

Water Resources Research®

RESEARCH ARTICLE

10.1029/2023WR036062

Key Points:

- Sulfate, zinc, and copper concentrations are increasing regionally in streams affected by acid rock drainage throughout Colorado
- Declining streamflows are contributing to increasing concentrations, but increasing loads are likely an equal or greater contributor
- Trend slopes are positively correlated with mean annual temperature and elevation, suggesting melting of frozen ground is a major driver

Supporting Information:

Supporting Information may be found in the online version of this article.

Correspondence to:

A. H. Manning,
amanning@usgs.gov

Citation:

Manning, A. H., Petach, T. N., Runkel, R. L., & McKnight, D. M. (2024). Climate-driven increases in stream metal concentrations in mineralized watersheds throughout the Colorado Rocky Mountains, USA. *Water Resources Research*, 60, e2023WR036062. <https://doi.org/10.1029/2023WR036062>

Received 11 AUG 2023

Accepted 6 MAR 2024

© 2024 The Authors. This article has been contributed to by U.S. Government employees and their work is in the public domain in the USA.

This is an open access article under the terms of the [Creative Commons Attribution-NonCommercial-NoDerivs License](#), which permits use and distribution in any medium, provided the original work is properly cited, the use is non-commercial and no modifications or adaptations are made.

Climate-Driven Increases in Stream Metal Concentrations in Mineralized Watersheds Throughout the Colorado Rocky Mountains, USA

Andrew H. Manning¹ , Tanya N. Petach^{2,3}, Robert L. Runkel¹ , and Diane M. McKnight² 

¹U.S. Geological Survey, Denver, CO, USA, ²Civil, Environmental, and Architectural Engineering Department, University of Colorado, Boulder, CO, USA, ³Aspen Global Change Institute, Basalt, CO, USA

Abstract Increasing stream metal concentrations apparently caused by climate warming have been reported for a small number of mountain watersheds containing hydrothermally altered bedrock with abundant sulfide minerals (mineralized watersheds). Such increases are concerning and could negatively impact downstream ecosystem health, water resources, and mine-site remediation efforts. However, the pervasiveness and typical magnitude of these trends remain uncertain. We aggregated available streamwater chemistry data collected from late summer and fall over the past 40 years for 22 mineralized watersheds throughout the Colorado Rocky Mountains. Temporal trend analysis performed using the Regional Kendall Test indicates significant regional upward trends of ~2% of the site median per year for sulfate, zinc, and copper concentrations in the 17 streams affected by acid rock drainage (ARD; median pH ≤ 5.5), equivalent to concentrations roughly doubling over the past 30 years. An examination of potential load trends utilizing streamflow data from eight “index gages” located near the sample sites provides strong support for regionally increasing sulfate and metal loads in ARD-affected streams, particularly at higher elevations. Declining streamflows are likely contributing to regionally increasing concentrations, but increasing loads appear to be on average an equal or greater contributor. Comparison of selected site characteristics with site concentration trend magnitudes shows the highest correlation for mean annual air temperature and mean elevation (R^2 of 0.42 and 0.35, respectively, with all others being ≤0.14). Future research on climate-driven controlling mechanisms should therefore focus on processes such as melting of frozen ground directly linked to site mean temperature and elevation.

Plain Language Summary “Mineralized” watersheds contain bedrock with abundant sulfide minerals that, when weathered, often produce naturally acidic and metal-rich streamwater, known as acid rock drainage (ARD). Increasing metal concentrations have been recently identified in a small number of ARD streams, apparently due to climate change. These trends are concerning because, even at low concentrations, dissolved metals can negatively affect downstream ecosystem health and the quality of water resources. However, we currently do not know how widespread these upward metal trends are regionally, and thus the scope of potential environmental impacts. To address this issue, we aggregated available streamwater chemistry data collected over the past 40 years for mineralized watersheds throughout Colorado. In the 17 sampled ARD streams, we found significant regional upward trends in concentration of ~2% of the site median per year for two metals of primary environmental concern, zinc and copper. This rate of increase equates to concentrations roughly doubling over the past 30 years. We examined possible driving mechanisms for these marked concentration trends and conclude they are mainly due to increasing sulfide weathering rates (rising metal mass export) rather than simply declining streamflows (less dilution), with melting of frozen ground being a likely major driver of accelerated weathering.

1. Introduction

Numerous studies have reported increasing major ion concentrations in high-elevation streams and lakes in response to recent climate warming, suggesting that this is a globally common phenomenon (see recent reviews by Colombo et al., 2018; Crawford et al., 2019). Rising concentrations are generally attributed to accelerated weathering and/or enhanced solute mobility caused by melting of frozen ground or other changes in subsurface hydrogeochemical conditions. These trends have broad implications for the chemistry of surface water resources, given that mountain-sourced streams and rivers supply fresh water to a large fraction of the world’s population (Viviroli et al., 2007; Viviroli & Weingartner, 2004). Some of these studies are from “mineralized” watersheds

(e.g., Rue & McKnight, 2021; Thies et al., 2007; Todd et al., 2012), which contain hydrothermally altered bedrock with abundant sulfide minerals such as pyrite. Mineralized watersheds commonly produce natural acid rock drainage (ARD), with a pH < 5, elevated metal concentrations (e.g., aluminum, arsenic, cadmium, copper, nickel, lead, and zinc) near or above aquatic life standards, and major ion concentrations 1–2 orders of magnitude higher than in unmineralized watersheds (e.g., sulfate concentrations of 100–1,000 mg/L compared to a more typical 1–10 mg/L). The prospect of widely increasing solute concentrations in ARD-affected streams is particularly concerning; given their abnormally high metal concentrations, such increases could have an outsized negative impact on the health of downstream ecosystems and water resources. Furthermore, because mines are often located in mineralized watersheds, rising background metal concentrations could also complicate the process of establishing attainable water quality standards required for effective environmental management of mine sites (Runkel et al., 2018; Runnells et al., 1992).

However, the number of studies examining water quality trends over recent decades at ARD sites (unrelated to mine-site activities) are few, meaning that the ubiquity and typical magnitude of increasing sulfate (SO_4) and metal concentrations in mineralized mountain watersheds remain uncertain. To our knowledge, statistically significant climate-driven trends in water chemistry have been reported for only two ARD sites. In the upper Snake River in the Colorado Rocky Mountains, USA, Todd et al. (2012) observed significant increases in SO_4 and zinc (Zn) of ~ 3 mg/L/yr and ~ 30 $\mu\text{g/L/yr}$, respectively, during summer and fall from 1979 to 2011. Rue and McKnight (2021) reported a continuation of these trends through 2019, with associated increases in rare earth element concentrations. In the upper Elqui River basin in the Andes, north-central Chile, Flores et al. (2017) identified significant upward trends in annual average SO_4 and copper (Cu) concentrations for several (though not all) sample sites of 1–10 mg/L/yr and <100–900 $\mu\text{g/L/yr}$, respectively, from 1990 to 2012. Similar upward trends have been reported for two other ARD sites in the European Alps and the Andes, though these were not tested for statistical significance. Thies et al. (2007) observed an increase in SO_4 of ~ 9 mg/L/yr in fall from 1985 to 2005 in the Rasass See, an alpine lake in South Tyrol, Italy. Valenzuela-Diaz et al. (2020) found increases in median SO_4 and Cu concentrations in the Yerba Loca tributary of the Mapocho River, central Chile, from 2001 to 2017, with magnitudes similar to those reported by Flores et al. (2017). Finally, upward trends have been inferred (but not verified) at two additional sites in the Pyrenees, northern Spain, based on indirect observations, including expanding streambed precipitates (Zarroca et al., 2021) and increasing metal concentrations in recent lake sediments (Zaharescu et al., 2016). Given the limited available information, it remains difficult to gauge an appropriate level of concern regarding the phenomenon of increasing metal concentrations in ARD-affected streams.

The specific climate-linked mechanisms dominantly responsible for observed upward solute trends in mineralized watersheds are also uncertain. Mechanisms proposed in previous studies, accompanied by some amount of supporting evidence, include: (a) accelerating sulfide weathering rates resulting from new exposure of fresh sulfides to oxygen and liquid water due to either melting of ice-filled pores/fractures (Ilyashuk et al., 2018; Zarroca et al., 2021) or deepening of the vadose zone (from declining groundwater recharge; Manning et al., 2013); (b) mobilization of solutes previously sequestered in either rock glacier ice (mobilized by melting; Thies et al., 2007) or in wetlands bound to organics (mobilized by decreasing pH and/or oxidation from drying; Crouch et al., 2013); and (c) declining streamflows causing less dilution of evolved metal-rich sources of streamflow by short residence-time (less evolved) sources, as the latter decline first and most under dryer conditions (“dilution effect”; Byrne et al., 2020). Identification of controlling mechanisms is necessary to better understand and predict future stream chemistry trends. A key unanswered question linked to causal mechanisms is whether stream solute loads (mass flux, equal to streamflow multiplied by concentration) are increasing in addition to concentrations; if loads are not increasing, the observed concentration increases may be primarily attributable to the dilution effect (mechanism 3), with mechanisms 1 and 2 having little or no influence. A few studies have reported increasing solute loads in unmineralized mountain watersheds and invoked increasing sulfide weathering rates (e.g., Crawford et al., 2019; Heil et al., 2022; Mast, 2013), but studies in ARD-affected mountain streams have not directly evaluated temporal trends in load. Crouch et al. (2013) present both streamflow and Zn concentration data from the upper Snake River and identify increasing Zn concentrations under similar low-flow conditions from 1971 to 2011, implying increasing Zn loads, but temporal load trends are not quantitatively examined.

In this study, we address uncertainties regarding the spatial extent, magnitude, and cause of climate-driven metal increases in ARD-affected streams by aggregating available historical water chemistry data from the past 40 years

for 22 headwater streams with elevated metal concentrations draining mineralized zones throughout the Colorado Rocky Mountains. These data were augmented by a round of sampling performed in 2021 to provide a current endpoint for each time series. All data are from the late-summer and fall low-flow period, and legacy mine sites within the selected watersheds have not undergone remedial actions in recent decades. We then perform regional trend analysis on Zn and Cu concentrations, these being primary metals of concern at legacy mine sites in the region, as well as SO_4 and pH, which reflect overall sulfide weathering rates. Concurrent streamflow measurements were not available for the water chemistry data, but load trends were evaluated in addition to concentration trends using three different approaches employing relative variations in streamflow at “index gages” located near the stream chemistry sampling sites. The magnitude of concentration and load trend slopes at different sites were then compared to watershed characteristics associated with the different climate-linked causal mechanisms discussed above to identify correlations. The specific objectives of this study are to: (a) determine if the significant recent upward trends in solute concentrations observed in the upper Snake River (Rue & McKnight, 2021; Todd et al., 2012) are occurring at ARD-affected sites throughout the Colorado Rocky Mountain region, or instead represent a unique local phenomenon; (b) define typical magnitudes of upward concentration trends for the region, if present; (c) evaluate the possibility of significantly increasing loads across the region; and (d) use the derived trend information to gain additional insights into the primary climate-linked mechanisms driving upward trends, if present.

2. Methods

2.1. Water Chemistry Data Aggregation

Twenty-two stream sampling sites were selected for the regional trend analysis, all meeting the following criteria (Table S1 in Supporting Information S1; Figure 1): (a) the stream drains a mineralized watershed, being in an area of exposed hydrothermally altered bedrock and having maximum metal concentrations that approach or exceed typical aquatic life standards; (b) the watershed above the sample point is a relatively small, high-elevation headwater catchment (generally 2–20 km^2 and 3,000–4,000 m above sea level (masl)); (c) publicly available historical streamwater chemistry data are available for the site; and (d) no documented mine-site remediation or other anthropogenic activities that could substantially affect stream chemistry have occurred upstream of the site in recent decades. The sites tend to occur in clusters, following zones of hydrothermal alteration, but as a whole cover a mountainous region ~150 km wide by ~350 km long.

