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Decadal trends in solute concentrations, mass flux, and discharge reveal variable hydrologic and geochemical response to climate change in two alpine watersheds

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ABSTRACT

High-alpine environments are particularly sensitive to changes driven by climate change and experience more dramatic shifts in vegetation, snowmelt timing, and the relative ratio of rain to snow compared to other lower-elevation environments. These shifts drive changes in stream discharge and solute concentrations, long-term records of which may be archived in publicly available databases. Here, we use three decades of discharge and water quality data from two alpine watersheds along the Continental Divide in the Rocky Mountains of Colorado, USA, to quantify temporal trends in solute concentration and solute mass flux, which serve as integrators of watershed processes and are used to identify controls on how these watersheds respond to climate change over decadal timescales. By analyzing both solute concentrations and mass flux we are able to remove the effects of seasonal changes in discharge and separate hydrologic and geochemical drivers of changes in solute export from these two watersheds. While we find that concentrations of calcium, bicarbonate, and sulfate increase through time in both watersheds, increasing solute mass flux is found in one watershed but not the other, despite similar watershed characteristics such as elevation, precipitation, average temperature, and bedrock geology. We identify different dominant weathering mechanisms as the cause for the differences in watershed response to climate change. In one watershed, sulfide oxidation was the dominant weathering mechanism at the beginning of the record and stayed dominant through the three-decade period of data. This consistency in weathering mechanism likely controls why the solute flux did not change significantly. In contrast, in the other watershed, solute flux increased and water chemistry shows that the dominant weathering mechanism shifted from dominantly CO_2-driven to more influence from sulfide-oxidation driven weathering. This shift in weathering mechanism is accompanied by significantly increasing solute fluxes. This study demonstrates the importance of quantifying geological weathering in watershed response to climate change where two similar watersheds exhibit different responses–one hydrological and one combined hydrological and geochemical–that could not have been predicted from a simple analysis of the watershed characteristics. Such analyses are needed on a large scale to quantify the type and magnitude of watershed changes in water quality and quantity to climate change, and suggest that weathering mechanisms, in particular weathering driven by oxidation of trace sulfide minerals, plays an important role in the geochemical response of watersheds to climate change.

1. Introduction

High-altitude alpine watersheds are sensitive and reliable indicators of global climate change owing to their remoteness (Catalan et al., 2006) and to the steep climatic and environmental gradients that characterize mountain regions (Moser et al., 2019; Thompson et al., 2005). They are minimally influenced by local-scale anthropogenic changes, such as development or land-use change, which can confound trends in long-term stream chemistry and hydrology driven solely by climate variations (Bertani et al., 2016). Stream chemistry in outflows is mainly driven by weathering of rocks, fluid-flow paths, and vegetation (Camarero et al., 2009). Alpine watersheds thus offer valuable

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Abbreviations: C-Q, concentration discharge; DOC, dissolved organic carbon; LTER, Long Term Ecological Research; WEBB, Water, Energy, and Biogeochemical Budgets; EMMA, End-member mixing analysis.

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opportunities to understand and predict chemical changes in water in response to natural drivers, including climate change.

Systematic evaluation of long-term trends in hydrologic and geochemical data from watersheds can help elucidate how watersheds respond to changes in climate over decadal timescales and provide insight into watershed sensitivity to climate change. Climate change results in shifts in timing and type of precipitation and, in alpine systems in particular, increases in air temperature (Daly et al., 2010; Lukas et al., 2008). As precipitation patterns change and air temperature increases, the timing and amplitude of freeze-and-thaw cycles changes (Lipson et al., 2000; Monson et al., 2006; Schimel and Clein, 1996), melting of glaciers and permafrost increases (Gruber and Haeberli, 2007; Haeberli et al., 1993; Jones et al., 2019; Paul et al., 2004), snow melt and timing of peak discharge occurs earlier in the year (Clow, 2010), and vegetation responds to warmer soils and longer growing seasons (Richardson et al., 2018). Combined, these effects lead to altered fluid flow paths (Hill, 2008; Manning et al., 2008), increased mechanical weathering (Harrison et al., 2019; Mast et al., 1990; Meyer et al., 2009), and changes in groundwater stores through time (Leopold et al., 2015; Luce, 2018; Luce et al., 2014; Luce and Holden, 2009).

