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Evidence for accelerated weathering and sulfate export in high alpine environments

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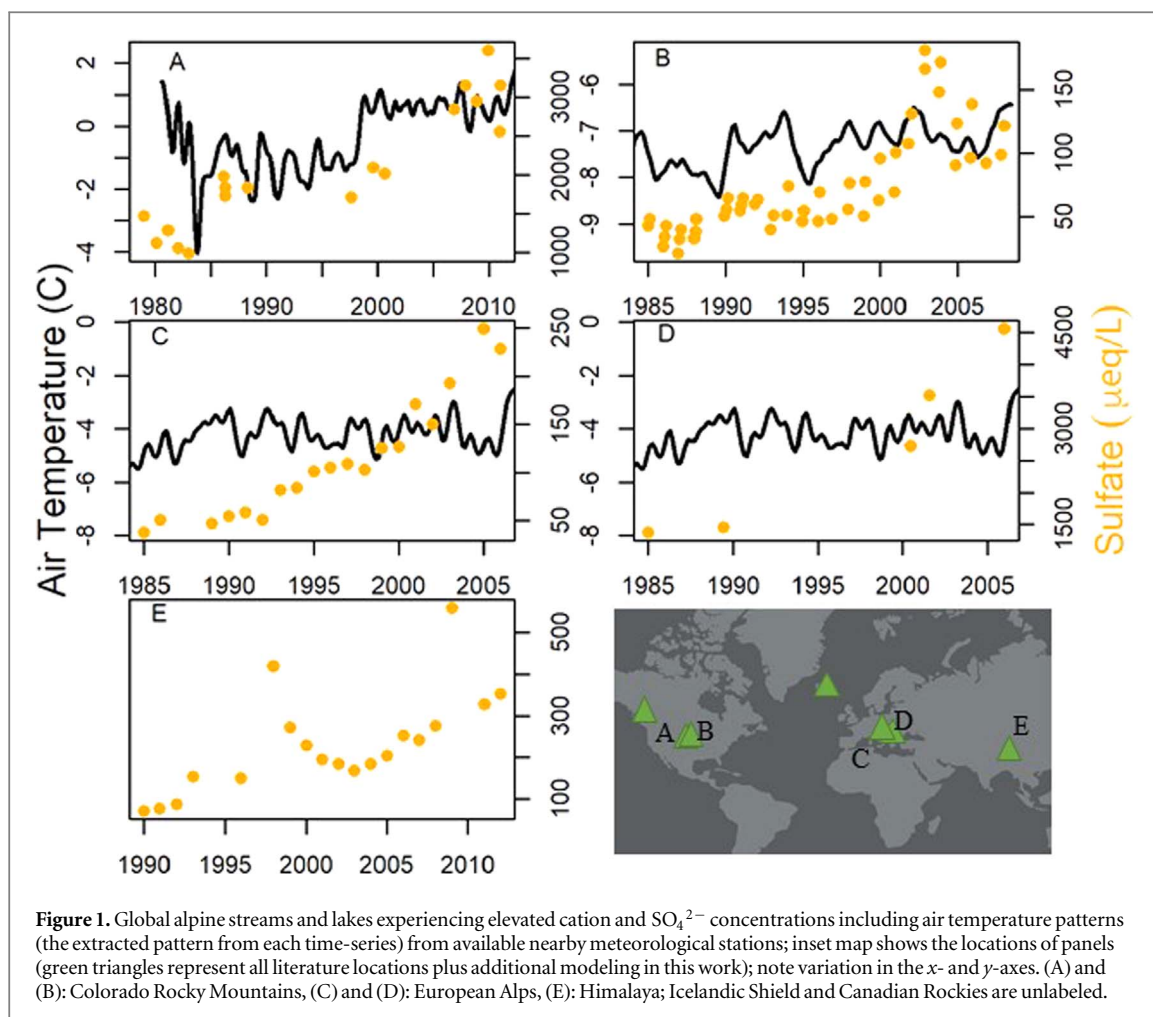
Abstract

High elevation alpine ecosystems—the 'water towers of the world'—provide water for human populations around the globe. Active geomorphic features such as glaciers and permafrost leave alpine ecosystems susceptible to changes in climate which could also lead to changing biogeochemistry and water quality. Here, we synthesize recent changes in high-elevation stream chemistry from multiple sites that demonstrate a consistent and widespread pattern of increasing sulfate and base cation concentrations or fluxes. This trend has occurred over the past 30 years and is consistent across multiple sites in the Rocky Mountains of the United States, western Canada, the European Alps, the Icelandic Shield, and the Himalayas in Asia. To better understand these recent changes and to examine the potential causes of increased sulfur and base cation concentrations in surface waters, we present a synthesis of global records as well as a high resolution 33 year record of atmospheric deposition and river export data from a long-term ecological research site in Colorado, USA. We evaluate which factors may be driving global shifts in stream chemistry including atmospheric deposition trends and broad climatic patterns. Our analysis suggests that recent changes in climate may be stimulating changes to hydrology and/or geomorphic processes, which in turn lead to accelerated weathering of bedrock. This cascade of effects has broad implications for the chemistry and quality of important surface water resources.