The complete database with all water chemistry data used for regional trend analysis is available in electronic format on the CUAHSI HydroShare data server (Petach, Manning, Runkel, & McKnight, 2023). Sources of data include the National Water Quality Monitoring Council’s Water Quality Portal, multiple publicly available reports, and samples collected from each site in 2021 as part of this study (Petach, Manning, Wanty, et al., 2023). The Water Quality Portal integrates data from the U.S. Geological Survey, the U.S. Environmental Protection Agency, and multiple state, federal, tribal, and local agencies (e.g., the Colorado Department of Health and Environment and Colorado River Watch). The publicly available reports include mainly USGS reports, scientific journal manuscripts, graduate student theses, and other state and federal agency reports. All 22 sites were sampled in late August and September 2021 to provide a current endpoint for each time series. Method descriptions for the measurement of field parameters and collection, treatment, preservation, and analysis of samples for major ion and trace element concentrations are presented in Petach, Manning, Wanty, et al. (2023).

Data were selected for inclusion in the database applying the following rationale. Measurements were included for the four constituents of primary interest: pH, SO_4 , Zn, and Cu. For comparability, samples had to be collected between July 15 and November 30, the typical late-summer to fall low-flow sampling period. The relatively few field analyses and samples collected prior to 1980 were excluded mainly due to often higher or uncertain detection limits, particularly for Cu. Included measurements are for dissolved constituent concentration (filtered sample aliquot), with measurements for total concentration (unfiltered sample aliquot; $n = 11$) only included if: (a) there were no companion measurements for dissolved concentration; (b) pH measurements for the site were dominantly <5.5 (Cu, Zn, and SO_4 are unlikely to be affected by precipitation and/or sorption reactions at low pH, so total and dissolved concentrations should be nearly equal); and (c) the median discrepancy in concentration between available pairs of total and dissolved measurements for the site was <15%. Measurements for samples collected on the same day were averaged, as these have no value individually for a multi-year trend analysis. A small number of highly anomalous measurements (<1%) were excluded, suspected to be the result of typographical or

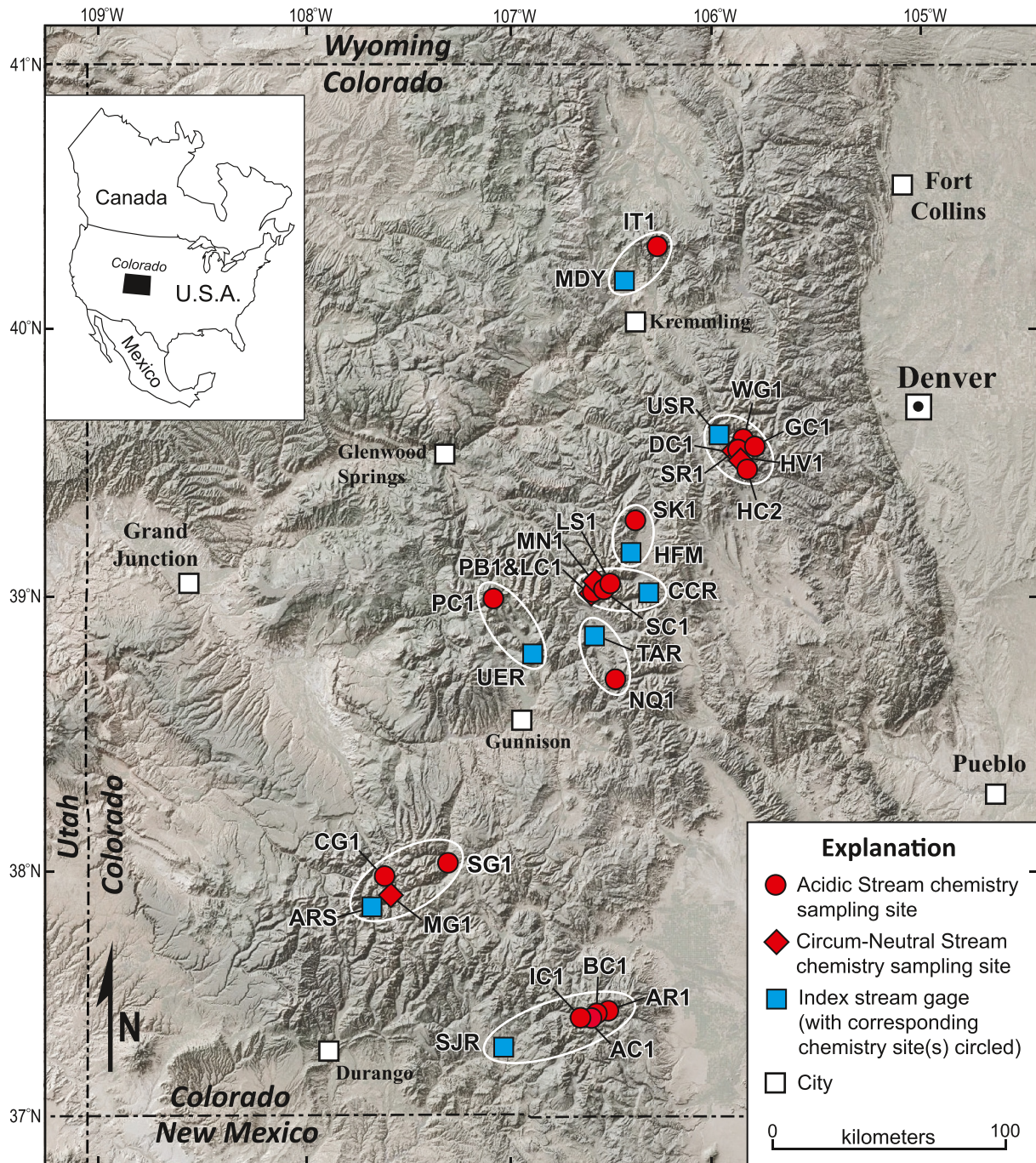


Figure 1. Map showing location of water chemistry sample sites and index gages. Corresponding sample sites and index gages are circled. Acidic sample sites have $\text{pH} \leq 5.5$, circum-neutral sample sites have $\text{pH} = 7\text{--}8$. Sample site and index gage information provided in Tables S1 and S2, respectively, in Supporting Information S1. Base from CalTopo, copyright 2019.

other processing errors (Text S1 in Supporting Information S1). Analytical method information was not provided for most samples, so the specific analytical methods used by different laboratories could not be compared. However, concentrations of SO_4 , Zn, and Cu are in general sufficiently high that potential measurement variations attributable to differences in analytical method would likely be small in comparison. All listed sample location coordinates were individually mapped and checked. Although samples from a given site were not necessarily all collected from the same exact location, all were collected from the same stream segment (with no intervening tributaries), with 93% located within ~ 200 m of the location listed in Table S1 in Supporting Information S1, and

the remainder within ~500 m. The resulting dataset includes a total of 634 measurements. The number of separate sampling events at each site ranges widely from 2 to 63 (upper Snake River site, SR1), but most sites (16 of 22) have 4–12, with a median of 5.

2.2. Trend and Correlation Analysis

Data from individual sites were evaluated for temporal trends using the Mann-Kendall Test (MKT; Mann, 1945; Helsel et al., 2020), following previous similar studies of streamwater chemistry changes over time (e.g., Mast, 2013; Todd et al., 2012). The Regional Kendall Test (RKT) was applied to data combined from multiple sites to test for a consistent temporal trend across the study region (Helsel & Frans, 2006). The RKT is appropriate for cases like ours where many sites may have too few data to yield significant trends, but collectively they may have the power to do so. Trends were considered statistically significant if the p value (probability that no temporal trend exists) was ≤ 0.05 . If multiple measurements were available at a site for a given constituent in the same year, these were averaged in the trend analysis to produce a single value for each year, given our interest in identifying trends over multiple decades. Trend direction and magnitude were estimated by computing the nonparametric Theil-Sen robust line (Helsel et al., 2020; Theil, 1950). For significant regional trends, the 90% confidence interval for the Theil-Sen line slope was computed using the nonparametric method employing the cumulative distribution function of the binomial distribution (Helsel et al., 2020). Uncertainty in trend slopes for the relative residual concentration are an exception, and were computed as explained in Section 2.3 below.

For each analyzed time series, measurements were normalized to the site median value for the observation period, enabling evaluation and comparison of relative changes in the measurement of interest across sites. Trend slopes presented throughout this paper are thus in units of percent of the site median per year (%/yr). We emphasize that this slope unit is linear, as the site median for the observation period is a constant value, and should not be confused with the commonly used nonlinear unit of percent of the prior year's value per year.

Given the pH dependence of in-stream precipitation and sorption reactions for Cu, Zn, and SO_4 , a difference in concentration trend behavior was anticipated for low-pH versus circum-neutral pH streams. Sites were thus divided into two categories based on pH: acidic sites ($n = 17$) with a median pH of ≤ 5.5 , and circum-neutral sites ($n = 5$) with a median pH of 7–8 (Table S1 in Supporting Information S1; Figure 1). Acidic sites also have median SO_4 , Zn, and Cu concentrations roughly 5–20 times higher than circum-neutral sites, these being 171 mg/L, 192 $\mu\text{g/L}$, and 60 $\mu\text{g/L}$, respectively, compared to 32 mg/L, 10 $\mu\text{g/L}$, 3.0 $\mu\text{g/L}$, respectively (Table S1 in Supporting Information S1). Therefore, circum-neutral sites have naturally somewhat elevated metal concentrations, but they are not truly acid rock drainage sites like the acidic sites. Circum-neutral sites are located close to the acidic sites within the same areas of hydrothermally altered bedrock (Figure 1). The likely source of SO_4 , Zn, and Cu at the circum-neutral sites is also sulfide mineral weathering, but largely within lower-grade propylitic alteration zones adjacent to the higher-grade (e.g., quartz-sericite-pyrite) zones that typically generate ARD (Rockwell & Bonham, 2017). Such prophylactically altered bedrock commonly generates water with slightly elevated SO_4 and metal concentrations, and is circum-neutral due to buffering with calcite, chlorite, and epidote (Verplanck et al., 2009).

Site SR1 was excluded in the acidic site RKTs and is presented separately because: (a) its inclusion could exert a disproportionate influence in the RKT because it has a much larger number of samples than the other sites ($n \approx 60$ compared to $n \leq 15$); and (b) it is the only site where prior quantitative trend analysis was performed, and a high-elevation major SO_4 and metal source zone was identified (Crouch et al., 2013; Todd et al., 2012). Thus, the site serves as a benchmark site against which other sites can be compared.

Selected site variables were compared to site concentration/load trend magnitude to identify correlations and gain insight into the relative importance of different possible controlling mechanisms. Rationale for site variable selection is provided below in Section 4. Mean annual air temperature and total annual precipitation for each site were computed from data obtained from PRISM (PRISM Climate Group, <https://www.prism.oregonstate.edu>), downloaded for the sample site location coordinates. Percentages of the watershed area above the sample site covered by wetlands (“wetlands coverage”) and rock glaciers (“rock glacier coverage”) were computed using GIS and digital maps of these features. The digital wetlands map was obtained from the U.S. Fish and Wildlife Service’s Seamless Wetlands Data website (U.S. Fish and Wildlife Service, <https://www.fws.gov/program/national-wetlands-inventory/download-state-wetlands-data>). The digital rock glacier map was obtained from the Portland State University Active Rock Glacier Inventory (PSUARGI; Johnson, 2020).

The R^2 value computed from linear regression was used to determine the strength of correlation between site concentration/load trend magnitude and individual site variables. We recognize that changes in concentration and load may be caused by multiple interlinked factors that may be correlated with each other, so a multiple linear regression analysis would be optimal for exploring correlations. Such an analysis was initially attempted, but the number of sites and data were found to be inadequate to enable this approach. We also recognize that a comprehensive exploration of correlations between site characteristics and concentration/load trends could include several site characteristics beyond those considered here. However, such a comprehensive analysis is beyond the scope of this study. The purpose of our exploratory analysis is to consider a handful of readily quantifiable site variables to provide a first-order examination of which potential driving mechanisms appear to play a major role in controlling the observed trends, and should thus be prioritized in future process-focused investigations.