These changes in the hydrologic cycle propagate to changes in geochemical processes. Rock weathering, driven by infiltration of dilute fluids from the surface, can respond to changes in the amount and timing of precipitation with climate change. As the amount of water that infiltrates into the sub-surface and the residence time of that water changes, where and how fast mineral reactions produce solutes will also change (e.g. Maher and Chamberlain, 2014). When groundwater elevation lowers in response to decreased infiltration and recharge, primary bedrock minerals can be exposed to dilute infiltrating fluids, enhancing mineral weathering. In the case of bedrock that contains sulfide minerals, like pyrite, this effect can be pronounced because oxygenated waters drive oxidation of the pyrite above the water table (Todd et al., 2012; Manning et al., 2013; Winnick et al., 2017). Additionally, increasing temperature with climate change has several indirect effects on rates of chemical weathering and riverine solute export. This includes factors such as melting of glaciers resulting in solute flux increases due to the export of previously stored solutes (Gislason et al., 2009) and the biological production and development of soils on previously glaciated terrains over longer time scales, which promote weathering and solute export. Crawford et al. (2019) compiled a list of studies that documented geochemical changes at shorter, more contemporary, time scales within 94 alpine streams and lakes across the globe. Interestingly, within some of the regional studies (e.g., Mast et al., 2011) some watersheds exhibited trends in geochemical observations while others did not.

Concentration-discharge (C-Q) relationships integrate information on the interactions between hydrologic processes and solute generation across a watershed and have been used extensively to categorize the transport dynamics of different solutes within watersheds. Briefly, C-Q relationships are most simply defined as dilution, where solute concentrations decrease with increasing discharge; flushing, where solute concentrations increase with increasing discharge; or chemostasis, where solute concentrations do not change with discharge (Godsey et al., 2009; Winnick et al., 2017). Dilution has been attributed to groundwater concentrations that are diluted by rain or melt water at high discharge (Li et al., 2017; Miller et al., 2016), short residence times and thus limited time for mineral dissolution (Chanat et al., 2002), and rapid depletion of stored solutes (Herndon et al., 2015; Hoagland et al., 2017). Flushing has been attributed to rising water tables tapping abundant near-surface solute supplies and increased hydrological connectivity between uplands and streams under high-flow conditions (Herndon et al., 2015; Pacific et al., 2010; Seibert et al., 2009; Winterdahl et al., 2014). Chemostasis implies chemical weathering rates and solute fluxes that do change with discharge (Godsey et al., 2009; Hornberger et al., 2001; Scanlon et al., 2001) and has been attributed to hydrologically responsive mineral dissolution rates over short-time scales (Li et al., 2017), buffering capacity of ion-exchange reactions (Clow and Mast, 2010), and pore waters approaching equilibrium as residence time increases (Ameli et al., 2017; Maher, 2011). Overall, stream water is a mix of many stores, including shallow, near-surface water, deeper groundwater, and precipitation or melting snowpack. C-Q relationships of solutes from watersheds can therefore be used to quantify the balance of these sources. During wetter periods of high discharge, from frequent storm events or melting snowpack, higher dissolved organic carbon (DOC) and solute exports suggest shallow soil water as a major source and key driver of solute concentration in streams (Boyer et al., 1997; Pacific et al., 2010; Seibert et al., 2009). During drier times, groundwater dominance in streams can bring a high level of geogenic solutes from depth (Kim et al., 2014).

