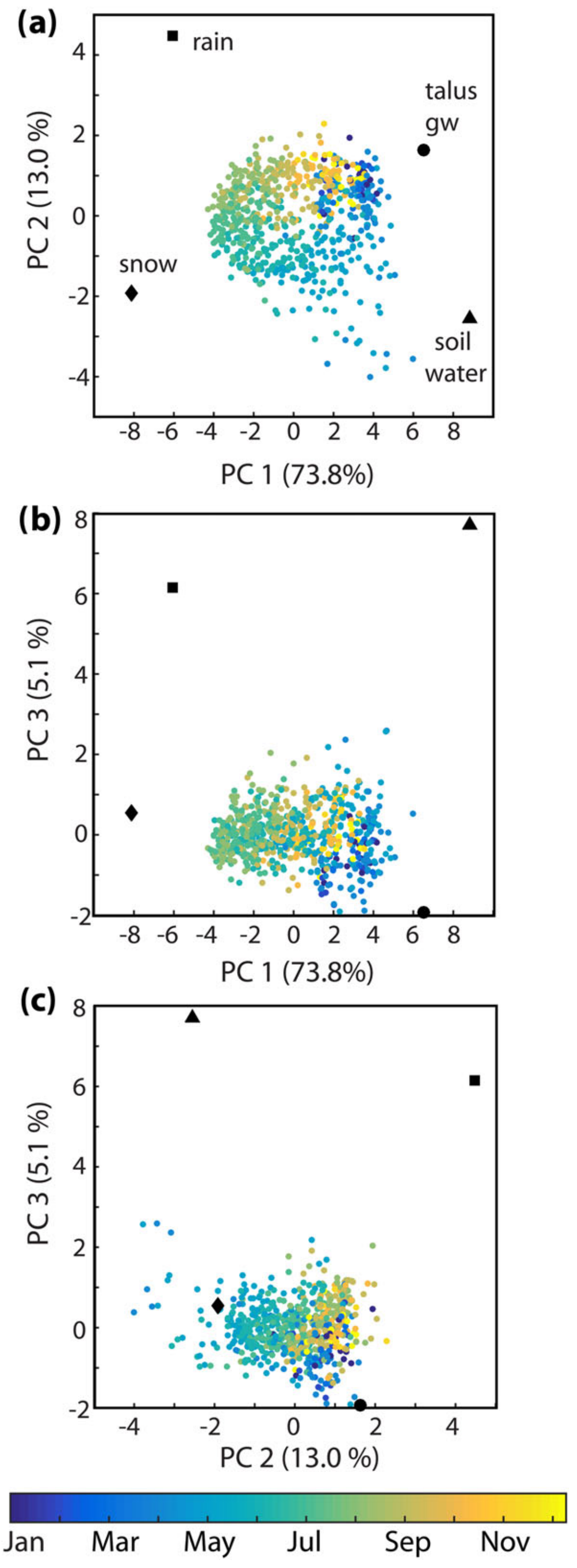

FIGURE 3 Stream samples and end members are plotted in **U** space; PC1 versus PC2 (a), PC1 versus PC3 (b), and PC2 versus PC3 (c). Stream samples are coloured according to the sample collection month. End-member median solute concentrations were projected into **U** space

of snow accumulation, melt, and water delivery in this high-elevation system (Figure 6). The talus-groundwater end member was the largest contributor to stream composition throughout the year, except for June and July, when the stream composition was dominated by snowmelt. The dilution and flushing of talus groundwater by melting snow is supported by the inverse relation between snow and talus-groundwater end-member percent contributions (Figure 6) and also by the inverse chemostatic relation between weathering product concentrations and streamflow (e.g., Clow & Mast, 2010; Godsey, Kirchner, & Clow, 2009). Contributions from soil-water were greatest during April and May, prior to peak snowmelt, and decreased in contribution in the subsequent summer months. As the soil-water contribution decreased through the summer, the influence from rain increased, reflecting inputs from summer storms. This is supported by the enrichment of $\delta^{18}O$ over the summer by increasing rain inputs and incongruent melting of the snowpack, allowing lighter $\delta^{18}O$ concentrations to reach the stream first and heavier $\delta^{18}O$ concentrations to reach the stream later in the summer. Increasing stream-water concentrations of Ca^{2+}, Mg^{2+}, Na^{+}, Si, and alkalinity during the summer also reflect decreased snow inputs and increased talus-groundwater bedrock-weathering material.

Over the 22-year study period, the annual percent contribution to Andrews Creek for each end member varied between wet and dry years and unexpectedly had different responses with regards to arrival and recovery of drought (Figure 7a). During the beginning of the study period (1994–2002), the watershed transitioned from wet conditions to drought-like conditions that coincided with increases in the talus-groundwater, soil-water, and rain percent contributions to Andrews Creek and a decrease in the snow end-member percent contribution. After 2002, the peak of drought, the system transitioned from below average annual precipitation (2002–2006) back to relatively normal-wet conditions, as the total annual precipitation increased each consecutive year after 2002, with the exception of 2006, 2007, and 2012. Although the peak of drought occurred in 2002, the percent snow contribution declined through 2005 while there was an increase in percent of talus water contribution (Figure 7b). From 2006 onward, the percent contribution from the snow end member increased and the talus-groundwater end member remained relatively stable, whereas the rain and soil-water end members changed without clear pattern (Figure 7 b). Over the study period, the rain contribution was small but sensitive to stochastic meteorological events, whereas there were relatively minor changes in the responses for other water sources (Figure 7c). These responses are most noticeable between 1997 and 2002. Soil-water and rain contributions were always small, whereas snow and talus-groundwater contributions were much larger.

Trend analysis using pSKT revealed that there was a statistically significant increase in the talus-groundwater percent contribution to Andrews Creek of 0.5% per year during May through October from WY 1994 to 2015, after correcting for monthly precipitation ($p < 0.0001$) (Table 1). During this time, there was a decrease in the percent contribution from the snow and rain end members of −0.4% per year and −0.1% per year, respectively ($p = 0.09$ and $p = 0.09$), a decrease of −0.6% per year for rain and snow combined ($p = 0.001$), and no trend in the soil-water end-member percent contribution ($p = 0.3$; Table 1).

3.5 | Seasonal and interannual discharge-weighted end-member contributions

We calculated end-member discharge-weighted contributions to evaluate volumetric contribution, seasonal behaviour, and