2.3. Load Trend Evaluation

Streamflow measurements were generally not made during collection of the streamwater samples in the dataset, so potential temporal trends in load could only be evaluated indirectly. We employed three approaches utilizing streamflow measured at index gages located as close as possible to the chemistry sampling sites (Figure 1, Table S2 in Supporting Information S1). Each approach assumes that, although the magnitude of streamflow at a sample site and corresponding index gage differ, their proximity means that they are affected by largely the same weather, so that relative variations in flow through time at the two locations should be similar. For example, if flow at an index gage on a given day in August is well above the median for that day due to an unusually large snowpack the preceding winter and/or high monsoon rainfall in preceding weeks, it is reasonable to assume that flow at the corresponding sample site has experienced a similar precipitation history and is thus elevated above the median by a similar amount. This principle underlies methods widely employed to estimate streamflow in ungaged basins (e.g., Razavi & Coulibaly, 2013). A limited number of streamflow measurements are available for one of the sample sites, SR1. Comparison of these flows to the mean flow for the same day at the associated index gage, USR, indicates a relatively good correlation with $R^2 = 0.85$ (Figure S1 in Supporting Information S1), consistent with our assumption. Eight index gages were selected using the following criteria, in addition to sample site proximity, to maximize the likelihood that variations in streamflow at the gages are generally representative of those at the sample sites: (a) the gage is located within the same mountain range as the sample site, on the lowest-order (highest-elevation) stream possible; (b) no major anthropogenic features are located upstream of the gage that could alter the natural flow regime, including major reservoirs, diversion ditches, or tunnels; and (c) the streamflow record is complete through the observation period for the corresponding sample site(s). Most sample sites are <30 km from their corresponding index gage (Figure 1, Table S1 in Supporting Information S1), the exceptions being site SG1 located 39 km from ARS, and the four southern San Juan Mountain sites (AC1, AR1, BC1, and IC1) located 38–46 km from SJR.

The first approach applied for evaluating load trends was a comparison of the relative magnitude of streamflow declines at the index gages to the relative magnitude of constituent concentration increases at the stream sampling sites. Mean monthly flows for August, September, and October from 1990 to 2021 were evaluated, these being the months and years during which the majority (76%) of the chemistry samples were collected. In the case of a constant load, over a period of 30 years, rates of decline in streamflow up to ~3% (of the observation period median) per year will produce corresponding rates of increase in relative concentration of approximately equal magnitude. This relationship is illustrated in Figure 2, which shows relative concentration increases caused by relative flow declines of -1, -2, -3, and -4%/yr. Regression lines fit to the relative concentration trends have slopes of 1.0%, 2.1%, 3.4%, and 5.3% (of the median) per year, respectively. The absolute value of the streamflow and corresponding concentration trend slopes are thus similar for the flow decline rates of -3%/yr or less, but this similarity breaks down at larger streamflow declines due to the increasingly non-linear response of the concentrations. Therefore, provided the rate of streamflow decline is $\leq 3\%/yr$, if the rate of the concentration increase exceeds the rate of streamflow decline, the declining streamflow (dilution effect) probably cannot fully account for the observed concentration increase. In this case, loads are likely increasing as well. Note that the total loss in streamflow produced by a decline rate of 3%/yr over 30 years is relatively large, equating to 62% of the initial streamflow. This decline rate is generally larger than what has been observed in the region (Leppi et al., 2012), as well as what is forecast for the next 30 years (Miller et al., 2021).

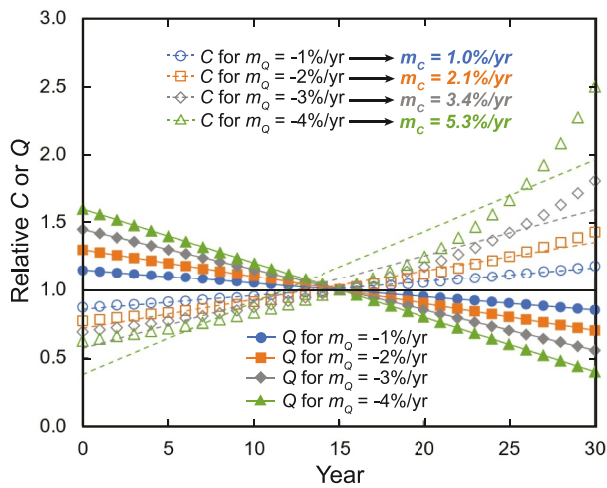


Figure 2. Increasing relative concentration (C) trends caused by different declining relative streamflow (Q) trends over a period of 30 years, assuming constant load. Relative C and Q are normalized to the median value for the observation period. C slope (m_C) and Q slope (m_Q) values are in units of percent of the observation period median per year (%/yr), with m_C being the slope of a regression line fit to the C values.

The second approach involved computing and evaluating trends in flow-adjusted concentrations, a method employed in previous water quality trend studies (e.g., Hirsch et al., 1991; Mast, 2013). Concentrations of relatively non-reactive solutes produced by mineral weathering, such as SO_4 and Zn (and likely Cu at $\text{pH} < 5$), generally increase with decreasing discharge in mountain streams (Heil et al., 2022; Li et al., 2022; Petach et al., 2021; Winnick et al., 2017). For each sample site, a relationship between concentration and streamflow was estimated for SO_4 , Zn, and Cu by a regression line fit to data on a C - Q plot of the log of the measured concentration (C_m) versus the log of the “index flow” (Q_I). For each C_m , Q_I was taken as the average of the mean daily flows for the week preceding sample collection (sample day and 6 days prior) at the corresponding index gage. This weekly average was used instead of the mean flow for the sample day alone to minimize inaccuracies potentially resulting from highly localized thunderstorms during summer monsoon cycles that might affect the index gage and sample site with different timing/intensity in the few days leading up to sample collection. The linear relationship derived from the C - Q plot (with slope = m_{CQ} and y-intercept = b_{CQ}) was used to compute a flow-based model concentration (C_Q) for each sample, using:

$$\text{Log}(C_Q) = m_{CQ} \times \text{Log}(Q_I) + b_{CQ} \quad (1)$$

The computed C_Q was then subtracted from C_m to produce a concentration residual, R ($R = C_m - C_Q$) and the trend analysis was performed on these residuals. A significant positive trend in R would suggest that changing flows alone cannot account for changing concentrations, and loads are thus increasing.

To account for the uncertainty in the site C - Q relationships, the 90% confidence interval for the slope of statistically significant concentration residual trends was computed using a Monte Carlo approach with 1,000 realizations in which the regression line representing the C - Q relationship for each site was randomly perturbed based on the standard error of m_{CQ} and of b_{CQ} . It should be noted that the assumption that relative variations in streamflow at the sample site are equal to those at the associated index gage provides another source of error in derived trend slopes for both the concentration residual and the “index load” described below. This source of error was not included in our computation of slope confidence intervals because, unfortunately, its magnitude cannot be quantified. We therefore caution that uncertainty in the concentration residual and index load trend slopes is likely greater than that indicated by the computed confidence intervals.

The third approach applied was an examination of trends in “index load”. An index load was computed for each concentration measurement by multiplying the concentration by the index flow, obtained as described above. A significant trend of increasing index load would provide evidence that actual loads are increasing as well. As previously mentioned, a limited number of streamflow measurements were available for sample site SR1, collected in late summer and fall from 1981 to 2021 ($n = 21$; Boyer et al., 1999; McKnight et al., 2002; USEPA, 2023; Petach, Manning, Wanty, et al., 2023). These were used to derive a linear relationship between streamflow at the site and at its corresponding index gage, USR ($R^2 = 0.85$; Figure S1 in Supporting Information S1). This relationship was used to estimate flow at site SR1 and compute “estimated loads”, instead of index loads, for each concentration measurement. Of the 21 flow measurements, seven were made at the time of sample collection from 2009 to 2021, so measured loads were computed for these seven sample events. Estimated and measured loads were combined in the same data series for performing MKTs for SR1. These measured and estimated flows for site SR1 were also used to compute the concentration residuals used in the second load evaluation approach described above.

3. Trend Analysis Results

3.1. Concentration Trends

Concentration trends for individual sites and for the region are presented in Table S3 in Supporting Information S1 and Figure 3. Concentration versus time plots for individual sites are shown for Zn in Figures S2 (acidic

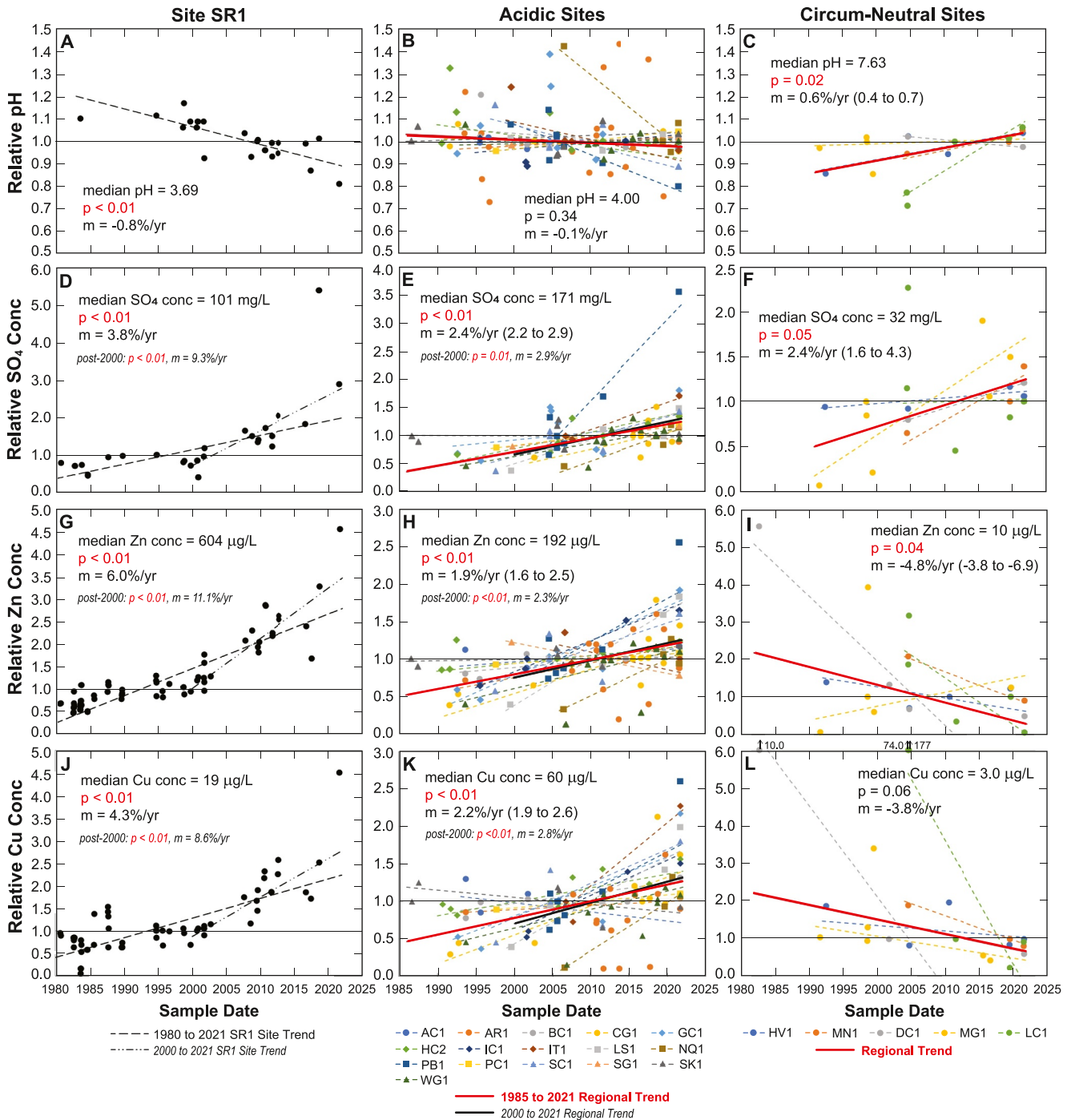


Figure 3. Relative pH and relative sulfate (SO₄), Zn, and Cu concentration versus sample date for site SR1 (a), (d), (g) and (j), acidic sites (pH ≤ 5.5; (b), (e), (h) and (k)), and circum-neutral sites (pH = 7–8; (c), (f), (i) and (l)). Plotted relative values are measured concentration normalized to the site median for the observation period. Dashed lines are Theil-Sen robust lines showing trends for individual sites, and solid red line is regional Theil-Sen robust line indicating regional trend. For SR1 and acidic sites, a separate Theil-Sen robust line is also shown for the post-2000 period for SO₄, Zn, and Cu. Mann-Kendall Test p-value is shown for SR1 and Regional Kendall Test p-value for acidic and circum-neutral sites, appearing in red when statistically significant (≤0.05). Trend slope (*m*) is shown in units of percent of site median for the observation period per year (%/yr), with 90% confidence interval shown in parentheses for the full period regional trend *m* (1985–2021) when *p* ≤ 0.05. Median concentration is shown to provide reference frame for absolute concentration values.