In addition to C-Q relationships, which reveal transport controls within watersheds, solute mass flux out of a watershed conveys information regarding geochemical weathering controls within watersheds (Creasey et al., 1986). Analysis of a watershed's solute mass flux is needed for interpreting changes in total solute inputs and geochemical processing (i.e., weathering processes) through time but is largely absent from C-Q and climate-change impact studies. An increase in solute concentration might appear to be driven by increased solute production; however, it can be caused solely by a decrease in discharge with no change in the total mass produced through geochemical processes. In this case, changing hydrology is responsible for the change in solute concentrations with no change to geochemical processes. Recently, Arora et al. (2020) investigated differential C-Q relationships along a reach of river to better understand solute behavior between upstream and downstream sites. The differential C-Q approach captures the difference in concentration in a river segment over the difference in discharge, thereby accounting for gains, losses, or fractional solute turnover between sampling stations, and quantifying changes in mass flux. However, this analysis can only be applied where there are multiple sampling locations for both discharge and water chemistry along a stream reach. A mass flux analysis removes the component of changing discharge driven by seasonal or long-term hydrologic changes and allows for isolation of changes in geochemical processes.

This study quantifies temporal trends in discharge and stream chemistry from two comparable alpine watersheds (e.g., geology, climate, area, vegetation, aspect, and elevation) in the Rocky Mountains of Colorado, USA, to identify changing hydrological and geochemical behavior over a period of increasing average temperatures and changes in precipitation patterns related to climate change (Daly et al., 2010; Lukas et al., 2008) and identify reasons for those changes. We analyzed datasets collected in the Green Lakes Valley (Albion Creek) from the Niwot Ridge Long Term Ecological Research (LTER) Site and Andrews Watershed (Andrews Creek), part of the Water, Energy, and Biogeochemical Budgets (WEBB) program. They are located 28 km apart, both at an elevation >3200 m along the U.S. Continental Divide (Fig. 1). These locations were selected because of the availability of chemical and hydrologic monitoring data as early as 1993 and because of similarities in characteristics as noted above. Similar location and elevation should lead to similar precipitation and temperatures, similar geology and area should result in similar amount and type of solutes, and similar vegetation should lead to similar cycling of nutrients and solutes. Similar geomorphology is present at both sites, including the presence of talus slopes, permafrost, and steep cliffs. Data were analyzed using a combination of instantaneous solute C-Q and mass flux-discharge relationships along with statistical temporal-trend analysis (seasonal Mann-Kendall tests) to assess temporal variability in hydrogeochemical behavior for each of these two sites. This approach allows for separation of hydrologic and geochemical changes through time, an important step in identifying processes that drive long-term behavior of headwater catchments and sensitivity of alpine watersheds to long-term shifts in climate. This research tests the hypothesis that these two alpine watersheds would behave similarly through time, with increases in solute concentrations and instantaneous mass flux (simply referred to mass flux