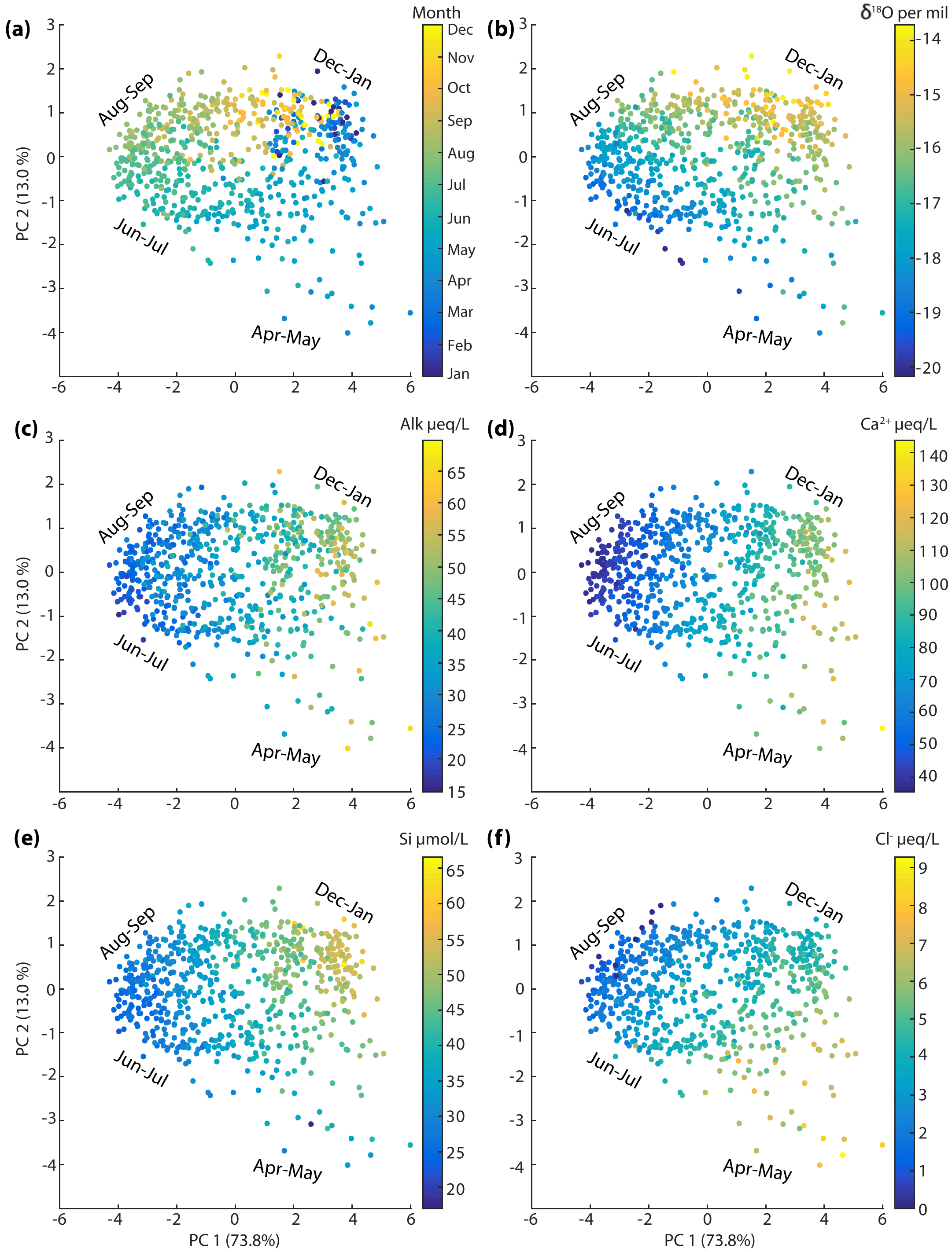

FIGURE 4 Stream sample chemistry characteristics defined in **U** space; coloured by sample collection month (a), $\delta^{18}O$ per mil (b), alkalinity µeq/L (c), Ca^{2+} µeq/L (d), Si µmol/L (e), and Cl^{-} µeq/L (f). Stream samples are only plotted on the PC1 and PC2 "axes" for easier comparison between solutes

interannual variations of a water source. The discharge-weighted contribution to Andrews Creek for each end member showed distinct seasonal patterns, characteristic of the seasonal hydrograph (Figure 6j) During December to April, the streamflow of Andrews Creek was less than 0.005 m^3/s on average and was mostly composed of talus groundwater. During April and May, Andrews Creek increased by an order of magnitude from 0.004 to 0.05 m^3/s on average, marked the rising limb of the annual hydrograph, and transitioned from a system dominated by talus-groundwater towards a more snow and soil-water influenced stream. The snow end member is the main contributor to Andrews Creek streamflow in June, but the remaining end members of soil water, rain, and talus groundwater also increased their streamflow contributions to Andrews Creek (0.02, 0.003, and 0.07 m^3/s, respectively). During July and August, the annual hydrograph recession limb, the percent and discharge-weighted contribution of soil water decreased as the percent and volumetric contribution of the rain end member increased (Figure S11). Snow still contributed the most to Andrews Creek

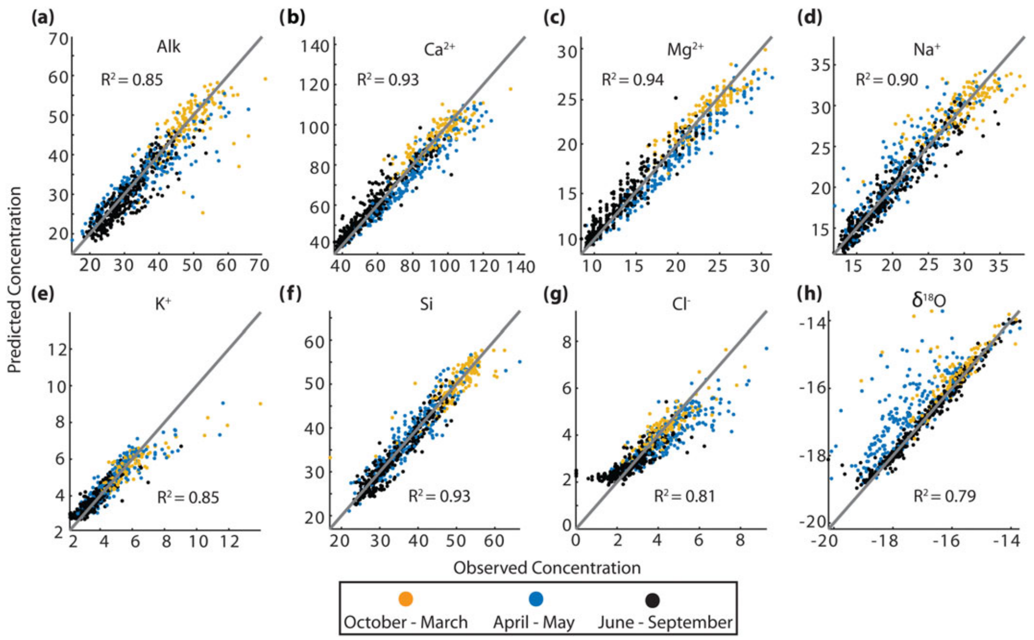

FIGURE 5 Comparison of predicted with observed solute concentrations within Andrews Creek using the four end-member mixing analysis. All units are in μeq/L, except for $\delta^{18}O$ (per mil) and Si (μmol/L). Sample colours correspond to collection period

streamflow during this time, whereas the talus groundwater contributed the second most. From September through December, talus-groundwater dominated streamflow again, whereas rain, soil water, and snow had decreased discharge-weighted contributions to streamflow.

Interannual changes in source-water contributions reflected variations in annual precipitation (Figure 7a; Figure S8). Hydrologic displacement was evident in Andrews Creek as talus-groundwater inputs responded to short-term variability in snow contribution (Figure 7a). Discharge-weighted contributions from snow and talus groundwater increased when precipitation amounts were greatest (i.e., 2011) and decreased during drought (i.e., 2002; Figures 7a and S12). This is expected because talus groundwater and snow contribute the most to Andrews Creek streamflow and there is a statistically significant, positive relationship between annual precipitation and yearly-averaged Andrews Creek streamflow ($p < 0.001$; Figure S6). Although there were no significant trends in discharge-weighted end-member contributions from WY 1994 to 2015 except for a small decrease in combined rain and snow contributions of 0.0006 m^3/s per year (Table 1), there appeared to be shorter-term variations in response to wet and dry conditions lasting longer than a year (Figure 7). For instance, yearly averaged snow and talus groundwater end-member discharge-weighted contributions during the first part of the study period (1994–2002) were significantly correlated to annual precipitation (Kendall tau = 0.78 and 0.67; p = 0.002 and p = 0.01, respectively) as the local atmospheric conditions became drier. Whereas the yearly-averaged snow and talus groundwater end-member discharge-weighted contributions were less correlated with annual precipitation when the watershed shifted into a drought recovery phase from 2003 to 2015 (Kendall tau = 0.46 and 0.15; p = 0.03 and p = 0.5, respectively). The driest year, WY 2002, had the lowest stream discharge and discharge-weighted contribution from snow and talus groundwater, but WY 2005 had the lowest snow percent contribution and a steady talus groundwater percent contribution (Figures 7c and S12). Thus, the solute concentration effects of WY 2002 were not apparent until WY 2005 implying there is chemical memory within the system. The rain end-member discharge-weighted contribution remained relatively stable from WY 1994 to 2005, where it peaked, and decreased after that. During the dry years, there was an increase in discharge-weighted contribution (and percent contribution) from the soil water end member to Andrews Creek (WY 2001–2005), which may imply the soil-water contributions are independent of the overall annual precipitation inputs.