sites) and S3 (circum-neutral sites) in Supporting Information S1 as an example to illustrate more clearly the variation in sample number and trend strength across different sites. In Figure 3 and all following time-series plots, the dependent variable (on y-axis) is normalized to the site median value for the observation time period to facilitate plotting of multiple sites on a single graph and to enable direct comparison of relative rates of change between different sites. These normalized values are referred to as the “relative concentration”, “relative residual concentration”, and “relative index load”. Computed linear trend slopes are therefore in units of percent of the site median value per year (%/yr).

Site SR1 has a significant downward trend in pH of $-0.8\%/yr$ and significant upward trends in SO_4 , Zn, and Cu of 3.8% , 6.0% , and $4.3\%/yr$, respectively. Rates of increase for SO_4 and Zn are similar to those reported by Todd et al. (2012) for September for the period from 1979 to 2011 ($\sim 3\%$ and $\sim 5\%$, respectively), though slightly greater, suggesting that concentrations are continuing to increase at the site at similar or perhaps slightly greater rates. The SO_4 , Zn, and Cu concentration trends all appear to become steeper around the year 2000, suggesting that post-2000 (current) rates of increase could be larger than those computed for the entire observation period. An acceleration in rates of change around the year 2000 is consistent with the fact that the southwestern U.S. entered a regional “megadrought” at this time, which is ongoing (Williams et al., 2020). A second MKT was thus performed for the period 2000–2021, and resulting p and m values are also indicated on the plots in Figure 3 and in Table S3 in Supporting Information S1. Post-2000 upward trends are significant for all three constituents and have slopes of 9.3% , 11.1% , and $8.6\%/yr$ for SO_4 , Zn, and Cu, respectively, roughly twice the magnitude of the 1980–2021 trends.

Some acidic sites display downward trends in pH like SR1, but overall acidic sites display no significant regional pH trend. However, for SO_4 , Zn, and Cu, the considerable majority of acidic sites display upward trends like SR1, and the RKT indicates significant positive regional trends of $2.4\%/yr$ for SO_4 , $1.9\%/yr$ for Zn, and $2.2\%/yr$ for Cu. This result provides strong evidence that the increasing SO_4 and metal concentrations observed at SR1 in recent decades are not unique, and such increases are occurring widely in ARD-affected watersheds throughout Colorado (but SR1 trend magnitudes are apparently on the high end). Though not as pronounced as at SR1, concentrations throughout the region also appear to rise more rapidly after the year 2000, so separate RKTs again were performed for the post-2000 period (and the same was done for the streamflow, concentration residual, and index load trends presented below). Post-2000 positive trends are significant, with slopes of 2.9% , 2.3% , and $2.8\%/yr$ for SO_4 , Zn, and Cu, respectively. These slopes are again larger than those for the 1985–2021 trends, but by a smaller amount (20%–30%) than at site SR1.

Circum-neutral sites have a significant regional upward trend in SO_4 of $2.4\%/yr$, consistent with SR1, acidic sites, and many other non-ARD mountain streams and lakes globally (e.g., Rogora et al., 2020; Salerno et al., 2016; Steingruber et al., 2021). However, in contrast to SR1 and acidic sites, circum-neutral sites have a significant regional positive trend in pH of $0.6\%/yr$ and borderline-significant regional negative trends in Zn and Cu of $-4.8\%/yr$ and $-3.8\%/yr$, respectively. A possible explanation is that these trends are caused by changes in instream processes involving photosynthesis resulting from decreased streamflow. A decrease in stream depth caused by declining streamflow will likely lead to increased light penetration and an associated increase in photosynthesis, a process known to increase stream pH (Andersen et al., 2017; Hamid et al., 2020). Effects of photosynthesis on stream pH would be further enhanced by decreased flows leading to an increase in the ratio of photosynthetically active benthic area to streamwater volume. The increasing stream pH may in turn explain the negative trends in Cu and Zn concentrations; when stream pH increases, sorption of cations such as Cu and Zn on hydrous metal oxides generally increases, resulting in decreased dissolved concentrations (Runkel et al., 1999). These processes would likely have a negligible effect on stream pH at the acidic sites due to the much higher initial H^+ activity. Note that information was not available regarding pH measurement or probe calibration procedures for most samples in the dataset. Therefore, the pH trends should be considered with some caution, particularly for the circum-neutral sites for which accurate field pH measurements require greater care. Though the circum-neutral site trends are interesting and warrant consideration, further evaluation of these processes is beyond the scope of the present study. The remainder of our trend analysis focuses exclusively on the acidic sites, these being of primary environmental concern for potential negative downstream impacts.

3.2. Potential Load Trends

Trends in mean monthly streamflow for August, September, and October at the eight index gages are presented in Table S4 in Supporting Information S1 and Figure 4. All gages display downward trends for all 3 months, the

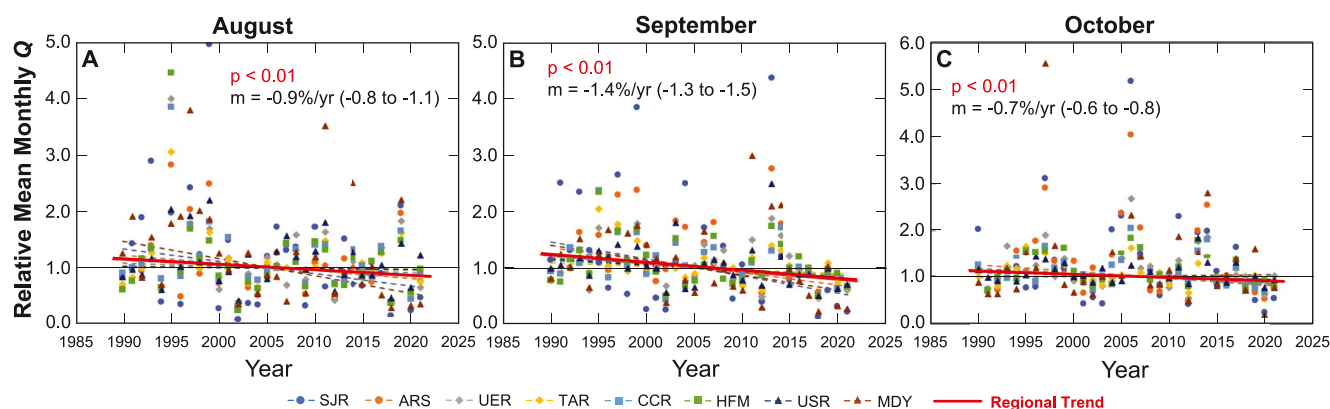


Figure 4. Relative mean monthly streamflow (Q) versus year for August (a), September (b), and October (c) for index stream gages. Plotted relative values are mean monthly flow normalized to the site median for the observation period. Dashed lines are Theil-Sen robust lines showing trends for individual gages, and solid red line is regional Theil-Sen robust line indicating regional trend. Regional Kendall Test p -value is shown, appearing in red when statistically significant (≤ 0.05). Regional trend slope (m) is shown in units of percent of site median for the observation period per year (%/yr), with 90% confidence interval shown in parentheses.

single exception being a positive trend at MDY for October. Regional Kendall Tests for each month indicate significant downward regional trends of $-0.9\%/yr$ for August, $-1.4\%/yr$ for September, and $-0.7\%/yr$ for October. These negative trends suggest that the positive regional concentration trends observed for acidic sites are caused at least in part by declining streamflows (dilution effect). However, the magnitude of rates of streamflow decline are only about half the magnitude of regional concentration increases (absolute value of $\sim 1\%/yr$ compared to $\sim 2\%/yr$). This difference suggests that the dilution effect can only account for about half of the regional concentration increases, and that loads are also generally increasing. Post-2000 rates of streamflow decline are not substantially greater than those for the whole observation period, being either insignificant (August) or within $0.2\%/yr$ of those for 1990–2021 (September and October). The same is true for post-2000 flows specifically at gage USR, the index gage for site SR1.

Another characteristic of the mean monthly streamflow trends is that their magnitudes are relatively well correlated with elevation, with larger flow declines apparently occurring at lower elevation (Figure S4A in Supporting Information S1). This relationship calls into question our primary reliance on geographic proximity, rather than elevation similarity, for selecting index gages (see Text S2 and Figures S4B and S4C in Supporting Information S1 for more detailed analysis of this issue). However, the long-term flow declines shown in Figure S4A in Supporting Information S1 (0% to $-2\%/yr$) comprise a small component of the annual flow variations shown in Figure 4 (commonly $>30\%$ of the site median). Furthermore, the fact that the sample sites are all at higher elevations than their index gages means that long-term flow declines for the sample sites are generally overestimated, and trend slopes for concentration residual and index load are thus generally underestimated. The relationship in Figure S4A in Supporting Information S1 therefore does not compromise the reliability of our approach for determining whether loads may be increasing regionally. However, it does indicate an additional source of uncertainty in the magnitudes of the concentration residual and index load trend slopes computed for individual sites (Table S3 in Supporting Information S1), and is another reason why we place less emphasis on the index load trend slopes than the concentration trend slopes in the correlation analysis presented in Section 4.

Representative concentration versus index flow (C - Q) plots are shown in Figure 5 for Zn, the sites shown being acidic sites with ≥ 6 samples. Plots for SO_4 and Cu have similar characteristics. Regression lines generally have negative slopes, indicating lower concentrations at higher flows as expected. For multiple sites, samples plotting below the regression line are generally older than those plotting above it. This pattern is well defined for SR1, where it was first identified by Crouch et al. (2013). This pattern is consistent with a non-stationary C - Q relationship resulting from the Zn concentration increasing over time for a given flow range.

Trends in residual concentrations computed from the C - Q relationships are shown for SR1 and other acidic sites in Figure 6. Note that concentration residuals are normalized to the site median concentration, not the median residual. Site SR1 displays significant upward trends for SO_4 , Zn, and Cu of $3.7\%/yr$, $5.0\%/yr$, and $4.0\%/yr$, respectively. As with the concentrations, post-2000 residual concentration trends are significant and steeper for all three constituents, with slopes roughly twice the magnitude of those for the entire observation period.