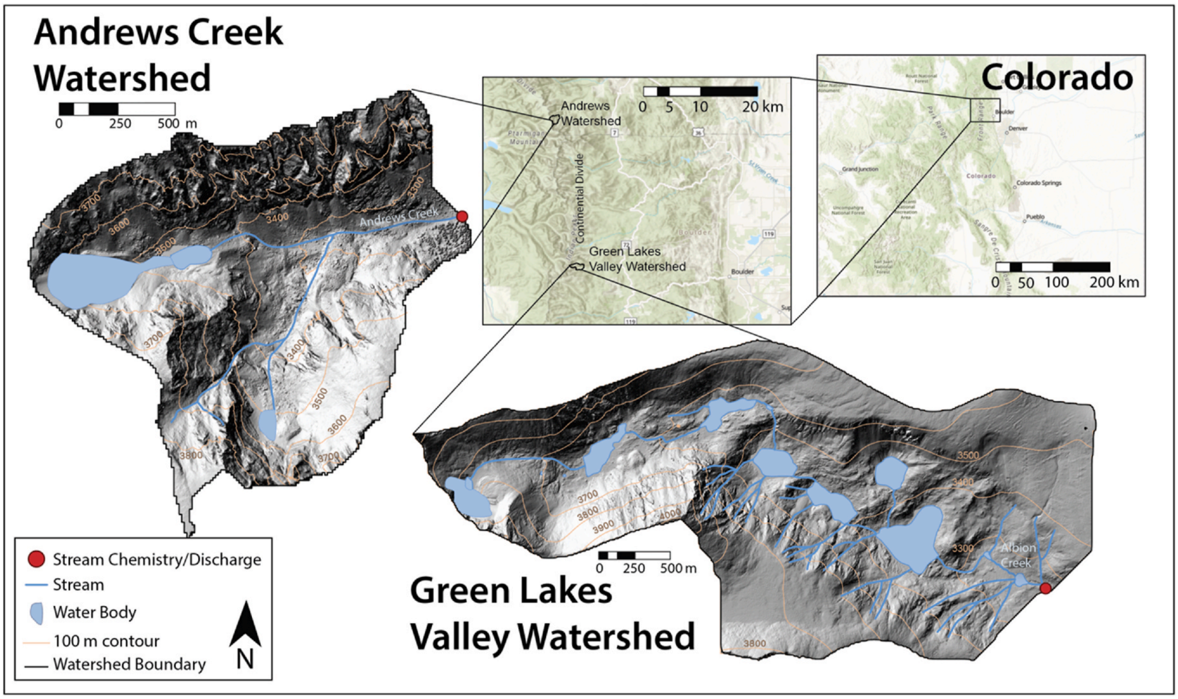

Fig. 1. Map of the Andrews and Green Lakes watersheds with Colorado inset map. Surface hydrology is from the U.S. Geological Survey National Hydrography Dataset (USGS, NHD, 2021a, 2021b) and LiDAR was downloaded from OpenTopography (Anderson, 2013; USGS LPC, 2014). Watersheds were delineated with StreamStats (Ries et al., 2017). The outlet sampling site of Green Lake Valley is Albion Creek. (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

here), given the two watersheds' analogous characteristics and the expected increase in weathering through time driven by climate change. This approach allows for separation of hydrologic and geochemical changes through time, an important step in identifying processes that drive long-term behavior of headwater catchments and sensitivity of alpine watersheds to long-term shifts in climate. The analysis is limited to instantaneous concentration and instantaneous mass flux to avoid extrapolation-induced uncertainty in both measures. Both instantaneous concentration and mass flux are indicators of long-term change but are not used here to evaluate changes in annual mass flux from these watersheds.

2. Site descriptions

2.1. Location and climate

Albion Creek (40.05°N, 105.59°W), the outlet of Green Lakes Valley watershed (7.1 km^2), and Andrews Creek (40.29°N, 105.68°W), the outlet of Andrews watershed (1.6 km^2), are east-facing glacial valleys that are located along the Continental Divide in Colorado, USA (Fig. 1). Albion Creek is 28 km south of Andrews Creek. At Green Lakes Valley, the elevation ranges from 4084 m at the Continental Divide to 3298 m at the outlet (Albion Creek), while at Andrews watershed the elevation ranges from 3910 m at the Continental Divide and 3219 m at the outlet (Andrews Creek). Both watersheds are topped by glaciers: the 8-ha Arikaree Glacier of Green Lakes Valley and the 10-ha Andrews Glacier of Andrews watershed. Estimated mean annual temperature of the Andrews watershed is 0.5 °C (Clow et al., 2003), with 65%–85% of precipitation falling as snow (Clow and Mast, 2010), while at Green Lakes Valley mean annual temperature is −3.7 °C (Williams et al., 1996) with almost 80% of the annual precipitation falling as snow (Caine, 1993). The combination of temperature and snowfall supports persistent snowpacks in these alpine watersheds through much of the year and a short growing season for the alpine vegetation (1–3 months) (Jones et al., 2019).

2.2. Geology

Andrews and Green Lakes Valley watersheds are dominantly comprised of steep rock walls, talus slopes, and glacially smoothed bedrock in the higher elevations with increasing vegetation (grasses, wet meadows, and coniferous forests) as elevation and slope decreases (Arthur, 1992; Mast, 1992; Williams et al., 2006). Bedrock of Andrews watershed consists of Precambrian gneiss and Silver Plume granite (Peterman and Hedge, 1968). The gneiss and granite have similar mineralogy and chemical composition (Mast, 1992). Primary mineralogy of the bedrock includes quartz, oligoclase, microcline, and biotite with trace amounts of calcite and pyrite (Mast, 1992). Secondary minerals found in the soil include smectite, kaolinite, and illite (Mast, 1992). Within Green Lakes Valley, the bedrock consists of Precambrian sillimanite-biotite gneiss and granite. The primary mineralogy includes plagioclase, quartz, and potassium feldspar. Mica (including biotite), calcite, and pyrite are minor to trace constituents in the rock materials of Green Lakes Valley (Birkeland et al., 2003). Smectite, illite, and kaolinite have also been reported for soils at Green Lakes Valley (Mahaney and Fahey, 1980). Calcite and pyrite in these sites are readily dissolved and represent an important potential source of solutes, including calcium and sulfur, to streams.