3.6 | Linking climate indices with water source availability and quality

Annual climate indices, water source percent contributions, and discharge-weighted contributions had moderate to weak Pearson correlations (Table 2). These correlations were most informative for interpreting percent and discharge-weighted contributions for wet versus dry atmospheric conditions, and correlations were greatest for climate indices that had moderate geographic regional scope (i.e., PMDI, PHDI, and PDSI), as opposed to those with very large geographic regional scope (i.e., NAO and PNA) or more localized scope (i.e., COMPI-14 and COMPI-25).

The magnitude and sign of the Pearson correlation coefficients between climate indices and the percent and discharge-weighted contributions varied among end member, climate index, and between the contribution types (Table 2). A positive correlation existed between most climate indices and the snow end-member contributions to Andrews Creek, reflecting a direct, positive relation between snowfall and streamflow (Table 2). An exception to this was the negative correlation between the PNA index and snow end-member percent and discharge-weighted contributions, which was likely related to a decrease in precipitation falling as snow due to warmer

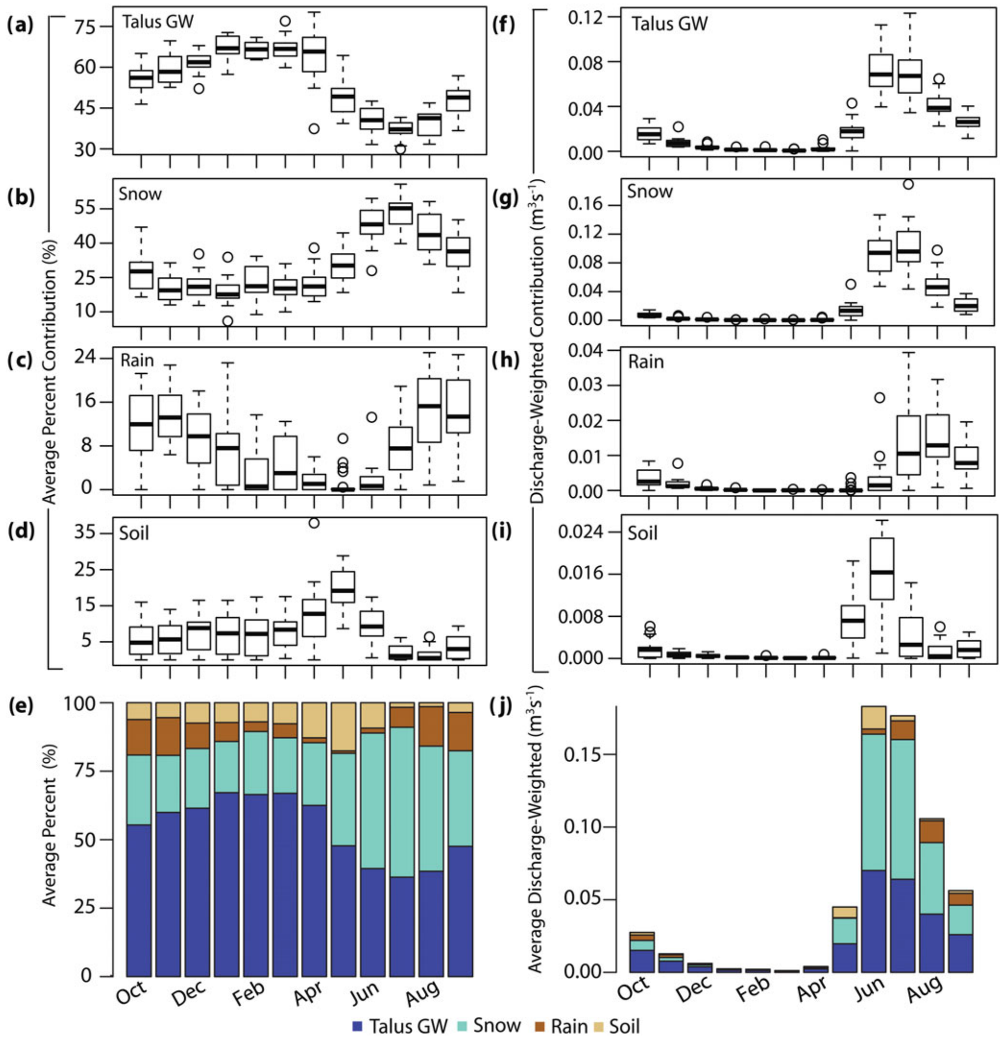

FIGURE 6 Monthly percent contributions from the talus groundwater (a), snow (b), rain (c), and soil water (d) end members from water year 1994 to 2015. Average monthly percent contribution from all the end members over the study period (e). Monthly discharge-weighted contributions from the (f) talus groundwater, (g) snow, (h) rain, and (i) soil end members from water year 1994 to 2015. Average weighted discharge from all end members over the study period (j)

than average temperatures in the western United States during a positive PNA teleconnection anomaly. This negative correlation also occurred between the PNA anomaly and the talus-groundwater discharge-weighted contributions, whereas the remaining correlations with the other climate indices for those sources remained positive. Similarly, talus groundwater had a large percent contribution to Andrews Creek, so when the overall streamflow decreased, a decrease in the discharge-weighted contribution occurred. The talus-groundwater percent contributions were negatively correlated with all of the chosen climate indices, except for with the PNA anomaly, reflecting that during wet years, there is a greater percentage of snow and in turn a lesser percentage of talus groundwater, soil water, and rain (as all end-member percent contributions must equal 100%). The soil-water and rain end-member percent contributions were also negatively correlated with the climate indices except for the PNA and NAO anomalies (Table 2). The rain end member contributed smaller percentage and volumetric amounts to the basin; thus, the correlations between contributions and climate indices were relatively weak. However, the soil-water end-member percent contribution had the greatest significant negative correlations to the chosen climate indices (positive percent contributions linked with negative climate index values) indicating that soil-water chemistry has an important influence on stream chemistry, especially during drier atmospheric conditions.

Among the climate indices examined, the moderate-sized regional scale indices (i.e., PDSI for the Platte and Colorado River basin) were the best overall at determining the contribution of a water source to the stream; however, different climate indices were better for predicting percent as opposed to discharge-weighted end-member contributions (Table 2). The PDSI for the Platte River basin and the Colorado River basin were the best overall climate indices for predicting end-member percent contributions (Table 2). However, the COMPI-25 and the PHDI for the Colorado River basin were best for envisioning end-member discharge-weighted contributions, with the next best being the PMDI Colorado index (Table 2). The worst overall correlations were between the NAO and PNA and all end-member contributions. The small regional-scale climate indices (COMPI-14 and COMPI-25) were better correlated with discharge-