Introduction

Mountain snow and ice supply approximately one third of global discharge to the ocean (Meybeck *et al* 2001), and provide freshwater to a large portion of the world's population (Viviroli *et al* 2007, 2011), especially in arid and semi-arid regions. The importance of mountains as water resources comes from the high-quality nature of water generated in alpine basins and because of the role of mountains as 'water towers' that supply domestic and agricultural use during dry seasons at lower elevations. Physical processes that occur in mountains are also important controls on river chemistry and sediment fluxes. High elevation regions dominate the global processes of sediment erosion and mineral weathering (Bluth and Kump 1994, Kirchner *et al* 2001). The chemical weathering of mountainous regions is a key control on river chemistry and alkalinity and therefore a vital contemporary control on the baseline water chemistry of downstream river networks (Meybeck 1987, Drever 1997).

Over the past two decades, a number of studies have noted increasing sulfate (SO_4^{2-}) and/or base cation (Ca^{2+}, Mg^{2+}) concentrations in high elevation lakes and streams on several continents (Sommaruga-Wögrath *et al* 1997, Thies *et al* 2007, Gislason *et al* 2009, Todd *et al* 2012). These studies often include a limited number of measurements made at particular points in time, but taken as a whole, this body of literature indicates that increased base cation and SO_4^{2-} concentrations are relatively common. We identify that such patterns have been observed in the literature in at least 94 different alpine streams and lakes around the globe (figure 1; also see table S1 which is available online at stacks.iop.org/ERL/14/124092/mmedia). Trends in stream/lake concentrations were between

Figure 1. Global alpine streams and lakes experiencing elevated cation and SO_4^{2-} concentrations including air temperature patterns (the extracted pattern from each time-series) from available nearby meteorological stations; inset map shows the locations of panels (green triangles represent all literature locations plus additional modeling in this work); note variation in the *x*- and *y*-axes. (A) and (B): Colorado Rocky Mountains, (C) and (D): European Alps, (E): Himalaya; Icelandic Shield and Canadian Rockies are unlabeled.

0.87 and 222 μeq l^{-1} yr^{-1} for SO_4^{2-}, and between 0.90 and 140 μeq l^{-1} yr^{-1} for base cations (Ca^{2+} and/or Mg^{2+}). Importantly, these records come from multiple continents and mountain ranges, including the Alps, Himalayas, Rockies, and the Icelandic Shield. Measurement locations are all at high elevations and/or high relief, contain metamorphic bedrock (excluding Iceland), have known periglacial or glacial conditions, and have experienced limited human disturbance to catchments.

There is some additional evidence of increasing SO_4^{2-} and/or cation increases in other cold regions, a phenomenon that has not been fully explored. For example, increasing cation and SO_4^{2-} flux has been observed for small and very large watersheds with varying levels of permafrost in Alaska's Yukon River Basin (Petrone *et al* 2006, Toohey *et al* 2016). These increasing trends have been attributed to changes in hydrology and increases in mineral weathering and sulfide oxidation (Toohey *et al* 2016). We also found trends of increasing SO_4^{2-} fluxes in a set of glaciated mountain catchments in British Columbia, Canada that are representative of the Canadian Rockies and the Coast Mountains (figures S2–S4). While these larger, soil-mantled catchments do not exclusively represent conditions in alpine environments, the increasing

mass flux is clearly in line with the broader global patterns.

The consistency of these patterns suggests the possibility of a broad global scale change in mountain systems. At present, only a few global phenomenon are plausible. They include: increasing atmospheric deposition of SO_4^{2-} and cations (direct mechanisms), or elevated carbon dioxide in the atmosphere, or global temperature increases and or changes in temperature patterns at high elevations (both being potential indirect mechanisms). In most cases, atmospheric deposition of SO_4^{2-} is declining in these systems and base cation deposition shows relatively little directional change in many locations (Tessier *et al* 2002, Lehmann *et al* 2005, Tørseth *et al* 2012); and we revisit this hypothesis later in the text. Elevated carbon dioxide is likely to enhance mineral weathering due to the 'acid attack' of carbonic acid upon minerals. However, carbon dioxide is not involved in the reactions likely responsible for SO_4^{2-} production (equation (1)). Further, the timescale for a weathering response to increasing CO_2 in the atmosphere is on the order of hundreds of years (Colbourn *et al* 2015). Climate change is left as the most likely global driver that could lead to a synchronous increase in cations and SO_4^{2-} in alpine environments, as has been suggested