2.3. Hydrology

Andrews watershed and Green Lakes Valley are drained by single first-order streams, Andrews Creek and Albion Creek, respectively, which flow continuously throughout the year. Hydrological studies have been conducted in Green Lakes Valley as part of the LTER program (Williams et al., 2001) and in Andrews watershed as part of the WEBB program (Clow, 2010). The seasonal flows show a classic snowmelt hydrograph, with discharge rising in May to a peak in late June and then declining into the autumn (Fig. 2A and B). At both sites the start of rising discharge and the timing of peak discharge have trended earlier in the season over the last 30 years (Clow, 2010; Cowie et al., 2017; Williams

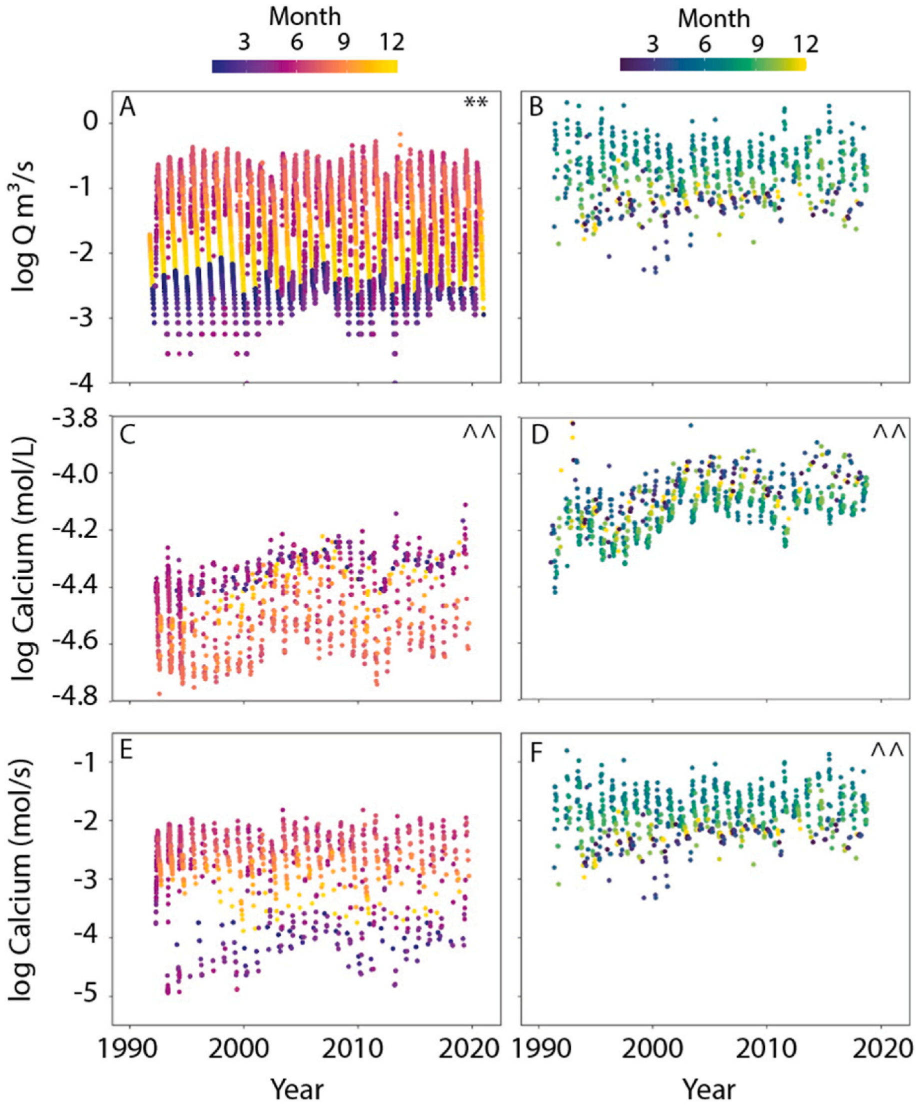

Fig. 2. Log discharge (Q, m^3/s), log Ca concentrations (mol/L), and log Ca flux (mol/s) from 1990 to 2020 at Andrews Creek (A,C,E respectively) and Albion Creek (B,D,F respectively). Discharge is higher in winter to spring with snow melt (yellow to purple/blue colors) compared to summer and fall months (orange colors A, green colors in B). Concentrations of calcium are lower in spring and early summer months during snow melt (yellow to purple/blue colors) compared to fall and winter months (orange colors C, green colors in D), concentrations of sulfate, bicarbonate, and silica show similar annual trends. Mass flux of Ca is generally lowest when Ca concentrations are highest due to lower discharge (E and F), with similar trend for higher flux during winter to spring with snow melt (yellow to purple/blue colors) compared to summer and fall months (orange colors E, green colors in F). Silica, sulfate, and bicarbonate concentrations and mass-flux generally follow the same annual trends as calcium (Supplemental Material Fig. S1). Trends through time are difficult to visualize in these data due to seasonality and short-term responses to drought. A seasonal Mann-Kendall test was used to evaluate these data for increasing and decreasing trends through time, slopes and p-values for concentrations and mass flux are reported in Table 1. (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

et al., 2001), consistent with hydrograph changes recorded across much of western North America (Stewart et al., 2005).