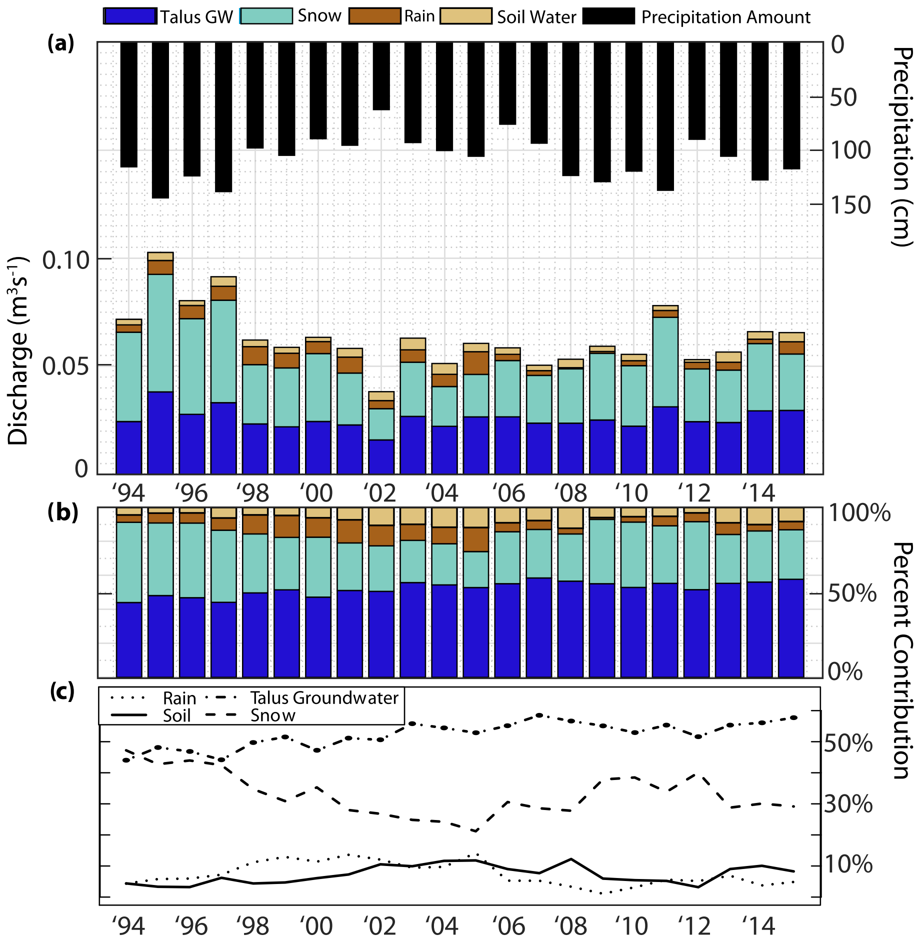

FIGURE 7 The yearly averaged end-member discharge-weighted contributions to Andrews Creek from water year 1994–2015, with the total annual precipitation recorded at the National Acid Deposition Program/National Trends Network precipitation gage—CO98 (a) (NADP, 2015). The yearly averaged percent contributions from each end member over the study period, each year should sum to 100% (b). Another perspective of yearly averaged percent contributions from each end member over the study period (c)

TABLE 1 Partial seasonal Kendall test results for monthly averaged end-member contributions and Andrews Creek discharge from May through October of water year 1994–2015

End member	Type	Kendall tau	SKT slope	*p* value
Talus GW	Percent contribution Weighted discharge	0.5 0.1	0.5 0.0003	0.00008* 0.2
Snow	Percent contribution Weighted discharge	−0.2 −0.1	−0.4 −0.0003	0.09 0.1
Rain	Percent contribution Weighted discharge	−0.2 −0.2	−0.06 0.0	0.09 0.07
Soil water	Percent contribution Weighted discharge	0.1 0.08	0.0 0.0	0.3 0.4
Rain + snow	Percent contribution Weighted discharge	−0.4 −0.2	−0.6 −0.0006	0.001* 0.02*
AC streamflow	Monthly average	−0.09	−0.0005	0.2

Note. Asterisks indicate strong trends ($p < 0.05$). SKT slope units are in percent per year for the percent contribution and cubic meters per second per year for the weighted discharge and streamflow. SKT = seasonal Kendall test; GW = groundwater; AC = Andrews Creek.

weighted contribution than percent contributions due to localized temperature and precipitation data that can more accurately account for streamflow conditions.

4 | DISCUSSION

EMMA was useful for identifying water sources to Andrews Creek (soil water, snow, talus groundwater, and rain), as well as their seasonal and interannual influence on stream chemistry and quantity. Soil water was a surprisingly important solute source to Andrews Creek because it had a relatively disproportionate influence on stream chemistry when compared with streamflow prior to peak stream discharge, delivering organic carbon and weathering products to Andrews Creek without increased volumetric input (Figures S5 and S11d). Talus-groundwater percent contribution increased significantly over the study period, without an increase in its discharge-weighted contribution. The increases in percent contribution from talus groundwater was matched by decreases in percent contributions from snow and rain, implying that talus groundwater provides hydrologic resilience to the system (Table 1). Moreover, we found a coherence between stream chemistry and regional to local-scale climate indices, suggesting that factors associated with these metrics influence water source contributions (Table 2).

4.1 | Inclusion and importance of soil water

Of the four significant end members generating Andrews Creek chemistry, the importance of the soil-water end member was the most

TABLE 2 Pearson correlation coefficients between general climate indices and end members' percent contribution and weighted discharge to Andrews Creek

	Percent contribution				Discharge-weighted contribution			
Climate indices	**Talus groundwater**	**Snow**	**Rain**	**Soil**	**Talus groundwater**	**Snow**	**Rain**	**Soil**
NAO index[a]	−0.29	0.09	0.12	0.04	0.05	0.10	0.04	0.01
PNA index[b]	0.38'	−0.33	0.15	0.07	−0.13	−0.34	0.22	0.09
COMPI-14[c]	−0.25	0.39'	−0.09	−0.41'	0.43'	0.45*	0.29	−0.29
COMPI-25[c]	−0.28	0.33	0.00	−0.40'	0.51*	0.52*	0.37'	−0.31
PDSI Platte[d]	−0.4'	0.59**	−0.28	−0.48*	0.32	0.54**	0.10	−0.30
PDSI Colorado[d]	−0.36	0.52*	−0.30	−0.36	0.41'	0.56**	0.04	−0.32
PHDI Platte[e]	−0.21	0.43*	−0.21	−0.48*	0.42'	0.48*	0.17	−0.34
PHDI Colorado[e]	−0.12	0.32	−0.21	−0.34	0.53*	0.50*	0.16	−0.34
PMDI Platte[f]	−0.12	0.37'	−0.24	−0.42'	0.44*	0.45*	0.17	−0.30
PMDI Colorado[f]	−0.10	0.31	−0.22	−0.31	0.56**	0.50*	0.16	−0.30

Note. All available contributions and climate indices were averaged for each water year and then compared. COMPI Region 14 corresponds to the Platte River drainage–Front range foothills, whereas Region 25 corresponds to the Northern Mountains. The continental divide separates these two regions. Pearson correlations with *p* values less than 0.1 are defined with an apostrophe, *p* values less than 0.05 are defined by one asterisk, and *p* values less than 0.01 are defined by two asterisks.

[a]North Atlantic Oscillation (NWSCPC, 2016a).

[b]Pacific/North American Oscillation (NWSCPC, 2016b).

[c]Colorado Modified Palmer Index for Region 14 and Region 25 (CCC, 2016).

[d]Palmer Drought Severity Index for the Platte River and Colorado River basin (NCDC, 2016).

[e]Palmer Hydrologic Drought Index for the Platte River and Colorado River basin (NCDC, 2016).

[f]Palmer Modified Drought Index for the Platte River and Colorado River basin (NCDC, 2016).

unexpected because adding this end member allowed us to give an explanation for some of the Andrews Creek samples within the **U** space that were nonconforming to the general mass of samples (Figure 3a). The ample number of stream samples collected over multiple seasons and decades allowed us to examine these unconstrained samples more thoroughly—leading to a residual analysis that substantiated a need for a fourth end member. Stream samples that were outside of the **U** space bounds in the three end-member analysis had distinct chemical signatures from April to May that were representative of ionic pulse solutes and solutes flushed from shallow soil horizons during early snowmelt. Thus, the addition of the soil-water end member to the analysis helped constrain some of these stream samples in **U** space (Figure 3) and was plausible given stream-chemistry observations and past documentation supporting the importance of this water source (Clow, 2010; Denning et al., 1991; Kampf, Markus, Heath, & Moore, 2015).