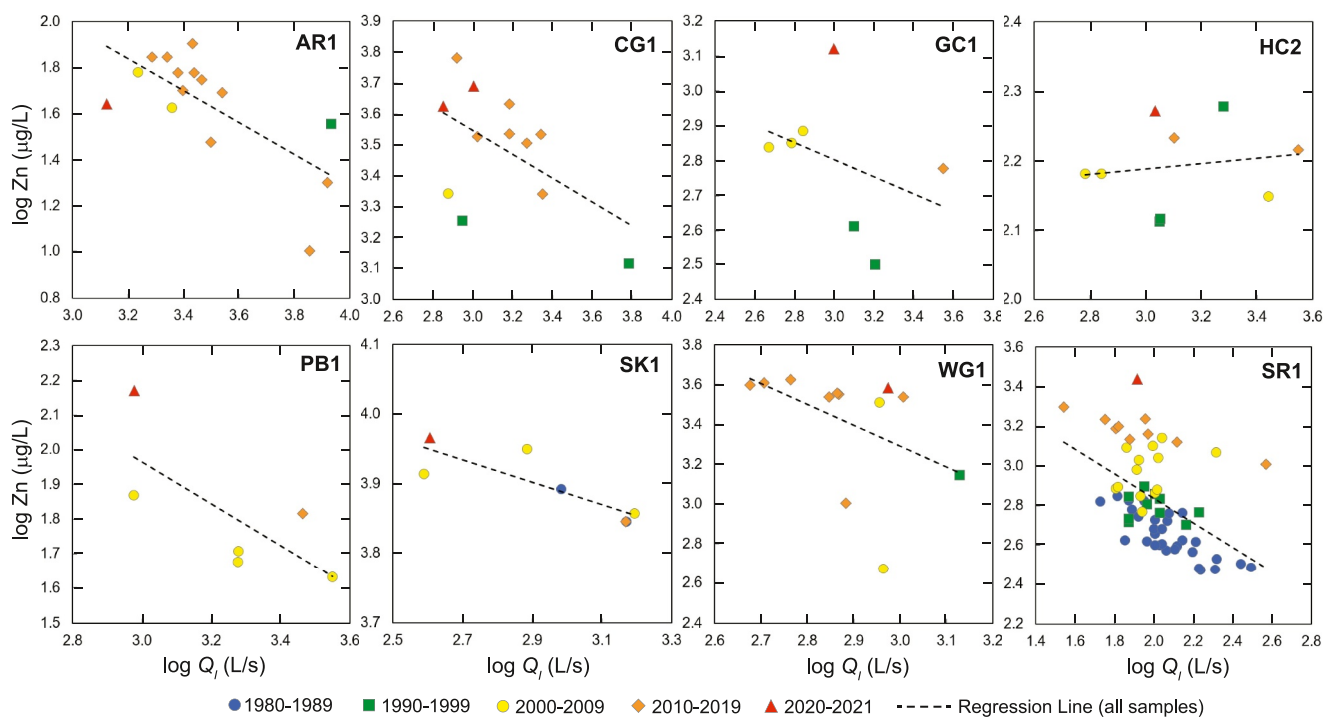


Figure 5. Log Zn concentration versus log index flow (Q_i) for acidic sites with ≥ 6 measurements, with regression line. For site SR1, flows are estimated flows at the site.

Concentration residuals are also generally increasing at the other acidic sites, with the RKT indicating significant positive regional trends for SO_4 , Zn, and Cu of 1.6%/yr, 1.2%/yr, and 1.6%/yr, respectively. These positive concentration residual trends at acidic sites provide additional support for loads generally increasing regionally along with concentrations. Magnitudes of the regional residual trends are less than those of the regional concentration trends by 0.6%–0.9%/yr. This difference is roughly consistent with the absolute value of declining trends in mean monthly streamflow, which suggest that the dilution effect on average probably does not account for more than $\sim 1\%$ /yr (or about half) of the regional increasing concentration trends. Regional post-2000 residual concentration trends are again significant and steeper than those for the entire observation period for all three constituents, particularly for Zn and Cu which have post-2000 slopes about twice the magnitude 1985–2021 slopes.

Trends in estimated/measured load (henceforth simply “estimated load”) for SR1 and index load for the other acidic sites are shown in Figure 7. Site SR1 displays significant positive trends in estimated load for SO_4 , Zn, and Cu of 3.2%/yr, 4.5%/yr, and 3.0%/yr, respectively. Post-2000 trends are once again steeper than trends for the entire observation period by about a factor of two, though only significant for SO_4 and Cu. An initial trend analysis for index load for all other acidic sites indicated no significant trends, with p-values of 0.13 for SO_4 , 0.62 for Zn, and 0.36 for Cu (Table S3 in Supporting Information S1). However, more consistent trends emerge when sites are separated into a high-elevation group, with a mean elevation (above the sample location) $> 3,450$ masl, and a low-elevation group, with a mean elevation $< 3,450$ masl (Figure 7). All six of the low-elevation sites display negative slopes in index load for all three constituents, whereas most of the high-elevation sites display positive slopes. High-elevation sites display significant regional positive trends for SO_4 and Cu of 1.6%/yr and 2.0%/yr, respectively. The regional trend for Zn at high-elevation sites is also positive at 1.2%/yr, but not significant ($p = 0.13$). The fact that the index load trends are less well defined than the residual concentration trends is not surprising, given that the former incorporates all the noise resulting from inconsistencies in the relationship between flow at the sample site and at the corresponding index gage, whereas this noise is dampened in computation of the residuals through use of the $C-Q$ plot regression lines. Post-2000 trends at the high elevation sites are once again steeper than those for the entire observation period by about a factor of two, but none of these are significant.

Taken together, the results of all three approaches for examining potential load trends provide strong support for regionally increasing loads in ARD-affected streams. The dilution effect is likely contributing to regionally increasing concentrations at acidic sites, but increasing loads appear to be on average at least an equal contributor.

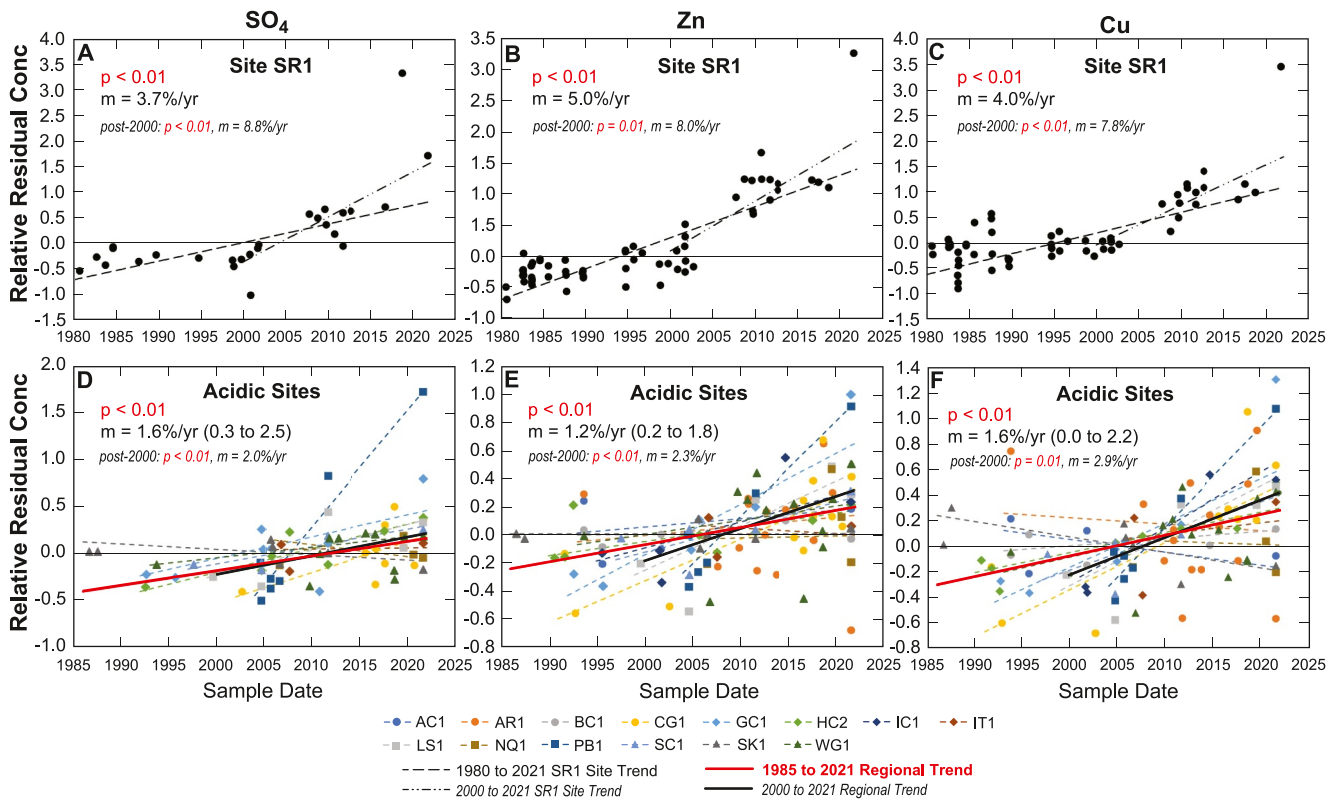


Figure 6. Relative residual sulfate (SO₄), Zn, and Cu concentration versus sample date for site SR1 (a), (b) and (c) and acidic sites (d), (e) and (f). Plotted relative values are residual concentrations normalized to the site median measured concentration for the observation period. Dashed lines are Theil-Sen robust lines showing trends for individual sites, and solid red line is regional Theil-Sen robust line indicating regional trend. A separate Theil-Sen robust line is also shown for the post-2000 period. Mann-Kendall Test p-value is shown for SR1 and Regional Kendall Test p-value for acidic sites, appearing in red when statistically significant (≤ 0.05). Trend slope (m) is shown in units of percent of site median for the observation period per year (%/yr), with 90% confidence interval shown in parentheses for the full period regional trend m (1985–2021).

The index load trends suggest that increasing loads are more likely to be found at higher elevation sites, pointing to an elevation dependence of important controlling mechanisms. Rates of increasing load apparently accelerated around the year 2000, whereas rates of streamflow decline apparently did not (both regionally and at gage USR associated with site SR1). This difference suggests that observed regional increases in concentration trend slope around the year 2000 were more likely caused by changing loads than changing streamflows.

4. Potential Driving Mechanisms

Quantification of the magnitude of concentration and index load trends for multiple ARD sites across Colorado presents an opportunity to compare these trend magnitudes to various site characteristics and gain insight into the relative importance of different potential driving mechanisms. The following variables were quantified for each acidic site (Table S5 in Supporting Information S1; see Section 2.2 for additional details), each being linked directly to one of the potential driving mechanisms listed in Section 1. As discussed in Section 2 above, we recognize that some of these variables could be linked to multiple driving mechanisms. However, the link between each site variable and its corresponding driving mechanism is sufficiently direct that a uniquely high degree of correlation between that variable and trend magnitudes (such that all other variables display weaker correlation) would provide clear support for the importance of that variable's corresponding mechanism. It should be noted that increasing atmospheric deposition of SO₄ is an unlikely potential cause of rising stream concentrations (Mast, 2013), as is glacier melting (Salerno et al., 2016) given the absence of glaciers at these study sites.

The “mean Q slope” is the average of the trend slopes for mean monthly streamflow for August, September, and October (Figure 4) for the associated index gage. This variable should reflect the degree of streamflow decline, and correlation with the concentration trend magnitude should thus reflect the importance of the dilution effect.