throughout the literature. The climate effect might work via more rapid weathering rates (kinetics), exposure of highly weatherable materials (thawing of ice and permafrost), or perhaps through both mechanisms

$$15O_2 + 14H_2O + 15FeS_2 = 8H_2SO_4 + 4Fe(OH)_3. \quad (1)$$
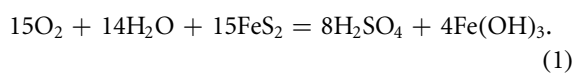
At a global scale, many high altitude regions are warming much faster than adjacent low-lying areas (Wang *et al* 2014). And there is evidence that climate has changed across these geographically diverse alpine sites; we show sites with a combination of rising SO_4^2, base cations, and rising air temperature in figure 1 (also see table S1). In the Alps, for example, the mean annual air temperature increased by more than 1 °C since 1980 up to the publication date (Thies *et al* 2007). Warming trends were also documented in the Rockies where mean annual and mean summer air temperatures have increased by 0.2 °C−1.2 °C per decade beginning in the 1980s (Todd *et al* 2012). In other regions such as the Himalaya (Salerno *et al* 2016), and in our study site in Colorado, the loss of glaciers and permafrost (Leopold *et al* 2015) are indirect evidence of a changing climate. However, alpine air temperatures can also show more complex patterns relative to the steady increases documented in the literature. In the high alpine of the Rocky Mountains for example, dampened diurnal air temperature ranges and teleconnections to atmospheric circulation patterns represented by the North Pacific Index and the El Niño-Southern Oscillation can lead to more complex temperature signals that are non-monotonic (Kittel *et al* 2009). Although there are well understood geologic time scale feedbacks between climate, mountain uplift, and mineral weathering (Gaillardet *et al* 1999, West *et al* 2005, Gislason *et al* 2009, Maher and Chamberlain 2014), relatively little is known about how climate might alter contemporary weathering or element release. However, it is clear that alpine and other high elevation/high latitude ecosystems are rapidly losing glacial and periglacial features and permafrost is thawing (Haeberli *et al* 1993, Paul *et al* 2004, Gruber and Haeberli 2007, Jones *et al* 2019), which has significant implications for changing both the hydrologic regime and biogeochemical cycling in these systems.

To investigate the emerging global pattern of elevated base cation and SO_4^{2-} concentrations in high elevation freshwater systems, we examined a long-term dataset from the Niwot Ridge Long Term Ecological Research Site located in Colorado, USA. This location was selected because of its high-resolution chemical and hydrologic sampling that extends back to 1984. We used a combination of mass balance and isotopic data, as well as findings from previous investigations, to determine the likely cause of elevated SO_4^{2-} and base cation flux from this alpine ecosystem.
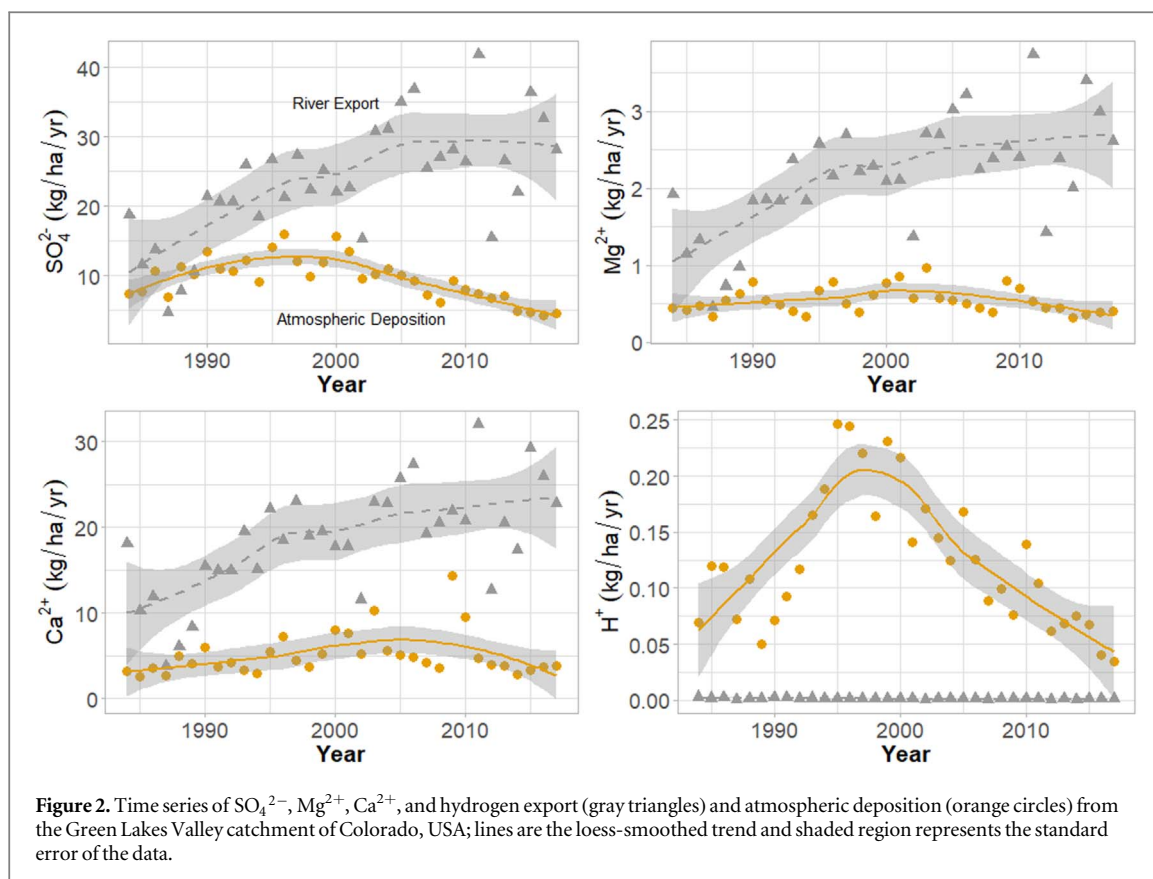
Methods