The inclusion of the soil-water end member allowed us to quantify inputs to Andrews Creek resulting from soil flushing, as we were able to define its impact on springtime stream chemistry and its disproportionate volumetric input. Often, soils are highly reactive due to the presence of cation exchange sites and organic matter, and have an outsized influence on solute flux relative to their discharge. This is evident in springtime chemistry at Andrews Creek, where stream samples collected in April and May emulated flushed soil-water chemistry, in which samples were characterized by $\delta^{18}O$ values between −18.5‰ to −16.5‰, high DOC, K^+, Cl^-, Ca^{2+}, and Mg^{2+} concentrations, and moderate alkalinity, Si, and Na^+ concentrations (Figures 4 and S5). Conceptually, solutes that accumulate in the soil from wet and dry deposition, weathering, and organic matter decay during late summer and fall are stored there through the winter and then flushed into the stream prior to and during snowmelt (Clow, Sickman, et al., 2003; Clow & Mast, 2010). High concentrations of Cl^- within this stream chemistry signature likely reflects flushing of wet and dry deposition that accumulated in soils during the previous summer and fall (Mast, Drever, & Baron, 1990). Wet and dry deposition of sulphur and nitrogen compounds in snow and rain also may provide protons to displace Ca^{2+} and Mg^{2+} from cation-exchange sites within the soil (Clow & Mast, 2010; Tranter et al., 1986); and these cation-exchange processes affect Ca^{2+} and Mg^{2+} much more than Na^+ (Baron & Mast, 1992; Clow & Mast, 2010). Therefore we would expect a soil-water signal to be distinguished from talus groundwater by higher stream concentrations of Ca^{2+} and Mg^{2+} in the April to May time period, without similarly high concentrations of Na^+ and Si. This is what was identified in the stream samples during this time (Figures 3 and 4).

The presence of a soil-water end member was also supported by peak DOC concentrations in the stream during April to May of each year (Figure S5c), as soil water is the primary reservoir of DOC within the catchment (Baron & Mast, 1992). Peak concentrations of K^+ within springtime stream samples suggest that biologically cycled K^+ is flushed from soil organic matter during spring snowmelt (Figure S5e) (Likens et al., 1994; Mast et al., 1990). Lastly, the relatively heavy $\delta^{18}O$ values in springtime stream water were consistent with early snowmelt-flushed soil water, which tends to be isotopically heavy due to rain or residual snowpack inputs from the preceding summer. The soil-water addition to the EMMA supports earlier hypotheses about the importance of soil-water flushing to stream chemistry (Clow & Mast, 2010). We would have ignored and underestimated the role of flushed soil-water inputs to Andrews Creek had we not included this water source, and this would have also affected the presumed contributions of other end members.

Capturing contributions from a soil-water end member within the alpine watershed is important for a multitude of reasons, but especially as we address drivers of chemostatic behaviour within catchments and the timing of water source solute fluxes (Godsey et al., 2009). The seasonal soil-water constituent inputs to streams are important as they are indicators that the soil moderates atmospheric pollutants from wet and dry deposition via cation exchange processes (Williams & Melack, 1991). In addition, the seasonal delivery of high DOC concentrations from soils to Andrews Creek provides nutrients to in-stream organisms and aids in terrestrial carbon cycling (Boyer, Hornberger, Bencala, & McKnight, 1997; IPCC, 2007). Previous works have recognized the importance of soil water in modifying stream chemistry (Campbell et al., 1995; Denning et al., 1991), but our results expand on this by comparing these contributions with climate variations. Our results also highlight the importance of soil-water contributions, the timing of contributions, and the significance of monitoring the export of inorganic solutes and organic carbon from alpine soils to streams as it may change by increasing springtime air temperatures and earlier melting of snowpack (Clow, 2010). Also, the enrichment of solutes within soil water during summer may be enhanced by evapotranspiration (e.g., Carey & Quinton, 2005; Dickinson, Chagué-Goff, Mark, & Cullen, 2002) and potentially during spring flush when more frequent and intense melt–freeze cycles concentrate ions at the base of the snowpack and release into the soil upon melt (Davis, Petersen, & Bales, 1995). This may ultimately change soil chemistry and the chemical interactions between snowmelt, soil water, and stream water. Flushing of soils could also occur with heavy rains; however, the exact controls that drive soil-water chemistry and delivery to Andrews Creek is an avenue for future investigation.

4.2 | Patterns and trends in interannual contributions

Monotonic trends among end-member contributions were explored from WY 1994 to 2015 during May to October using the pSKT, and the only statistically significant results were a percent increase in talus-groundwater contribution to Andrews Creek ($p < 0.0001$), percent decrease in snow plus rain contribution ($p = 0.001$), and a slight decrease in snow plus rain discharge-weighted contribution ($p = 0.02$). These results translate to Andrews Creek chemistry shifting towards greater base-cation concentrations and a heavier isotopic signature during the months of May through October, over the study period. Thus, the observed trend is likely the result of a combination of effects including the following: (a) an increase in talus-groundwater contribution and decrease in snow and rain contribution, (b) an increase of internal catchment sources where there is enhanced mineral weathering and/or melting of periglacial features containing greater base-cation concentrations, (c) an increase in dust deposition or enhanced evapotranspiration, or (d) an artefact of our chosen study period with regards to drought conditions.

An increase in talus-groundwater percentage over the study period without a significant trend identified in the talus-groundwater discharge-weighted contribution ($p = 0.2$) suggests that there is groundwater storage that sustains streamflow and provides resilience to the system, especially during and after dry periods or periods of drought. This is supported by a similar decrease in percent snow and rain contribution ($p = 0.09$, each respectively; $p = 0.001$ combined) and decrease in snow plus rain discharge-weighted contributions ($p = 0.02$; Table 1). However, the strong positive relation between annual precipitation and yearly averaged talus-groundwater discharge-weighted contributions indicates talus groundwater is recharged by precipitation that enters the basin; thus, the two are volumetrically related ($R^2 = 0.53$; Figure S8a). This is most pronounced in years with exceptional precipitation (WY 1995, 1997, and 2011) or lack of it (WY 2002; Figure 7a). The talus-groundwater discharge-weighted contribution to Andrews Creek may decrease if less precipitation enters the basin over time or if the precipitation received does not adequately recharge available reservoirs, as revealed by the drought in the early 2000s. Consequently, the watershed may be less resilient and more sensitive to atmospheric pollutants owed to the relatively quick renewal of talus groundwater by precipitation.

Another explanation for the increase in percent talus groundwater present in Andrews Creek could be that there is enhanced mineral weathering or melting of periglacial features due to increasing air temperatures and moisture availability that are providing more base cations to the stream over time (Heath & Baron, 2014; Kopáček et al., 2016; Williams, Knauf, Caine, Liu, & Verplanck, 2006). These processes could potentially amplify the trend of increasing percent talus groundwater revealed by the pSKT. If periglacial feature chemistry were different from talus groundwater or soil water and significant to altering stream chemistry, then we could possibly identify the influence of the source in **U** space.

Increased air temperatures or dust inputs might also amplify the increase in percent talus groundwater to Andrews Creek due to greater evapoconcentration and solute retention within streams during warmer/dry periods or with the addition of more solutes without increased flow/volume from dry dust deposition (Clow, Williams, & Schuster, 2016; Mosley, 2015). Dust was attributed to statistically significant increases in alkalinity, Ca^{2+}, and in Mg^{2+} concentrations within Loch Vale watershed snowpack between 1993 and 2014 (Clow et al., 2016). The melting of dust-deposited cations on snowpack throughout the summer would amplify the trend of an increase in talus-groundwater percent contribution to Andrews Creek.