Water storage within Green Lakes Valley and Andrews watershed occurs as snowpack, snowfields, glaciers, rock glaciers, wetlands, lakes, permafrost, shallow alluvial aquifers, and talus-slope groundwater reservoirs (Clow et al., 2003; Cowie et al., 2017). Talus slopes have large potential groundwater-storage capacities and help sustain baseflow (Clow et al., 2003). End-member mixing analysis (EMMA) of Andrews watershed (Foks et al., 2018) and Green Lakes Valley (Cowie et al., 2017) showed that snow and talus-groundwater were the most important sources of discharge in these two catchments. For Andrews watershed, talus-groundwater has become a more dominant contributor to discharge than snow over time, signifying how crucial it is to the resilience of a watershed's discharge to fluctuations in snowpack (Foks et al., 2018). However, fluctuations in discharge contributions from different sources through time could influence stream chemistry (i.e., dilute snow melt versus concentrated talus groundwater) (Campbell et al., 1995; Clow and Mast, 2010; Clow and Sueker, 2000).

3. Statistical analysis of data records

Several major base cations and weathering products were examined but here we focus on elements that can inform overall weathering trends of calcite, pyrite, and silicates. Calcium, silica (as SiO_2), sulfate, and bicarbonate (determined from alkalinity or acid neutralization capacity) concentration and mass flux-discharge relationships were evaluated for both Andrews watershed and Green Lakes Valley using long-term records of discharge and water chemistry from the outlets of these watersheds, Albion Creek and Andrews Creek, respectively. We calculate mass flux (mol sec^{-1}) as the product of concentration (C, mol m^{-3}) and discharge (Q, m^3 sec^{-1}), consistent with terminology used in many studies on mass export from watersheds. For Albion Creek, water chemistry (Caine, 2018) and discharge data (Caine, 1993) from 1993 to 2020 were retrieved from the Niwot Ridge LTER site data page (https://portal.edirepository.org/nis/home.jsp). For Andrews Creek, part of the Loch Vale LTER site, water chemistry and discharge data for 1993–2020 were retrieved from USGS NWIS (https://co.water.usgs.gov/lochvale/data.html).