We calculated mass balance budgets for SO_4^{2-}, Ca^{2+}, Mg^{2+}, and other constituents for the Green Lakes Valley catchment in Colorado, USA using long-term records of atmospheric deposition, water chemistry, and stream flow. The outlet of the Green Lakes Valley corresponds to the Albion site described in the supplementary material (watershed area = 7.1 km²). Water chemistry (Caine 2018) and stream flow data (Caine 1993), as well as climatological data were retrieved from the Niwot Ridge Long Term Ecological Research site data page (http://niwot.colorado.edu/data). Climate data are presented from an alpine monitoring location (D1) and a sub-alpine station (C1).

To estimate monthly flux of chemical constituents from the watershed, we used the Weighted Regressions on Time, Discharge, and Season (WRTDS) model (Hirsch *et al* 2010) contained within the EGRET package for the statistical programming language R (R Core Team 2018). WRTDS was chosen for stream flux modeling specifically because of its capabilities for decadal water quality data, which include: an ability to detect changes in concentration and flux; relationships between concentration, discharge, and season are allowed to change over time; the model produces a time-series of both actual fluxes and fluxes where the effect of inter-annual flow variability has been removed, known as the flow-normalized flux. The flow-normalized flux can be used to infer changes in the watershed that have an impact on stream chemistry that are independent of the variability in stream flow. The flow-normalized flux does not include the random variability driven by the random variability in discharge (see supplementary material '*Flow Normalized Trends in Chemical Flux*'). Confidence intervals for the change in flow-normalized flux, as well as likelihood estimates of flux trends were calculated using the block bootstrap procedures (Hirsch *et al* 2015) built for WRTDS in the R package EGRETci.

Rates of wet atmospheric deposition of SO_4^{2-}, Ca^{2+}, Mg^{2+}, and H^+ were retrieved from the National Atmospheric Deposition Program (NADP) monitoring site to the north of the stream outlet (NTN Site C002). Dry deposition was not measured at the NADP site, therefore we applied a constant dry deposition rate to all years using recent estimates made near the NADP sample collector (Oldani *et al* 2017).

We analyzed average daily air temperatures, and calculated degree days (sum of average daily temperatures) at a monthly time step for all months using a long-term climate record from the alpine meteorological station in the watershed (D1 site, 3743 m.a.s.l.). We also present de-trended mean air temperatures for D1 and a nearby sub-alpine climate station (C1, 3018 m.a.s.l.). We assessed the relationship between monthly degree days at D1 and flow-normalized flux from the Green Lakes Valley in seasonal

Figure 2. Time series of SO_4^{2-}, Mg^{2+}, Ca^{2+}, and hydrogen export (gray triangles) and atmospheric deposition (orange circles) from the Green Lakes Valley catchment of Colorado, USA; lines are the loess-smoothed trend and shaded region represents the standard error of the data.

bins (April–June, July–September, October–December, January–March) with linear regression using the statistical programming language R.

A survey of $\delta^{34}S$ of dissolved SO_4^{2-} at Green Lakes Valley was completed during summer 2018. Water samples of $\delta^{34}S$ were taken from seeps, snowmelt and groundwaters flowing below and around the rock glacier adjacent to Green Lake 5 ($n = 10$). $BaCl_2 \cdot 2H_2O$ was added to 100 ml solution to induce SO_4^{2-} precipitation from these low-concentration waters. The ^{34}S analyses were done by isotope ratio mass spectrometry at the University of California, Santa Cruz (see supplementary material '*Water Chemistry Sampling*').