As with any trend analysis, the window of observation can play a role in the outcome of trends, and our study period, governed by the period of record, happened to include a time of transitioning atmospheric conditions. To briefly investigate if the period of wet years prior to the drought influenced our pSKT, we removed the first four years of the study period and reran the analysis. The same significant trend was identified by the pSKT for the years 1998 through 2015, with the addition of significant decreasing trends in the percent and discharge-weighted (volumetric) rain end-member contributions (Table S4). Only contributions from May to October of each year in the study period were evaluated by the pSKT, so the decrease in rain contributions and increase in talus groundwater may propose that the timing, type, and delivery of precipitation is changing. In addition to this, temporal variation in end-member chemistry could potentially reduce the accuracy of contribution estimates to Andrews Creek; however, without residence times defined for each end member, it would be difficult to determine how each end members' chemical changes have influenced the stream.

Over the study period, there have been changes in percent water source contributions to Andrews Creek, but the combination of other influences cannot be ignored, which can control changes in the stream chemistry and skew results of the pSKT. Generally, water source contributions have been responding to climate variables, such as precipitation, seemingly making Andrews Creek less resilient; however, any resilience within Andrews Creek is owed to the relative continual supply of talus groundwater.

4.3 | Climate and water source contributions

Pearson correlations between end-member contributions and climate indices provided insight to how climate variability can alter water source influence within alpine environments. Climate indices had different correlation responses to percent versus discharge-weighted contribution. The NAO and PNA had the overall worst correlations with all climate indices, which was expected because these are large teleconnection patterns that may be difficult to detect on a basin-scale study and the NAO does not significantly influence climate in Midwestern North America. The PDSI Platte and PDSI Colorado indices, which calculate the intensity of long-term droughts in those basins, had the best overall correlations with all of the end-member percent contributions and had significant correlations with the snow percent contribution. There was also a significant correlation between the soil-water percent contribution and the PDSI Platte. The PDSI model uses antecedent moisture, present precipitation, surface air temperature, and potential evaporation demand (Thornthwaite equation) in a hydrologic model for estimating soil moisture content (Palmer, 1965). Streamflow has been correlated to PDSI in the past (Piechota & Dracup, 1996); however, the percent contribution in our case is more related than the discharge-weighted contributions derived from the EMMA. This suggests that the PDSI for both the Colorado and Platte River basins are useful in examining percent water source contributions to alpine catchments, especially for snow as it is the largest contribution to precipitation in the catchment.

The COMPI-25 and the PHDI Colorado were best overall for estimating end members' discharge-weighted contributions, with the PMDI Colorado close behind. This is expected as the PHDI is a measure of how water sources are impacted by long-term droughts, and the correlation with discharge-weighted contributions inherently contains stream discharge information. The COMPI-25 is a localized Palmer drought index that uses inputs from weather stations within a region defined by climatic similarities and homogeneity. This region encompasses the northern mountains in the Colorado River basin and some of the alpine–subalpine watersheds on the eastern side of the Continental Divide (Andrews Creek watershed is included in Region 25). The PHDI Colorado and the PMDI Colorado also cover regions on the western side of the continental divide. Although Andrews Creek watershed lies within the Platte River drainage, its similarities in climate with the northern mountains in the Colorado River basin results in better correlations between discharge-weighted contributions and climate indices defined for the Colorado River watershed. This indicates that western continental slope processes may govern eastern continental slope discharge within alpine watersheds similar to Andrews Creek. In the case of discharge-weighted contributions, localized to moderate spatial coverage climate indices are best for understanding streamflow dynamics in our system, especially talus-groundwater and snow inputs because these two end members are dominant.

5 | CONCLUSIONS

Our research explores the hydrologic resilience of an alpine stream and how its water source contributions have altered during climate variability. We found that the talus-groundwater percent contribution had significantly increased over the study period, whereas there were statically significant decreases in percent snow plus rain contributions and no large changes in the soil-water percent contribution. Talus groundwater was found to be crucial in sustaining what little resilience there is in this watershed. This is evident in the effects of the 2002 drought, which were observed for several years after (until 2005), indicating a potential for the system to retain memory through changing atmospheric climate conditions (Figure 7b and 7c). In addition, the discharge-weighted contributions of the talus groundwater respond to precipitation and showed significant correlations with Palmer drought indices on a local and moderate geographic scale, implying talus groundwater is still susceptible to changes in climate. The correlations between climate indices and snow were mostly significant to moderate, soil water had mostly moderate correlations with climate indices, whereas there were mostly weaker correlations with rain contributions. Teleconnection patterns were not significantly correlated to contributions as the moderate to local scale climate indicators. The implication of these findings are that variations in water sources reflect variations in climate. In a changing climate, especially during drought, we may expect talus groundwater to be more important in terms of providing support to headwater streamflow while expecting talus-groundwater and soil water to become more influential components to headwater stream chemistry during drier atmospheric conditions.

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REFERENCES

Bachmann, S. A. (1994). Hydrology of a subalpine wetland complex in Rocky Mountain National Park, Colorado (Doctoral dissertation). Colorado State University, Fort Collins, Colorado.

Barnett, T. P., Adam, J. C., & Lettenmaier, D. P. (2005). Potential impacts of a warming climate on water availability in snow-dominated regions. *Nature*, *438*(7066), 303–309.

Baron, J., & Mast, M. A. (1992). Regional characterization and setting for the Loch Vale watershed study. In *Biogeochemistry of a subalpine ecosystem* (pp. 12–27). New York: Springer.

Baron, J. S., Rueth, H. M., Wolfe, A. M., Nydick, K. R., Allstott, E. J., Minear, J. T., & Moraska, B. (2000). Ecosystem responses to nitrogen deposition in the Colorado Front Range. *Ecosystems*, *3*(4), 352–368.

Beniston, M. (2003). Climatic change in mountain regions: A review of possible impacts. *Climatic Change*, *59*, 5–31.

Boyer, E. W., Hornberger, G. M., Bencala, K. E., & McKnight, D. M. (1997). Response characteristics of DOC flushing in an alpine catchment. *Hydrological Processes*, *11*(12), 1635–1647.

Brooks, P. D., Williams, M. W., & Schmidt, S. K. (1998). Inorganic nitrogen and microbial biomass dynamics before and during spring snowmelt. *Biogeochemistry*, *43*(1), 1–15.

Campbell, D. H., Baron, J. S., Tonnessen, K., Brooks, P., & Schuster, P. (2000). Controls on nitrogen flux in alpine/subalpine watersheds. *Water Resources Research*, *36*(1), 37–48.

Campbell, D. H., Clow, D. W., Ingersoll, G. P., Mast, M. A., Spahr, N. E., & Turk, J. T. (1995). Processes controlling the chemistry of two snowmelt-dominated streams in the Rocky Mountains. *Water Resources Research*, *31*(1), 2811–2821.

Carey, S. K., & Quinton, W. L. (2005). Evaluating runoff generation during summer using hydrometric, stable isotope and hydrochemical methods in a discontinuous permafrost alpine catchment. *Hydrological Processes*, *19*(1), 95–114.

Christophersen, N., & Hooper, R. P. (1992). Multivariate analysis of stream water chemical data: The use of principal components analysis for the end-member mixing problem. *Water Resources Research*, *28*(1), 99–107.

Christophersen, N., Neal, C., Hooper, R. P., Vogt, R. D., & Andersen, S. (1990). Modelling streamwater chemistry as a mixture of soilwater end-members—A step towards second-generation acidification models. *Journal of Hydrology*, *116*(1–4), 307–320.

Clow, D. W. (2010). Changes in the timing of snowmelt and streamflow in Colorado: A response to recent warming. *Journal of Climate*, *23*(9), 2293–2306.

Clow, D. W., & Mast, M. A. (2010). Mechanisms for chemostatic behavior in catchments: Implications for CO_2 consumption by mineral weathering. *Chemical Geology*, *269*(1–2), 40–51.