Trends in discharge and water chemistry for Albion Creek and Andrews Creek were evaluated using the seasonal Mann-Kendall test, as described in Helsel and Hirsch (1992). The seasonal Mann-Kendall test is established on the basis that the trend is cyclically varying in relation to the seasons of the year. This test is a common tool used to analyze time series to identify significant increasing or decreasing monotonic trends (Hirsch et al., 1982) and is robust in dealing with missing data, skewed data, seasonality, and serial correlation (Helsel and Hirsch, 1992). The seasonal Mann-Kendall Test is a modified version of Mann-Kendall test that accounts for seasonality by computing the Mann-Kendall test on each of the seasons independently. Monthly scores are then added to get the test statistic. By adding the variances of the Mann-Kendall score statistic for each month, the variance of the test statistic is obtained. Here, the seasonal Mann-Kendall test was calculated through the rkt package within R to assess significance of trends in solute concentrations and mass flux from 1993 to 2020. The seasons were defined as individual months and all tests for statistical significance were evaluated at a significance level, α, of 0.05.

4. Results

4.1. Concentration, discharge, and mass-flux relationships at Andrews Creek

Discharge at Andrews Creek ranged from 0.0003 to 0.7 m^3/s with maximum values observed in June and July and minimum values observed in April and May over the entire study period (Fig. 2A). Solute concentrations ranged from 1.8 to 7.5 $\times$ 10^{-5} mol/L for calcium (Figs. 2C), 8.3 $\times$ 10^{-6} to 5.2 $\times$ 10^{-5} mol/L for sulfate, 1.4 $\times$ 10^{-5} to 8 $\times$ 10^{-5} mol/L for bicarbonate, and 3.5 $\times$ 10^{-5} to 1.4 $\times$ 10^{-4} mol/L for silica (Figure SI-1). Solute concentrations were higher during winter months when discharge was low. Minimum concentrations generally occurred in August to September on the falling limb of the hydrograph, after which concentrations increase through the fall and winter months with maximum solute concentrations in May before snowmelt (Fig. 2C). A pattern of hysteresis over annual timescales is apparent in C-Q plots for all solutes in examined in Andrews Creek (e.g., calcium, Fig. 3A) where rising limb (spring) concentrations prior to peak discharge are generally greater than falling limb (late summer) concentrations over similar discharge values. Solutes within each watershed tend to exhibit the same C-Q relations, but these relations are different between the two watersheds (Fig. 4). The log of solute mass flux versus discharge shows a positive linear trend for all solutes examined (Fig. 5 A, C, E). After peak discharge mass flux decreases but retains a linear trend, indicating a decrease in solute mass flux for a given discharge. This observation is denoted by an arrow in Fig. 5A as an example for Ca and visible for bicarbonate in Figure SI-1 and sulfate in Figure SI-2 in data colored by month. The seasonal Mann-Kendall test revealed increasing trends through all time for concentrations of calcium ($p = 7.1 \times 10^{-4}$), sulfate ($p = 4.1 \times 10^{-4}$), and bicarbonate ($p = 2.5 \times 10^{-5}$) but not for mass flux of the same solutes (Table 1). Additionally, there was no significant trend through time in concentration ($p = 0.06$) or mass flux for silica ($p = 0.31$). Discharge at Andrews Creek decreased over the three-decade study period (Fig. 2A) with a Seasonal Mann-Kendall test p-value = 0.007 (Table 2).

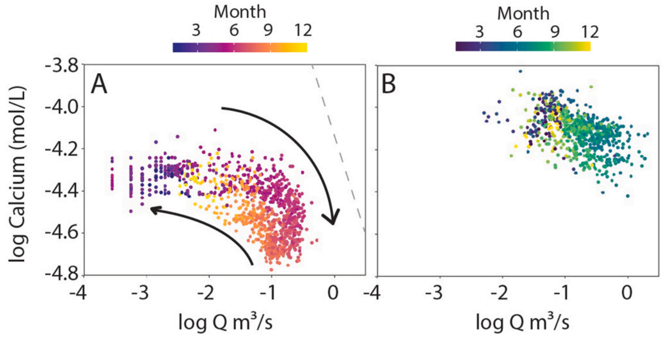

Fig. 3. C-Q plots of calcium concentrations from 1990 to 2020 in Andrews Creek (A) and Albion Creek (B) with symbols colored by month. Dashed grey line in (A) indicates a power law slope = 1, characteristic of dilution behavior. In Andrews Creek (A), C-Q data show hysteresis over annual time scales with concentrations in the rising limb of the snowmelt hydrograph higher than those in the falling limb (direction denoted by arrows). Hysteresis is also observed in bicarbonate and sulfate, but not silica (Figure SI-1 and SI-2). Hysteresis is not observed in C-Q relationships in Albion Creek Ca concentrations (B) or in C-Q data of other solutes (Figures SI-3 and SI-4).