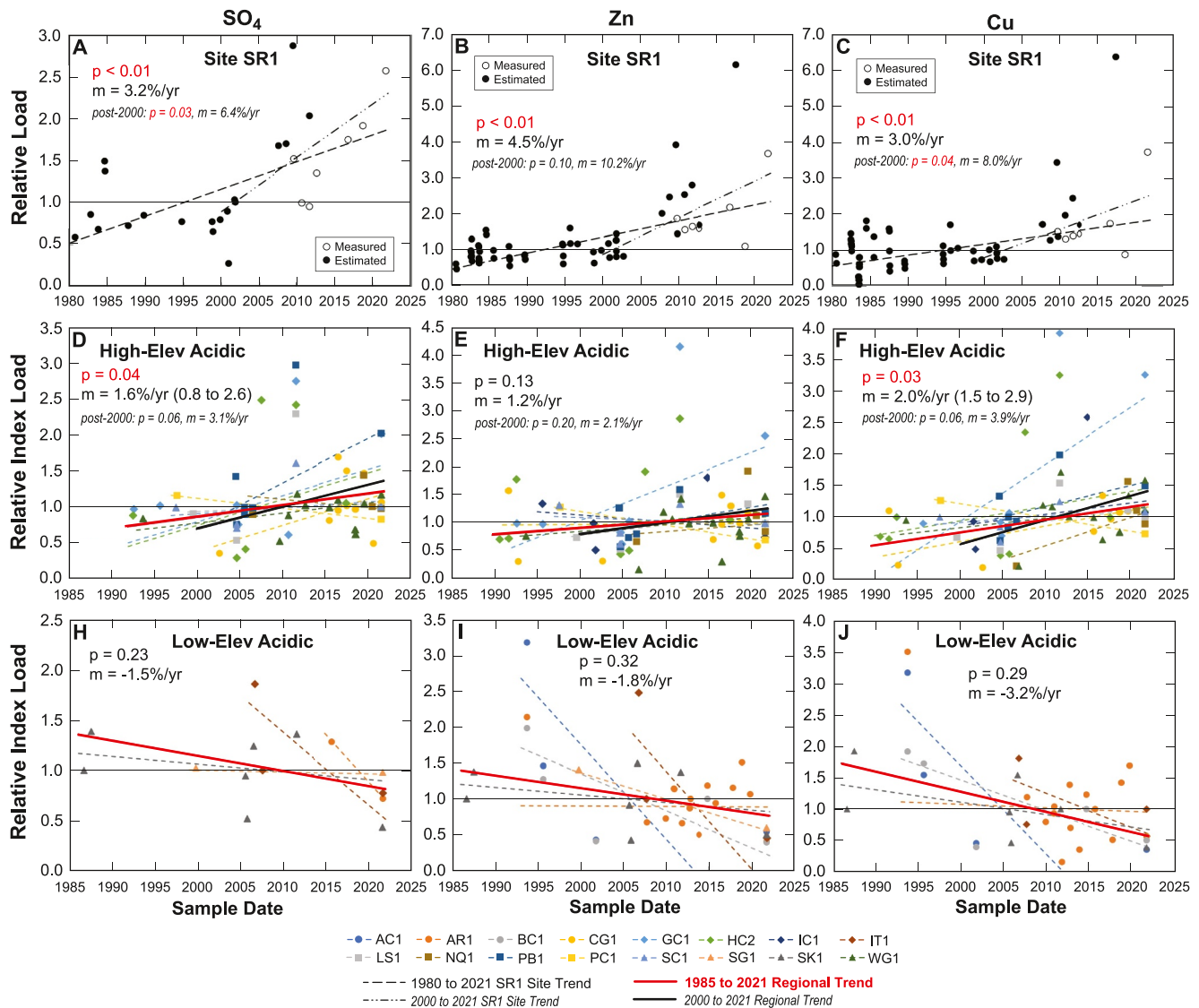


Figure 7. Relative estimated (and measured) sulfate (SO₄), Zn, and Cu load versus sample date for site SR1 (a), (b) and (c), and relative index SO₄, Zn, and Cu load for high-elevation acidic sites (d), (e) and (f) and low-elevation acidic sites (h), (i) and (j). High-elevation sites have mean elevation (above sample point) > 3,450 masl, and low-elevation sites have mean elevation < 3,450 masl. Plotted relative values are estimated/index loads normalized to the site median for the observation period. Dashed lines are Theil-Sen robust lines showing trends for individual sites, and solid red line is regional Theil-Sen robust line indicating regional trend. A separate Theil-Sen robust line is also shown for the post-2000 period for SR1 and the high-elevation acidic sites. Mann-Kendall Test p-value is shown for SR1 and Regional Kendall Test p-value for acidic sites, appearing in red when statistically significant (≤ 0.05). Trend slope (m) is shown in units of percent of site median for observation period per year (%/yr), with 90% confidence interval shown in parentheses for the full period regional trend m (1985–2021) when $p \leq 0.05$.

The “MAAT” is the median of the mean annual air temperatures for the period from 1990 to 2020 (Figure S5A in Supporting Information S1). The MAAT for most sites in the 1980s was between -2.0 and 2.0°C (Figure S6 in Supporting Information S1), meaning that some (but not all) of the sampled watersheds likely contained permafrost at that time (Janke, 2005), and all likely contained seasonally frozen ground due to subzero mean winter temperatures. The 1990–2020 MAAT medians are generally $\sim 1^\circ\text{C}$ warmer (Figure S6 in Supporting Information S1), indicating that some sites have transitioned from negative to positive MAATs, and all sites have probably experienced some decline in the spatial extent and seasonal persistence of frozen ground. We assume that sites with the coldest MAATs had the most frozen ground initially, and therefore loss of frozen ground has probably been the most extensive at these coldest sites in recent decades. A correlation between MAAT and the concentration/load trend magnitude may thus reflect the importance of accelerating weathering rates caused by the melting of frozen ground. Because frozen ground acts like an aquitard, melting of ground ice could open up

new pathways for groundwater flow, enabling shallow oxygenated groundwater to access deeper levels of the bedrock where anoxic conditions previously existed due to isolation from active groundwater flow and the atmosphere (Colombo et al., 2018; Ilyashuk et al., 2018). This groundwater could then begin oxidizing fresh sulfides in the deeper bedrock previously protected from weathering, and transport the resulting SO_4 and metals to the stream.

The “MAAT slope” and “PPT slope” are slopes for the mean annual air temperature and total annual precipitation trends for the period from 1990 to 2020 (Figure S5 in Supporting Information S1). Because groundwater recharge is directly dependent on both temperature and precipitation, these variables indicate potential changes in recharge, which could in turn drive changes in water table position. A correlation between these variables and the concentration/load trend magnitude could thus reflect the importance of accelerating weathering rates caused by falling water tables under warmer and drier conditions. A drop in the water table could expose fresh sulfides to oxygen in the vadose zone that were previously isolated below the water table under saturated anoxic conditions (Manning et al., 2013; Mast, 2013). This process would increase groundwater SO_4 and metal concentrations, which would then increase stream concentrations as groundwater enters the stream. The “wetland coverage” and “rock glacier coverage” are the percentage of the watershed above the sample point covered by mapped wetlands and rock glaciers. We assume that the greater the extent of these features, the more likely they are to influence streamwater chemistry. A correlation between wetland coverage and the concentration/load trend magnitude might indicate the importance of the mobilization of metals previously bound to organics in wetlands as a result of greater oxidation during more frequent/intense drying, and/or by decreasing pH (Crouch et al., 2013). A correlation between rock glacier coverage and the concentration/load trend magnitude might indicate the importance of the mobilization of metals previously trapped in rock glacier ice as this ice melts, given that such meltwater is often elevated in solutes (Colombo et al., 2018; Thies et al., 2007). The mean elevation was additionally examined, given its clear relation to index load trends observed in Figure 7.

All the above site variables were plotted against the trend slopes for both concentration and index load for SO_4 , Zn, and Cu (Figure S7 in Supporting Information S1), as well as the average trend slope for all three constituents (“mean trend slope”). Plots for site variables displaying R^2 values >0.2 for either concentration or index load are shown in Figure 8. In the following discussion, we place greater emphasis on correlations with the concentration mean trend slope than correlations with the index load mean trend slope because, as noted in Sections 2.3 and 3.2 above, the magnitudes of the latter are more uncertain.

The MAAT shows the strongest correlation with concentration trend slope of all the variables tested ($R^2 = 0.42$; Figure 8a), and its correlation with index load trend slope is also relatively high ($R^2 = 0.40$). This result suggests that enhanced sulfide weathering due to melting of frozen ground is a primary contributor to observed increasing metal concentrations and loads. Mean elevation is also relatively well correlated with the mean trend slope for both concentration and index load (R^2 of 0.35 and 0.47; Figure 8b). This correlation is expected given the known strong correlation between elevation and MAAT, and the previously established fact that index load slopes are mainly negative for low-elevation sites and positive for high-elevation sites (Figure 7). The relationship between mean elevation and concentration trend slope helps explain the dominantly negative index load trend slopes at the low-elevation sites. Mean Q slope for the index gages is strongly correlated with the gage elevation ($R^2 = 0.71$; Figure S4A in Supporting Information S1), such that larger streamflow declines are apparently occurring at lower elevation. The relatively large streamflow declines combined with the relatively small (generally near-zero) concentration increases at the low-elevation sites should produce declining loads.

The MAAT slope appears poorly correlated with both concentration and index load trend slopes when all sites are plotted, with R^2 values <0.1 (Figures S7E and S7F in Supporting Information S1). However, all four sites located in the southern San Juan Mountains (AC1, AR1, BC1, and IC1; Figure 1) plot in a group apart from the rest of the sites, suggesting that the relationship between warming temperatures and concentration/load trends in this area is fundamentally different from the rest of the study region. Note that the only other site variable displaying a similar isolated cluster in Figure S7 in Supporting Information S1 is PPT slope when plotted against the concentration trend slope (Figure S7I in Supporting Information S1), and in this case the sites in this isolated cluster are not all from the same location. When the four southern San Juan Sites are removed, the R^2 values increase to 0.14 and 0.47 for the concentration and index load trend slopes, respectively (Figure 8c). The R^2 value for the index load trend slope is sufficiently high to suggest that enhanced sulfide weathering due to falling water tables may be contributing to increasing metal loads across much of the study region. However, the R^2 value for concentration