Results
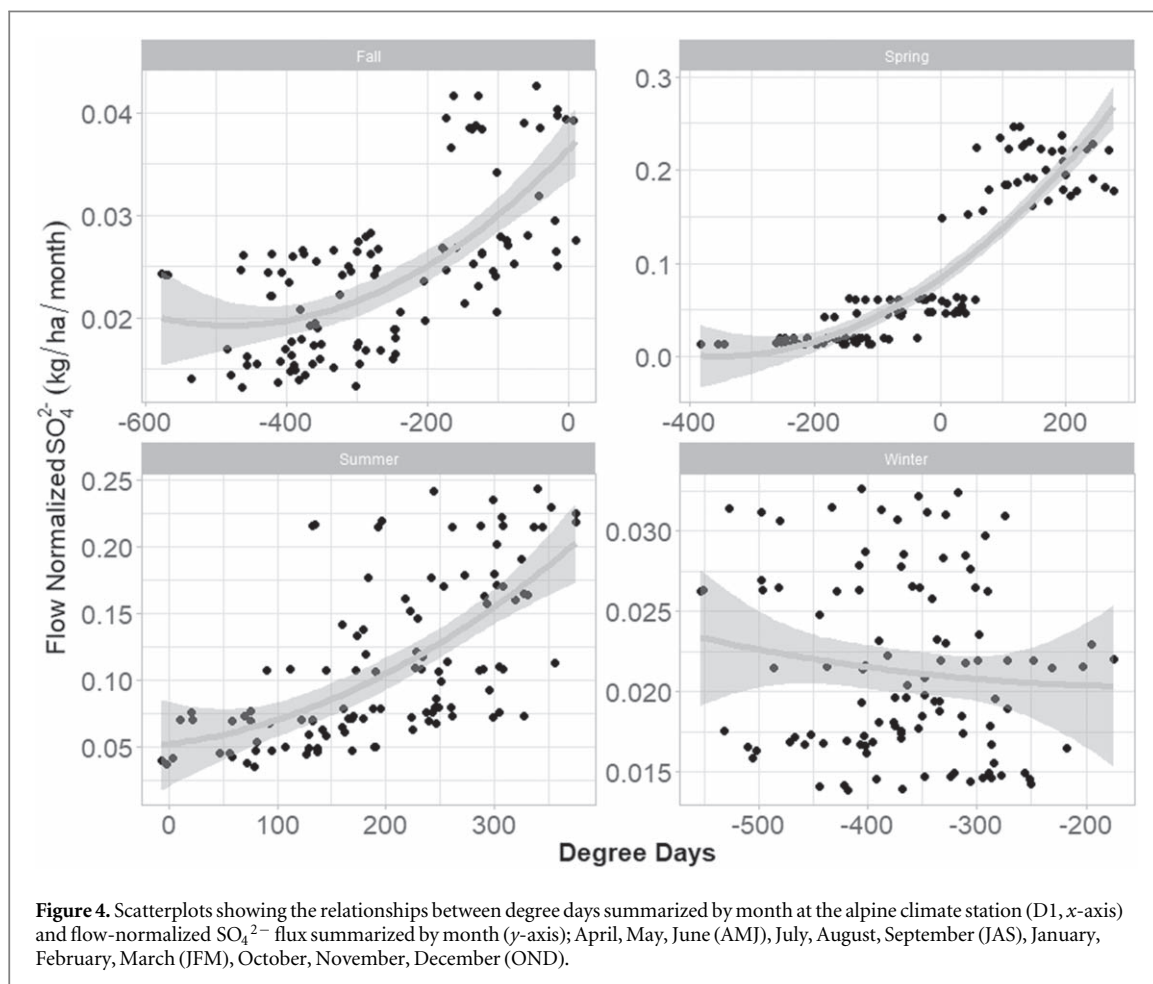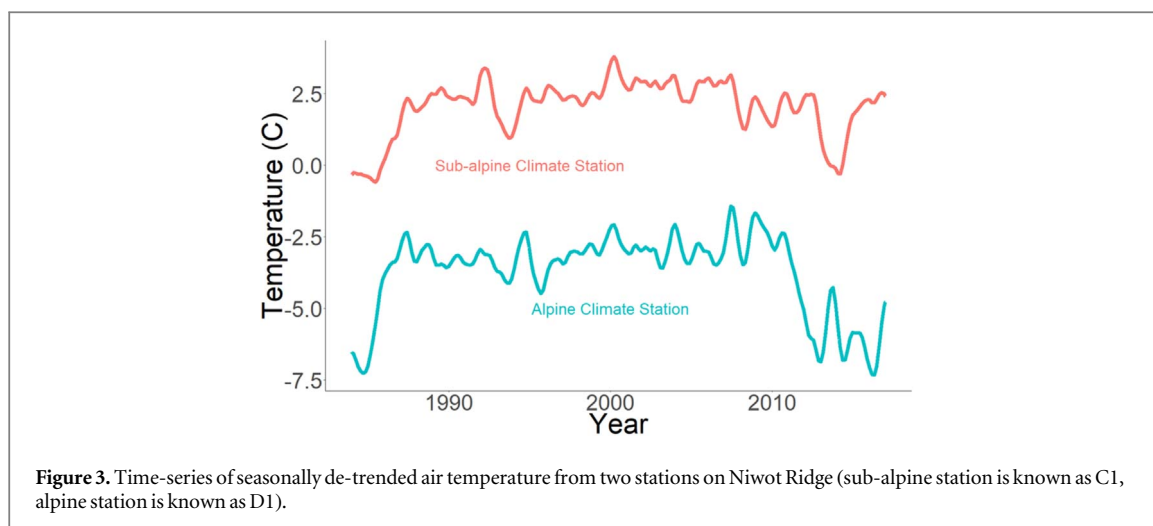
Modeling of SO_4^{2-} and cation flux using water chemistry and stream flow data from the Green Lakes Valley catchment, a remote and undisturbed alpine watershed within the Niwot Ridge study area, revealed robust changes in the mass of elements leaving the watershed over a 33 year period (figure 2). The increases in stream export were the result of increased concentrations at all water flows and over all seasons after controlling for variation in stream flow (figures S7–S9). In this watershed, SO_4^{2-} fluxes increased by over 200% between 1984 and 2015 while Mg^{2+} and Ca^{2+} fluxes approximately doubled over the same time period. These large increases were not simply due to chance, as the likelihood that flow-normalized SO_4^{2-}, Ca^{2+}, and