Clow, D. W., Schrott, L., Webb, R., Campbell, D. H., Torizzo, A., & Dornblaser, M. (2003). Ground water occurrence and contributions to streamflow in an alpine catchment, Colorado Front Range. *Groundwater*, *41*(7), 937–950.

Clow, D. W., Sickman, J. O., Striegl, R. G., Krabbenhoft, D. P., Elliott, J. G., Dornblaser, M., … Campbell, D. H. (2003). Changes in the chemistry of lakes and precipitation in high-elevation national parks in the western United States, 1985–1999. *Water Resources Research*, *39*(6).

Clow, D. W., & Sueker, J. K. (2000). Relations between basin characteristics and stream water chemistry in alpine/subalpine basins in Rocky Mountain National Park, Colorado. *Water Resources Research*, *36*(1), 49–61.

Clow, D. W., Williams, M. W., & Schuster, P. F. (2016). Increasing aeolian dust deposition to snowpacks in the Rocky Mountains inferred from snowpack, wet deposition, and aerosol chemistry. *Atmospheric Environment*, *146*, 183–194.

Colorado Climate Center (CCC), Dept. of Atmospheric Science, Colorado State University. (2016). Colorado modified Palmer drought index [Dataset for Region 14 (Platte-Foothills) and Region 25 (Northern Mountains)] Retrieved from http:// climate.colostate.edu/palmerindex.php

Creed, I. F., Spargo, A. T., Jones, J. A., Buttle, J. M., Adams, M. B., Beall, F. D., … Yao, H. (2014). Changing forest water yields in response to climate warming: Results from long-term experimental watershed sites across North America. *Global Change Biology*, *20*(10), 3191–3208.

Darken, P. F., Zipper, C. E., Holtzman, G. I., & Smith, E. P. (2002). Serial correlation in water quality variables: Estimation and implications for trend analysis. *Water Resources Research*, *38*(7).

Davis, R. E., Petersen, C. E., & Bales, R. C. (1995). Ion flux through a shallow snowpack: Effects of initial conditions and melt sequences. In K. A. Tonnessen, M. W. Williams, & M. Tranter (Eds.), *Biogeochemistry of seasonally snow-covered catchments, IAHS publications-series of proceedings and reports-international association hydrological sciences* (Vol. 228) (pp. 115–126).

Denning, A. S., Baron, J., Mast, M. A., & Arthur, M. (1991). Hydrologic pathways and chemical composition of runoff during snowmelt in Loch Vale watershed, Rocky Mountain National Park, Colorado, USA. *Water, Air, and Soil Pollution*, *59*(1–2), 107–123.

Dickinson, K. J., Chagué-Goff, C., Mark, A. F., & Cullen, L. (2002). Ecological processes and trophic status of two low-alpine patterned mires, south-central South Island, New Zealand. *Austral Ecology*, *27*(4), 369–384.

Ernakovich, J. G., Hopping, K. A., Berdanier, A. B., Simpson, R. T., Kachergis, E. J., Steltzer, H., & Wallenstein, M. D. (2014). Predicted responses of arctic and alpine ecosystems to altered seasonality under climate change. *Global Change Biology*, *20*(10), 3256–3269.

Foster, L. M., Bearup, L. A., Molotch, N. P., Brooks, P. D., & Maxwell, R. M. (2016). Energy budget increases reduce mean streamflow more than snow–rain transitions: Using integrated modeling to isolate climate change impacts on Rocky Mountain hydrology. *Environmental Research Letters*, *11*(4), 044015.

Fuss, C. B., Driscoll, C. T., Green, M. B., & Groffman, P. M. (2016). Hydrologic flowpaths during snowmelt in forested headwater catchments under differing winter climatic and soil frost regimes. *Hydrological Processes*, *30*(24), 4617–4632.

Godsey, S. E., Kirchner, J. W., & Clow, D. W. (2009). Concentration–discharge relationships reflect chemostatic characteristics of US catchments. *Hydrological Processes*, *23*(13), 1844–1864.

Granat, L. (1972). On the relation between pH and the chemical composition in atmospheric precipitation. *Tellus A*, *24*(6), 550–560.

Guttman, L. (1954). Some necessary conditions for common-factor analysis. *Psychometrika*, *19*(2), 149–161.

Heath, J., & Baron, J. S. (2014). Climate, not atmospheric deposition, drives the biogeochemical mass-balance of a mountain watershed. *Aquatic Geochemistry*, *20*(2–3), 167–181.

Hofmann, A., Roussy, D., & Filella, M. (2002). Dissolved silica budget in the north basin of Lake Lugano. *Chemical Geology*, *182*(1), 35–55.

Hooper, R. P. (2003). Diagnostic tools for mixing models of stream water chemistry. *Water Resources Research*, *39*(3).

Hooper, R. P., Christophersen, N., & Peters, N. E. (1990). Modelling streamwater chemistry as a mixture of soilwater end-members—An application to the Panola Mountain catchment, Georgia, USA. *Journal of Hydrology*, *116*(1–4), 321–343.

Ingersoll, G. P., Mast, M. A., Nanus, L., Manthorne, D. J., Handran, H. H., Hulstrand, D. M., & Winterringer, J. (2005). *Rocky mountain snowpack chemistry at selected sites, 2003 (No. USGS-OFR-2005-1332)*. Reston, VA: U.S. Geological Survey.

Intergovernmental Panel on Climate Change (IPCC) 2007. Climate change 2007: Impacts, adaptation and vulnerability. Contribution of Working Group II to the Fourth Assessment. Report of the Intergovernmental Panel on Climate Change. M.L. Parry, O.F. Canziani, J.P. Palutikof, P.J. van der Linden and C.E. Hanson, Eds. Cambridge University Press, Cambridge, UK, 976 pp.

Intergovernmental Panel on Climate Change (IPCC) 2014. Climate change 2014: Synthesis report. Contribution of Working Groups 1, II and III to the Fifth Assessment. Report of the Intergovernmental Panel on Climate Change. Core Writing Team, R.K. Pachauri and L.A. Meyer, Eds. IPCC, Geneva, Switzerland, 151 pp.

Jepsen, S. M., Harmon, T. C., Meadows, M. W., & Hunsaker, C. T. (2016). Hydrogeologic influence on changes in snowmelt runoff with climate warming: Numerical experiments on a mid-elevation catchment in the Sierra Nevada, USA. *Journal of Hydrology*, *533*, 332–342.

Johannessen, M., & Henriksen, A. (1978). Chemistry of snow meltwater: Changes in concentration during melting. *Water Resources Research*, *14*(4), 615–619. https://doi.org/10.1029/WR014i004p00615

Kaiser, H. F. (1960). The application of electronic computers to factor analysis. *Educational and Psychological Measurement.*, *20*(1), 141–151.

Kaiser, H. F. (1961). A note on Guttman's lower bound for the number of common factors. *British Journal of Statistical Psychology*, *14*(1), 1–2.

Kampf, S., Markus, J., Heath, J., & Moore, C. (2015). Snowmelt runoff and soil moisture dynamics on steep subalpine hillslopes. *Hydrological Processes*, *29*, 712–723. https://doi.org/10.1002/hyp.10179

Kampf, S. K., & Lefsky, M. A. (2016). Transition of dominant peak flow source from snowmelt to rainfall along the Colorado Front Range: Historical patterns, trends, and lessons from the 2013 Colorado Front Range floods. *Water Resources Research*, *52*, 407–422.

Kapnick, S., & Hall, A. (2012). Causes of recent changes in western North American snowpack. *Climate Dynamics*, *38*(9–10), 1885–1899.

Kopáček, J., Kaňa, J., Bičárová, S., Fernandez, I. J., Hejzlar, J., Kahounová, M., … Stuchlík, E. (2016). Climate change increasing calcium and magnesium leaching from granitic alpine catchments. *Environmental Science & Technology*, *51*(1), 159–166.