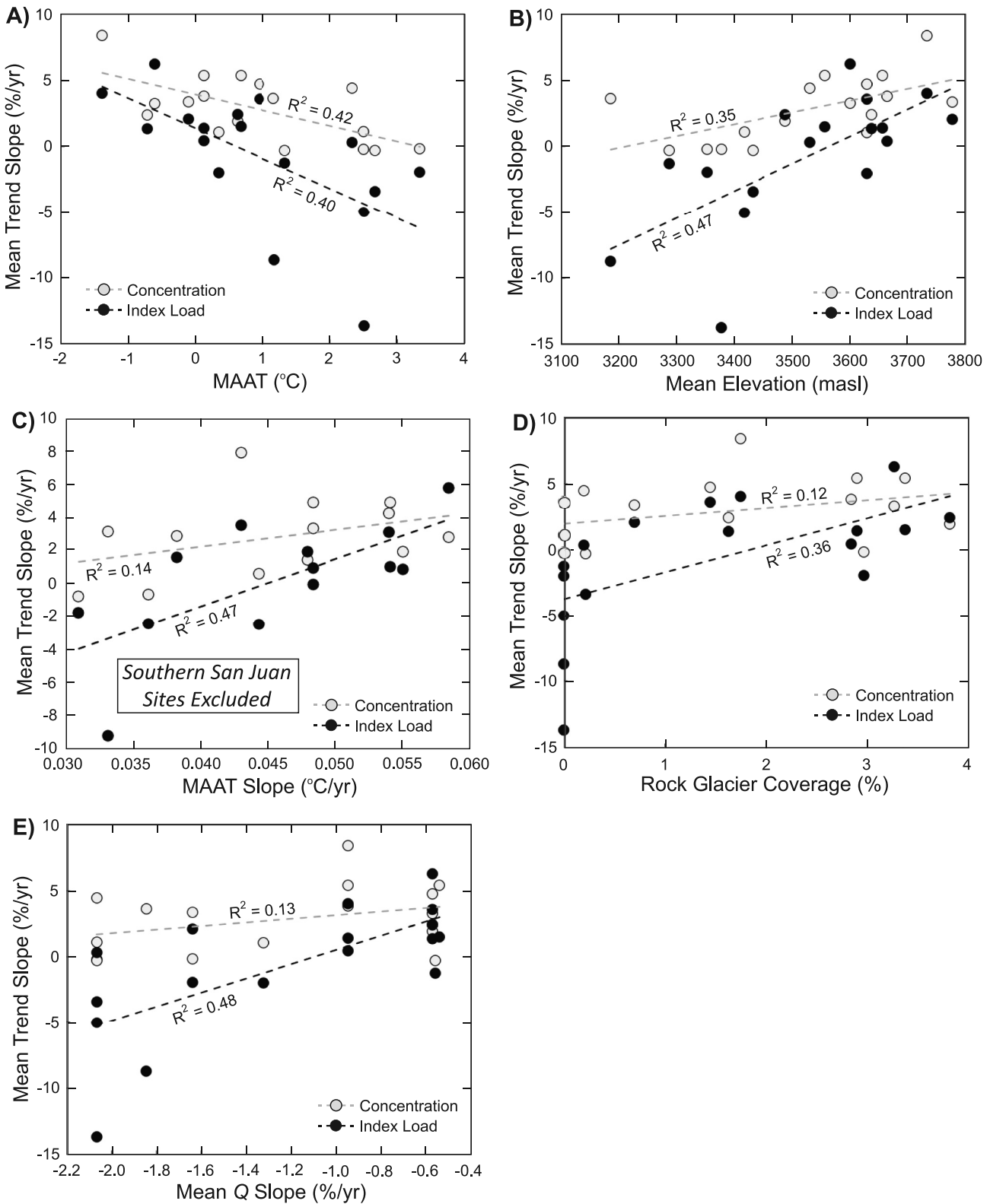


Figure 8. Mean trend slope for concentration and index load versus selected site variables defined and explained in main text, including: (a) mean annual air temperature (MAAT); (b) mean elevation; (c) MAAT slope for the period of 1990–2020, excluding southern San Juan Mountain sites; (d) rock glacier coverage; and (e) mean streamflow (Q) slope for the period of 1990–2021. Mean trend slope for concentration and index load and mean Q slope are in units of percent of the site median per year (%/yr). Regression lines with R^2 values are also shown.

trend slope is relatively low. Furthermore, the PPT slope is poorly correlated with both concentration and index load trend slopes with R^2 values <0.15 (Figures S7I and S7J in Supporting Information S1); while this lack of correlation is not evidence against declining recharge (which could be occurring due to increasing temperature alone), it provides no further evidence to support it. Together, the MAAT slope and PPT slope correlations suggest that falling water tables may be partly responsible for increasing concentrations and loads, but this mechanism probably does not play a primary role across the region.

The correlation between rock glacier coverage and concentration trend slope is relatively poor ($R^2 = 0.12$; Figure 8d). The R^2 value for index load trend slope is substantially higher at 0.36, but this reduces to 0.11 when sites with 0% rock glacier coverage (i.e., where factors other than rock glaciers must be drivers) are removed. The mobilization of metals from melting rock glacier ice therefore does not appear to be a major contributor to regional concentration and load increases. However, it should be recognized that our analysis does not consider the degree of rock glacier activity (largely controlled by the amount of ice they contain), which clearly could be an important factor dictating the amount of water they release and their relative impact on local stream chemistry. Comparison of activity level and other more detailed rock glacier characteristics to the concentration and load trend slopes might therefore yield higher correlations. Mean Q slope is poorly correlated with the concentration trend slope ($R^2 = 0.13$; Figure 8e), and the slope of the regression line, though slight, is opposite of that expected for the dilution effect, with larger (more negative) streamflow declines associated with somewhat smaller concentration increases. The low R^2 and reversed slope suggest that factors other than the dilution effect are mainly driving observed concentration increases. This situation should also lead to smaller load increases (perhaps even decreases) at sites with larger declines in streamflow. Such is the case here, with the index load regression line having a positive slope and a considerably higher R^2 value of 0.48. Finally, wetland coverage is poorly correlated with both the concentration and index load trend slopes ($R^2 < 0.1$), suggesting that mobilization of metals from wetlands is not a major regional driver of increasing concentrations and loads.

Our correlation analysis therefore points to accelerating sulfide weathering rates from melting of frozen ground as perhaps the most important driving mechanism for observed regional increases in concentration and load at acidic sites. This conclusion aligns with the observation of Crouch et al. (2013) that a major source of metals and acid in the upper Snake River is in the upper reaches of a single tributary, within a high-elevation talus hillslope that may have begun to gradually thaw in the summer. Our analysis also supports a potentially substantial, though likely secondary, regional contribution from accelerating sulfide weathering driven by falling water tables. This conclusion is consistent with that of Manning et al. (2013), who combine coupled numerical modeling with direct subsurface observations from a deep borehole at the top of the upper Snake River watershed and find that a falling water table is another plausible driver of increasing stream metal concentrations. Though our analysis does not find correlations supporting a major regional role for other proposed driving mechanisms, we must emphasize that the analysis is insufficiently robust to broadly rule out the importance of any specific mechanism, especially at any particular site.

This study highlights the need for additional research focused on climate-driven controlling mechanisms, and recommends that such research prioritize those, such as melting of frozen ground, with a strong link to mean annual air temperature and elevation. This future work should include, first, continued monitoring of stream chemistry and flow at ARD sites with historical records, like the ones presented here, to track ongoing changes and better constrain the occurrence and magnitudes of trends in concentration and load. Second, these growing datasets could be used to perform considerably more robust correlation analyses than performed here, employing more rigorous multi-variate analysis and possibly machine learning to better identify the relative importance of and inter-relationships between different potential controlling mechanisms. These analyses could also include a larger number of more specific site variables that might be more directly linked to potential drivers. For example, permafrost models have been developed for some mountain areas (e.g., Janke, 2005) and such a model could be used to develop an extent-of-permafrost metric for inclusion in these analyses. As another example, we simply considered the presence or absence of rock glaciers in our analysis, but, as previously noted, the degree of rock glacier activity could be an important factor controlling their relative influence on local streamwater chemistry, and thus should be included in a more rigorous study. Third, future research should include a limited number of multidisciplinary focused field studies that collect extensive detailed geological, hydrological, chemical, and biological datasets from a single or small number of ARD watershed(s) where stream metal concentrations are increasing. Such studies should include geophysical techniques and subsurface measurements from boreholes and

groundwater monitoring wells to directly observe and map ground ice, ground temperature dynamics, groundwater flow conditions, and sulfide weathering processes.

Improved process-level understanding and process models developed from focused field studies combined with empirical models developed from broad-scale monitoring and correlation analyses together provide the greatest opportunity to understand and successfully forecast increasing metal concentrations and loads in ARD-affected streams in mountainous regions. Importantly, ARD-affected streams in Arctic regions could be undergoing changes similar to those in mountainous regions. Numerous studies have identified widespread surface water degradation across Arctic regions that is generally attributed to pervasive permafrost melting, though few of these have focused on heavy metal concentrations in mineralized zones (Colombo et al., 2018). However, the sudden emergence of “rusting rivers” reported by O’Donnell et al. (2023) provides new evidence that the climate-related changes in ARD streams in Colorado could be occurring in the Arctic in an extreme form. In just the past few years, these rivers have rapidly degraded from containing clear, circum-neutral, dilute water to containing low-pH, metal-rich, ARD water with extensive iron precipitation, apparently due to melting of ground ice in mineralized zones. An improved understanding and ability to predict increasing metal concentrations and loads in ARD-affected streams is therefore urgently needed in both mountainous and Arctic regions globally to effectively protect downstream ecosystems, manage water resources, and plan mine site remediation under a changing climate.

5. Conclusions

Statistically significant regional upward trends in SO_4 , Zn, and Cu concentration suggest that metal concentrations are generally increasing in mountain streams affected by acid rock drainage throughout Colorado due to climate warming. Regional upward trend magnitudes for the period 1986 to 2021 for these three constituents are substantial at 1.9%–2.4% (of the site median concentration) per year, meaning that concentrations on average have approximately doubled over the past 30 years. Regional trend magnitudes apparently accelerated around the year 2000, being 2.3%–2.8% per year for the more recent period of 2000–2021. An examination of potential load trends utilizing streamflow data from gages located near the sample sites provides strong support for regionally increasing SO_4 , Zn, and Cu loads in streams affected by acid rock drainage. Declining streamflows are likely contributing to regionally increasing concentrations, but increasing loads appear to be on average an equal or greater contributor. Load increases appear to be mainly occurring at higher-elevation sites (mean elevation >3,450 masl, or 65% of sites in this study), with loads at lower-elevation sites largely declining due to larger streamflow declines coupled with smaller (near-zero) concentration increases. Comparison of selected site characteristics with the magnitude of concentration and load trend slopes suggests that accelerating sulfide weathering rates from melting of frozen ground may be the most important driving mechanism for observed regional increases in concentration and load at acid rock drainage sites. Mean annual air temperature and mean elevation display the highest correlation with concentration trend slope (R^2 of 0.42 and 0.35, respectively, with all others being ≤ 0.14). Future research of specific controlling mechanisms driven by climate change should therefore prioritize those such as melting of frozen ground that are closely linked to mean annual air temperature and elevation.

Data Availability Statement

All data are available in electronic format on the CUAHSI HydroShare data server (Petach, Manning, Runkel, & McKnight, 2023) at: <http://www.hydroshare.org/resource/443675d7bcf64b6da19d9307882997b0>.

References

- Andersen, M. R., Kragh, T., & Sand-Jensen, K. (2017). Extreme diel dissolved oxygen and carbon cycles in shallow vegetated lakes. *Proceedings of the Royal Society of London*, *B284*(1862), 20171427. <https://doi.org/10.1098/rspb.2017.1427>
- Boyer, E. W., McKnight, D. M., Bencala, K. E., Brooks, P. D., Anthony, M. W., Zellweger, G. W., & Harnish, R. E. (1999). Streamflow and water quality characteristics for the upper Snake River and Deer Creek catchments in Summit County, Colorado: Water years 1980 to 1990. In *University of Colorado Institute of Arctic and Alpine Research Occasional Paper* (Vol. 53, p. 81). Retrieved from <https://www.colorado.edu/instaar/research/publications/instaar-occasional-papers>
- Byrne, P., Onnis, P., Runkel, R. L., Frau, I., Lynch, S. F. L., & Edwards, P. (2020). Critical shifts in trace metal transport and remediation performance under future low river flows. *Environmental Science and Technology*, *54*(24), 15742–15750. <https://doi.org/10.1021/acs.est.0c04016>
- Colombo, N., Salerno, F., Gruber, S., Freppaz, M., Williams, M., Fratianni, S., & Giardino, M. (2018). Review: Impacts of permafrost degradation on inorganic chemistry of surface fresh water. *Global and Planetary Change*, *162*, 69–83. <https://doi.org/10.1016/j.gloplacha.2017.11.017>

Acknowledgments

This work was funded by National Science Foundation Graduate Research Fellowship Program Award Number 1650115, a fellowship from the University of Colorado at Boulder’s Department of Civil, Environmental and Architectural Engineering, and the U.S. Geological Survey’s Mineral Resources Program. Any use of trade, product, or firm names is for descriptive purposes only and does not imply endorsement by the U.S. Government.