Mg^{2+} flux was upward trending equaled 0.988 for all constituents. Silica fluxes (figure S10) also showed an upward trend (likelihood = 0.762), but the magnitude of the increase (34%) was lower than other weathering products such as Ca^{2+}. The lower silica fluxes are consistent with precipitation of secondary Si minerals as proposed by Williams *et al* (2006).

Warm periods were evident at Niwot Ridge for both the alpine climate station (D1) and the sub-alpine climate station (C1) records (figure 3). At the sub-alpine climate station, a warm period began in approximately 1984, increasing nearly 3 °C by 2009, and then slightly decreasing by 2017. Mean annual temperatures at the sub-alpine site have consistently been above the 0 °C threshold for the study period. Mean annual temperatures at the highest elevations were still below 0 °C for the period of record, but warming of nearly 5 °C occurred between 1984 and 2010. Air temperatures at D1 decreased from 2010 onward. When aggregated at a monthly time step, average temperatures have increased over time in specific months. For example, July and September trends at the alpine station were significant as assessed with the Mann-Kendall test (*p*-values of 0.01 and 0.05, respectively).

Watershed SO_4^{2-} and cation export increased (figure 2) during a period of increased air temperatures in the Green Lakes Valley (figure 3). The long-term extent of the Green Lakes Valley stream measurements combined with nearby, high-quality meteorological data allow us to further explore the link between

Figure 3. Time-series of seasonally de-trended air temperature from two stations on Niwot Ridge (sub-alpine station is known as C1, alpine station is known as D1).

Figure 4. Scatterplots showing the relationships between degree days summarized by month at the alpine climate station (D1, *x*-axis) and flow-normalized SO_4^{2-} flux summarized by month (*y*-axis); April, May, June (AMJ), July, August, September (JAS), January, February, March (JFM), October, November, December (OND).

air temperature, SO_4^{2-}, and base cation fluxes. An analysis of the monthly sum of average daily air temperature (degree days) versus flow-normalized SO_4^{2-} flux shows a very strong relationship for Spring, Summer, and Fall seasons, but not for the winter season (figure 4). This pattern of increased fluxes with increasing air temperatures is also the case for base cation flux (figures S11, S12). Importantly, the

flow-normalized flux removes inter-annual variation in discharge. The air temperature and flux trends at Niwot are both non-monotonic (figure 3). For example, during the recent cooling phase after 2010, the ion fluxes also decreased, which suggests that ionic flux may respond to both increasing and decreasing air temperatures. Meanwhile, CO_2 in the atmosphere has risen unabated (see http://scrippsco2.ucsd.edu/).