Lawson, C. L., & Hanson, R. J. (1974). *Solving least squares problems*. New York: John Wiley and Sons, Inc. 1974

Lepori, F., Barbieri, A., & Ormerod, S. J. (2003). Effects of episodic acidification on macroinvertebrate assemblages in Swiss Alpine streams. *Freshwater Biology*, *48*(10), 1873–1885.

Libiseller, C., & Grimvall, A. (2002). Performance of partial Mann–Kendall tests for trend detection in the presence of covariates. *Environmetrics*, *13*(1), 71–84.

Likens, G. E., Driscoll, C. T., Buso, D. C., Siccama, T. G., Johnson, C. E., Lovett, G. M., … Reiners, W. A. (1994). The biogeochemistry of potassium at Hubbard Brook. *Biogeochemistry*, *25*(2), 61–125.

Liu, F., Williams, M. W., & Caine, N. (2004). Source waters and flow paths in an alpine catchment, Colorado Front Range, United States. *Water Resources Research*, *40*(9).

Marchetto, A., (2015). Package "rkt". Mann–Kendall test, seasonal and regional Kendall tests. R package version 1.4. https://cran.r-project.org/web/packages/rkt/rkt.pdf.

Mast, M. A., Drever, J. I., & Baron, J. (1990). Chemical weathering in the Loch Vale watershed, Rocky Mountain National Park, Colorado. *Water Resources Research*, *26*(12), 2971–2978.

Mast, M. A., Kendall, C., Campbell, D. H., Clow, D. W., & Back, J. (1995). Determination of hydrologic pathways in an alpine-subalpine basin using isotopic and chemical tracers, Loch Vale Watershed, Colorado, USA. IAHS Publications-Series of Proceedings and Reports-International Association Hydrological Sciences. 228, 263–270.

Meixner, T., Manning, A. H., Stonestrom, D. A., Allen, D. M., Ajami, H., Blasch, K. W., … Walvoord, M. A. (2016). Implications of projected climate change for groundwater recharge in the western United States. *Journal of Hydrology*, *534*, 124–138.

Mosley, L. M. (2015). Drought impacts on the water quality of freshwater systems; review and integration. *Earth-Science Reviews*, *140*, 203–214.

National Atmospheric Deposition Program (NADP). (2015). National trends network site operation manual version 2.3. National atmospheric deposition program office, Illinois State Water Survey, Champaign (IL).

National Atmospheric Deposition Program / National Trends Network (NADP/NTN). (2016). Daily data for site: CO98 (Rocky Mountain National Park - Loch Vale), 10-01-1993 to 09-30-2015 [Data set]. Accessed: 01 February 2016. http://nadp.sws.uiuc.edu/nadpdata/dailyRequest.asp?site=CO98.

National Climatic Data Center (NCDC), National Oceanic and Atmospheric Administration. (2016). Division: Colorado Drainage Basin and Platte Drainage Basin, 10–1993 to 09–2015 [Data set]. Accessed: 13 July 2016. https://www7.ncdc.noaa.gov/CDO/CDODivisionalSelect.jsp

National Weather Service Climate Prediction Center (NWSCPC), National Oceanic and Atmospheric Administration. (2016a). North Atlantic Oscillation (NAO): Historical Index [Data set]. Accessed: 13 July 2016. http://www.cpc.ncep.noaa.gov/data/teledoc/nao.shtml

National Weather Service Climate Prediction Center (NWSCPC), National Oceanic and Atmospheric Administration. (2016b). Pacific/North American (PNA): Historical Index [Data set]. Accessed: 13 July 2016. http://www.cpc.ncep.noaa.gov/data/teledoc/pna.shtml

Palmer, W. C. (1965). *Meteorological drought (Vol. 30)*. Washington, DC: U. S: Department of Commerce, Weather Bureau.

Piechota, T. C., & Dracup, J. A. (1996). Drought and regional hydrologic variation in the United States: Associations with the El Niño–Southern Oscillation. *Water Resources Research*, *32*(5), 1359–1373. https://doi.org/10.1029/96WR00353

Sullivan, T. J., Cosby, B. J., Tonnessen, K. A., & Clow, D. W. (2005). Surface water acidification responses and critical loads of sulfur and nitrogen deposition in Loch Vale watershed, Colorado. *Water Resources Research*, *41*(1).

Taylor, S., Feng, X., Kirchner, J. W., Osterhuber, R., Klaue, B., & Renshaw, C. E. (2001). Isotopic evolution of a seasonal snowpack and its melt. *Water Resources Research*, *37*(3), 759–769. https://doi.org/10.1029/2000WR900341

Tranter, M., Brimblecombe, P., Davies, T. D., Vincent, C. E., Abrahams, P. W., & Blackwood, I. (1986). The composition of snowfall, snowpack and meltwater in the Scottish Highlands—Evidence for preferential elution. *Atmospheric Environment (1967)*, *20*(3), 517–525.

U. S. Geological Survey (USGS). (2016). Rocky mountain regional snowpack chemistry monitoring study. [Data set] Accessed: 01 February 2016. http://co.water.usgs.gov/projects/RM_snowpack/html/data.html.

U.S. Geological Survey (USGS). (2015). USGS National Elevation Dataset (NED) 1/3 arc-second n41w106 1 × 1 degree ArcGrid 2015: U.S. Geological Survey.

U.S. Geological Survey, National Geospatial Program (USGS NGP). (2016). USGS National Hydrography Dataset (NHD) Best Resolution HU4–1019 20161102 for HU-4 Sub-region FileGDB 10.1 Model Version 2.2.1: U.S. Geological Survey.

Water, Energy, and Biogeochemical Budgets Program (WEBB). (2016). Andrews Creek stream chemistry data from 10-1993 to 09-2015. [Data set] Accessed: 01 February 2016. http://co.water.usgs.gov/lochvale/data.html.

Webb, R. M., & Parkhurst, D. L. (2017). Water, energy, and biogeochemical model (WEBMOD), user's manual, version 1. U.S. Geological Survey Techniques and Methods 6-B35.

Wheeler, J. A., Hoch, G., Cortés, A. J., Sedlacek, J., Wipf, S., & Rixen, C. (2014). Increased spring freezing vulnerability for alpine shrubs under early snowmelt. *Oecologia*, *175*(1), 219–229.

Williams, M. W., Brown, A. D., & Melack, J. M. (1993). Geochemical and hydrologic controls on the composition of surface water in a high-elevation basin, Sierra Nevada, California. *Limnology and Oceanography*, *38*, 775–797.

Williams, M. W., Knauf, M., Caine, N., Liu, F., & Verplanck, P. L. (2006). Geochemistry and source waters of rock glacier outflow, Colorado Front Range. *Permafrost and Periglacial Processes*, *17*(1), 13–33.

Williams, M. W., & Melack, J. M. (1991). Solute chemistry of snowmelt and runoff in an alpine basin, Sierra Nevada. *Water Resources Research*, *27*(7), 1575–1588.

Wipf, S., Stoeckli, V., & Bebi, P. (2009). Winter climate change in alpine tundra: plant responses to changes in snow depth and snowmelt timing. *Climatic Change*, *94*(1–2), 105–121.

SUPPORTING INFORMATION

Additional supporting information may be found online in the Supporting Information section at the end of the article.

Additional details on Andrews Creek data used in this study, EMMA and PCA methods, and PCA results (Sections 1, 2, and 3, respectively). Details regarding two precipitation collectors used at CO98 during the span of the study (Section 4). Table of additional pSKT results (Section 5). Additional stream chemistry characteristics in **U** space (Section 6). Plots presenting precipitation relationships between end-member contributions and Andrews Creek (Section 7). Plots presenting relationships between climate indices and Andrews Creek discharge, and end-member contributions (Sections 8 and 9). Plots presenting end-member contribution relationships over time (Section 10). Spring average air temperature and average precipitation over the study period (Section 11).

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