- Crawford, J. T., Hinckley, E. S., Litaor, M. I., Brahney, J., & Neff, J. C. (2019). Evidence for accelerated weathering and sulfate export in high alpine environments. *Environmental Research Letters*, *14*(12), 124092. <https://doi.org/10.1088/1748-9326/ab5d9c>
- Crouch, C. M., McKnight, D. M., & Todd, A. S. (2013). Quantifying sources of increasing zinc from acid rock drainage in an alpine catchment under a changing hydrologic regime. *Hydrological Processes*, *27*(5), 721–733. <https://doi.org/10.1002/hyp.9650>
- Flores, M., Núñez, J., Oyarzún, J., Freixas, G., Maturana, H., & Oyarzún, R. (2017). Surface water quality in a sulfide mineral-rich arid zone in North-Central Chile: Learning from a complex past, addressing an uncertain future. *Hydrological Processes*, *31*(3), 498–513. <https://doi.org/10.1002/hyp.11086>
- Hamid, A., Bhat, S. U., & Jehangir, A. (2020). Local determinants influencing stream water quality. *Applied Water Science*, *10*(1), 24. <https://doi.org/10.1007/s13201-019-1043-4>
- Heil, E., Warix, S., Singha, K., & Navarre-Sitchler, A. (2022). Decadal trends in solute concentrations, mass flux, and discharge reveal variable hydrologic and geochemical response to climate change in two alpine watersheds. *Applied Geochemistry*, *144*, 105402. <https://doi.org/10.1016/j.apgeochem.2022.105402>
- Helsel, D. R., & Frans, L. M. (2006). Regional Kendall Test for trend. *Environmental Science and Technology*, *40*(13), 4066–4073. <https://doi.org/10.1021/es051650b>
- Helsel, D. R., Hirsch, R. M., Ryberg, K. R., Archfield, S. A., & Gilroy, E. J. (2020). Statistical methods in water resources. *U.S. Geological Survey Techniques and Methods, Book*, (Vol. 4, pp. 458). Chapter A3. <https://doi.org/10.3133/tm4a3>
- Hirsch, R. M., Alexander, R. B., & Smith, R. A. (1991). Selection of methods for the detection and estimation of trends in water quality. *Water Resources Research*, *27*(5), 803–813. <https://doi.org/10.1029/91WR00259>
- Ilyashuk, B. P., Ilyashuk, E. A., Psenner, R., Tessadri, R., & Koinig, K. A. (2018). Rock glaciers in crystalline catchments: Hidden permafrost-related threats to alpine headwater lakes. *Global Change Biology*, *24*(4), 1548–1562. <https://doi.org/10.1111/gcb.13985>
- Janke, J. R. (2005). The occurrence of alpine permafrost in the Front Range of Colorado. *Geomorphology*, *67*(3–4), 375–389. <https://doi.org/10.1016/j.geomorph.2004.11.005>
- Johnson, G. (2020). *Active rock glacier inventory of the contiguous United States (PSUARGI)*. PANGAEA. <https://doi.org/10.1594/PANGAEA.918585>
- Leppi, J. C., DeLuca, T. H., Harrar, S. W., & Running, S. W. (2012). Impacts of climate change on August stream discharge in the Central-Rocky Mountains. *Climatic Change*, *112*(3–4), 997–1014. <https://doi.org/10.1007/s10584-011-0235-1>
- Li, L., Stewart, B., Zhi, W., Sadayappan, K., Ramesh, S., Kerins, D., et al. (2022). Climate controls on river chemistry. *Earth's Future*, *10*(6), e2021EF002603. <https://doi.org/10.1029/2021EF002603>
- Mann, H. B. (1945). Non-parametric tests against trend. *Econometrica*, *13*(3), 245–259. <https://doi.org/10.2307/1907187>
- Manning, A. H., Verplanck, P. L., Caine, J. S., & Todd, A. S. (2013). Links between climate change, water-table depth, and water chemistry in a mineralized mountain watershed. *Applied Geochemistry*, *37*, 64–78. <https://doi.org/10.1016/j.apgeochem.2013.07.002>
- Mast, M. A. (2013). Evaluation of stream chemistry trends in US Geological Survey reference watersheds, 1970–2010. *Environmental Monitoring and Assessment*, *185*(11), 9343–9359. <https://doi.org/10.1007/s10661-013-3256-6>
- McKnight, D. M., Hornberger, G. M., Bencala, K. E., & Boyer, E. W. (2002). In-stream sorption of fulvic acid in an acidic stream: A stream-scale transport experiment. *Water Resources Research*, *38*(1), 1005. <https://doi.org/10.1029/2001WR000269>
- Miller, O. L., Miller, M. P., Longley, P. C., Alder, J. R., Bearup, L. A., Pruitt, T., et al. (2021). How will baseflow respond to climate change in the Upper Colorado River Basin? *Geophysical Research Letters*, *48*(22), e2021GL095085. <https://doi.org/10.1029/2021GL095085>
- O'Donnell, J. A., Carey, M. P., Koch, J. C., Baughman, C. A., Hill, K., Sullivan, P., et al. (2023). *Rusting of the Arctic: Causes of metal mobilization from thawing permafrost and consequences for aquatic ecosystems* (pp. C21E–C1286). American Geophysical Union Fall Meeting.
- Petach, T. N., Manning, A. H., Runkel, R. L., & McKnight, D. M. (2023). *Streamwater pH, sulfate, copper, and zinc concentration data collected from 1980 to 2021 in mineralized watersheds throughout the Colorado Rocky Mountains*. HydroShare. Retrieved from <http://www.hydroshare.org/resource/443675d7bcf64b6da19d9307882997b0>
- Petach, T. N., Manning, A. H., Wanty, R. B., Runkel, R. L., & McGee, B. N. (2023). *Chemistry and flow data from headwater streams draining hydrothermally altered areas in Colorado*. U.S. Geological Survey data release. <https://doi.org/10.5066/P99UJDPC>
- Petach, T. N., Runkel, R. L., Cowie, R. M., & McKnight, D. M. (2021). Effects of hydrologic variability and remedial actions on first flush and metal loading from streams draining the Silverton caldera, 1992–2014. *Hydrological Processes*, *35*(11), e14412. <https://doi.org/10.1002/hyp.14412>
- Razavi, T., & Coulibaly, P. (2013). Streamflow prediction in ungauged basins: Review of regionalization methods. *Journal of Hydrologic Engineering*, *18*(8), 958–975. [https://doi.org/10.1061/\(ASCE\)HE.1943-5584.0000690](https://doi.org/10.1061/(ASCE)HE.1943-5584.0000690)
- Rockwell, B. W., & Bonham, L. C. (2017). *Digital maps of hydrothermal alteration type, key mineral groups, and green vegetation of the western United States derived from automated analysis of ASTER satellite data*. U.S. Geological Survey data release. <https://doi.org/10.5066/F7CR5RK7>
- Rogora, M., Somaschini, L., Marchetto, A., Mosello, R., Tartari, G. A., & Paro, L. (2020). Decadal trends in water chemistry of Alpine lakes in calcareous catchments driven by climate change. *Science of the Total Environment*, *708*, 135180. <https://doi.org/10.1016/j.scitotenv.2019.135180>
- Rue, G. P., & McKnight, D. M. (2021). Enhanced rare earth element mobilization in a mountain watershed of the Colorado Mineral Belt with concomitant detection in aquatic biota: Increasing climate change-driven degradation to water quality. *Environmental Science and Technology*, *55*(21), 14378–14388. <https://doi.org/10.1021/acs.est.1c02958>
- Runkel, R. L., Kimball, B. A., McKnight, D. M., & Bencala, K. E. (1999). Reactive solute transport in streams: A surface complexation approach for trace metal sorption. *Water Resources Research*, *35*(12), 3829–3840. <https://doi.org/10.1029/1999WR90025>
- Runkel, R. L., Verplanck, P. L., Kimball, B. A., & Walton-Day, K. (2018). Cinnamon Gulch revisited: Another look at separating natural and mining-impacted contributions to instream metal load. *Applied Geochemistry*, *95*, 206–217. <https://doi.org/10.1016/j.apgeochem.2018.04.010>
- Runnells, D. D., Shepherd, T. A., & Angino, E. E. (1992). Metals in water. Determining natural background concentrations in mineralized areas. *Environmental Science and Technology*, *26*(12), 2316–2323. <https://doi.org/10.1021/es00036a001>
- Salerno, F., Rogora, M., Balestrini, R., Lami, A., Tartari, G. A., Thakuri, S., et al. (2016). Glacier melting increases the solute concentrations of Himalayan glacial lakes. *Environmental Science and Technology*, *50*(17), 9150–9160. <https://doi.org/10.1021/acs.est.6b02735>
- Steingruber, S. M., Bernasconi, S. M., & Valenti, G. (2021). Climate change-induced changes in the chemistry of a high-altitude mountain lake in the central Alps. *Aquatic Geochemistry*, *27*(2), 105–126. <https://doi.org/10.1007/s10498-020-09388-6>
- Theil, H. (1950). A rank-invariant method of linear and polynomial regression analysis, I, II, and III. *Proceedings of the Royal Netherlands Academy of Sciences*, *53*, 386–392, 521–525, and 1397–1412. https://doi.org/10.1007/978-94-011-2546-8_20

- Thies, H., Nickus, U., Mair, V., Tessadri, R., Tait, D., Thaler, B., & Psenner, R. (2007). Unexpected response of high alpine lake waters to climate warming. *Environmental Science and Technology*, *41*(21), 7424–7429. <https://doi.org/10.1021/es0708060>
- Todd, A. S., Manning, A. H., Verplanck, P. L., Crouch, C., McKnight, D. M., & Dunham, R. (2012). Climate-change-driven deterioration of water quality in a mineralized watershed. *Environmental Science and Technology*, *46*(17), 9324–9332. <https://doi.org/10.1021/es3020056>
- USEPA. (2023). *Peru Creek 3062_Subscription.mdb database*. U.S. Environmental Protection Agency. Retrieved from https://response.epa.gov/site/doc_list.aspx?site_id=8722
- Valenzuela-Díaz, M. J., Navarrete-Calvo, A., Caraballo, M. A., McPhee, J., Garcia, A., Correa-Burrows, J. P., & Navarro-Valdivia, L. (2020). Hydrogeochemical and environmental water quality standards in the overlap between high mountainous natural protected areas and copper mining activities (Mapocho river upper basin, Santiago, Chile). *Journal of Hydrology*, *588*, 125063. <https://doi.org/10.1016/j.jhydrol.2020.125063>
- Verplanck, P. L., Nordstrom, D. K., Bove, D. J., Plumlee, G. S., & Runkel, R. L. (2009). Naturally acidic surface and ground waters draining porphyry-related mineralized areas of the Southern Rocky Mountains, Colorado and New Mexico. *Applied Geochemistry*, *24*(2), 255–267. <https://doi.org/10.1016/j.apgeochem.2008.11.014>
- Viviroli, D., Dürr, H. H., Messerli, B., Meybeck, M., & Weingartner, R. (2007). Mountains of the world, water towers for humanity: Typology, mapping, and global significance. *Water Resources Research*, *43*(7), W07447. <https://doi.org/10.1029/2006WR005653>
- Viviroli, D., & Weingartner, R. (2004). The hydrological significance of mountains: From regional to global scale. *Hydrology and Earth System Sciences*, *8*(6), 1016–1029. <https://doi.org/10.5194/hess-8-1017-2004>
- Williams, A. P., Cook, E. R., Smerdon, J. E., Cook, B. I., Abatzoglou, J. T., Bolles, K., et al. (2020). Large contribution from anthropogenic warming to an emerging North American megadrought. *Science*, *368*(6488), 314–318. <https://doi.org/10.1126/science.aaz9600>
- Winnick, M. J., Carroll, R. W. H., Williams, K. H., Maxwell, R. M., Dong, W., & Maher, K. (2017). Snowmelt controls on concentration-discharge relationships and the balance of oxidative and acid-base weathering fluxes in an alpine catchment, East River, Colorado. *Water Resources Research*, *53*(3), 2507–2523. <https://doi.org/10.1002/2016WR019724>
- Zaharescu, D. G., Hooda, P. S., Burghilea, C. I., Polyakov, V., & Palanca-Soler, A. (2016). Climate change enhances the mobilisation of naturally occurring metals in high altitude environments. *The Science of the Total Environment*, *560–561*, 73–81. <https://doi.org/10.1016/j.scitotenv.2016.04.002>
- Zarroca, M., Roqué, C., Linares, R., Salminci, J. G., & Gutiérrez, F. (2021). Natural acid rock drainage in alpine catchments: A side effect of climate warming. *The Science of the Total Environment*, *778*, 146070. <https://doi.org/10.1016/j.scitotenv.2021.146070>