Discussion

Potential mechanisms for increased SO_4^{2-} and base cation fluxes

The strong relationship between degree days and stream chemistry fluxes at Green Lakes Valley (and similar types of relationships elsewhere) suggests that elevated air temperatures are related to increases in stream chemical export but shed little light on the reasons why. There are several proximal mechanisms that could be responsible for elevated SO_4^{2-} as well as base cation flux in response to the distal cause (warming) at Niwot Ridge. These include: (1) increased decomposition of organic matter, (2) desorption of ions from soils and mineral sites, (3) ion release from glacier and ice storage, and (4) increased weathering of silicate and sulfide minerals. Additionally, there are also two direct mechanisms that could lead to elevated ion flux as presented earlier: increased atmospheric deposition of SO_4^{2-} and base cations, or CO_2 induced weathering increases of silicate minerals. All of these mechanisms will operate on different timescales.

At Green Lakes Valley, there is evidence available to refute some of these alternative hypotheses and there is growing support for a weathering source of ions. In principle, atmospheric deposition of SO_4^{2-} and cations could increase the watershed flux from both wet (precipitation) and dry deposition (e.g. dust) sources. However, watershed mass balance calculations of SO_4^{2-}, Mg^{2+}, Ca^{2+}, and hydrogen ions indicate that atmospheric deposition (wet plus dry sources) cannot account for the increases in flux from Green Lakes Valley (figure 2). The same result has been found for some of the other global sites (Thies *et al* 2007, Mast *et al* 2011), and is aligned with patterns observed in much of the temperate Eastern US and Europe where atmospheric nutrient and ion deposition has strongly decreased as a result of emissions controls (Dillon *et al* 2003, Mitchell *et al* 2011). To balance the riverine flux of SO_4^{2-} from the Green Lakes Valley would require approximately six years of cumulative atmospheric deposition at current rates, or approximately 10 years of pre-industrial emissions (assuming a 1 kg S/ha/yr deposition flux).

Rising temperatures should increase rates of organic matter decomposition in alpine watersheds, which could lead to increased SO_4^{2-} and base cation concentrations in streams if these elements (S, Ca, Mg) are bound to organic matter. If this were the case at Niwot Ridge, we would expect a cascade of changes in the system including the release of dissolved organic carbon (DOC) and higher ecosystem respiration rates from terrestrial sites. At Green Lakes Valley, we do not see broad scale evidence for increased decomposition. Over the 33 year period of record at Green Lakes Valley, DOC flux has actually decreased (figure S19), but other recent work suggests some increases in alpine

decomposition (Knowles *et al* 2019), showing mixed evidence of changing decomposition.

Desorption of SO_4^{2-} stored on mineral and soil exchange sites could result in hydrologic flux from the catchment (e.g. Sharpley 1990). Sulfate desorption would be most likely caused (on these timescales) by the displacement of SO_4^{2-} on ion exchange sites by another ion with more favorable adsorptive characteristics and/or higher concentrations. There is no evidence for anion concentration increase in deposition to Green Lakes Valley, where precipitation SO_4^{2-} and NO_3^- concentrations are actually decreasing over this time period. Melting ice has also been suggested as a source of increasing ion flux (Caine 2010), but information on the mass of ice reservoirs, and their potential concentrations of ions are essentially unknown. Finally, the chemical reactions likely responsible for elevated SO_4^{2-} flux (equation (1)) do not involve CO_2, and a mechanism linking both cation and SO_4^{2-} increases has not been elaborated. Furthermore, precipitation pH, surface water pH and alkalinity have all increased in the Green Lakes Valley, which does not support increasing acidity as a result of rising atmospheric CO_2.

Sulfide weathering

Enhanced mineral weathering has been noted as a potential cause of increased SO_4^{2-} and base cation concentrations in other alpine sites (Gislason *et al* 2009, Todd *et al* 2012). Sulfide minerals are present in many alpine catchments and these minerals also have high reactivity relative to silicates (Torres *et al* 2017). Sulfide minerals are known to occur in the Green Lakes Valley (see supplementary material '*Evidence of Sulfide Minerals*'), and in many of the sites shown in figure 1. Our review of the literature indicates that sulfide weathering occurs in many other alpine regions across the globe (see Darmody *et al* 2007, Szynkiewicz *et al* 2013, Salerno *et al* 2016). These general patterns of sulfide reactivity in alpine systems, combined with widespread occurrence of sulfide minerals (Craig and Vokes 1993, Vaughn 2013), illustrate the potential for enhanced weathering to drive elevated SO_4^{2-} and cation flux in high elevation systems. But the presence of sulfides alone is not enough evidence to support a weathering source of SO_4^{2-}.

At Green Lakes Valley, we carried out a small survey of $\delta^{34}S$ of dissolved SO_4^{2-} in stream water during summer 2018 to determine whether sulfide minerals were a probable source of SO_4^{2-} to surface waters. The $\delta^{34}S$ isotopic signature of SO_4^{2-} has been widely used to discern the contribution of sulfide oxidation to river SO_4^{2-} flux (Torres *et al* 2016; Burke *et al* 2018; Calmels *et al* 2007) as geologic S typically has much more negative ratios relative to atmospheric and biological sources. In the Green Lakes Valley, results show average surface water $\delta^{34}S$ of dissolved SO_4^{2-} values of $-2.13‰$ (range -4.28 to $-0.37‰$), which were within the range of expected

geologic sulfide values in Colorado (-1.7 to $-5.0‰$; Mast *et al* 2011), and much more depleted relative to atmospheric sources measured in alpine snowpacks throughout the mountain range ($+4.0$ to $+8.2‰$; Mast *et al* 2001). Additionally, inverse geochemical modeling —which offers a window into the reactions occurring in the subsurface—of water discharging from a rock glacier in the Green Lakes Valley suggested weathering of pyrite and potential release of base cations from associated weathering of silicate minerals (Williams *et al* 2006). Thus, the combination of mass balance calculations, isotopic tracing, and chemical modeling all point to sulfide weathering as a likely source of SO_4^{2-} to surface waters. But what might connect air temperatures to enhanced sulfide weathering?

Weathering of pyrite (a common sulfide) is thought to be limited, in part, by temperature. However, the temperature dependency at near-freezing conditions may be fairly small (see Todd *et al* 2012). Additional rate limiting mechanisms include exposure of fresh mineral surfaces (Das *et al* 2012, Ross *et al* 2018), the availability of water and oxygen, as well as a number of complex microscopic processes (Chandra and Gerson 2010). High erosion rates in glacial and periglacial environments have been shown to enhance pyrite oxidation rates (Calmels *et al* 2007, Darmody *et al* 2007), likely due to the exposure of fresh pyrite surfaces to oxygen and water. In other alpine catchments, rock glaciers appear to be important loci of enhanced SO_4^{2-} and cation flux (Williams *et al* 2006, Thies *et al* 2007, Caine 2010). The spatial patterns of chemical time-series in the Green Lakes Valley (figures S13–S15) only showed SO_4^{2-} increases below the rock glacier near Green Lake 5, but no changes in water downstream of the Arikaree Glacier at the head of the watershed, which suggests that the rock glacier may be an important local source of changing water chemistry.

Our decision to assess the relationship between air temperatures and fluxes follows the recognition that heating (and potential thaw/melt) of rock glaciers, talus, and other high porosity periglacial features can be driven by sensible heat exchange (Grueber and Haeberli 2007; Pruessner *et al* 2018; Mühll and Haeberli 1990), in addition to conductive heat flux. Thus, the accumulation of degree days represents a reasonable metric of potential thawing of the subsurface, as is the likely case for glaciers in the region (Hoffman *et al* 2007). We suggest that thawing of previously ice-filled flow paths allows for increased weathering at fresh mineral surfaces and that the connection to rapidly warming air temperatures is not simply a result of the kinetic limitations of sulfide oxidation. It is also possible that sulfides such as pyrite release protons that subsequently weather silicate minerals, but the connection to elevated cation fluxes is not yet understood.

Conclusion

The results synthesized for high elevation systems across the globe, including additional lines of evidence from the Green Lakes Valley, and larger permafrost regions of Alaska and the Canadian Rockies, suggest that alpine stream chemistry is changing as a result of recent warming-induced changes to bedrock weathering. These patterns suggest broad scale shifts in the geomorphology and biogeochemistry of high elevation watersheds that will lead to changes in stream chemistry. Preliminary work in British Columbia suggests the trends indicated here may also be present in lower elevation watersheds that supply large urban regions. The release of SO_4^{2-} and acidity from weathering of S-bearing minerals or from other physical reservoirs could have adverse effects on water supplies if the resulting decrease in pH is not countered by increasing alkalinity from other sources (such as rising base cation concentrations). Elevated cation concentrations could increase the potential for infrastructure corrosivity (e.g. Stets *et al* 2018), and increased water hardness with impacts on water usability. More generally, these changes are unlikely to be limited to just these dissolved constituents. Weathering reactions release a range of dissolved elements including metals. Although these elements are often not measured, increased metal discharge could lead to toxic loading to aquatic systems, as has been found in Colorado and the Alps (Thies *et al* 2007, Todd *et al* 2012), with potential negative consequences for biota and downstream water users. Such changes will be increasingly important to understand as the climate of alpine systems continues to change.

Data availability statement

The data that support the findings of this study are openly available. Data can be found at the Niwot Ridge LTER data catalog and via the Environmental Data Initiative. Also see the references for direct access to the data.

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