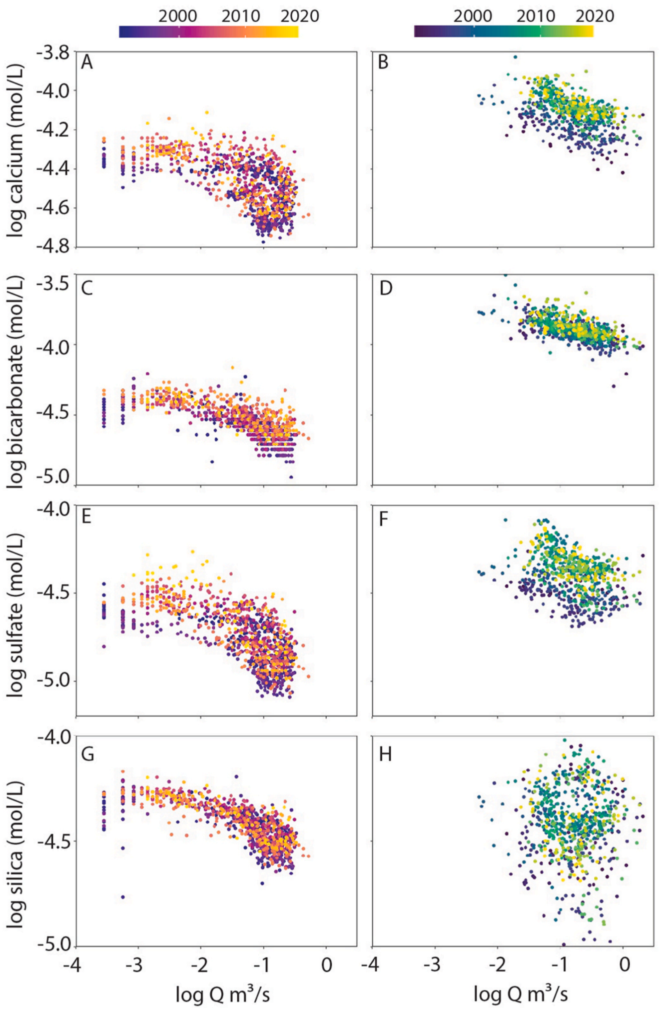

Fig. 4. C-Q plots for Andrews Creek (left column) and Albion Creek (right column) for log calcium concentration (A and B), log bicarbonate (C and D), log sulfate (E and F), and log silica (G and H) concentrations in mol/L plotted as a function of log discharge, colored by year.

4.2. Concentration, discharge, and mass-flux relationships at Albion Creek

Discharge at Albion Creek ranged from 0.003 to 5.5 m^3/s with maximum values observed in June and July and minimum values observed in April and May over the entire study period (Fig. 2B). Solute concentrations ranged from 2.1 $\times$ 10^{-4} to 2.2 $\times$ 10^{-4} mol/L for calcium (Figs. 2C), 1.1 to 8.2 $\times$ 10^{-5} mol/L for sulfate, 5.1 $\times$ 10^{-5} to 3.5 $\times$ 10^{-4} mol/L for bicarbonate, 1.6 $\times$ 10^{-6} to 1.8 $\times$ 10^{-4} mol/L for silica and were higher during winter months, when discharge is low (Fig. 2C). Minimum concentrations generally occurred in August to September on the falling limb of the hydrograph, after which concentrations increased through the fall and winter months with maximum solute concentrations in May before snowmelt. The log of solute mass flux versus discharge shows a positive linear trend (e.g., calcium, Fig. 3). Unlike Andrews Creek, no pattern of hysteresis in the concentration and mass flux-discharge relationships were observed. The seasonal Mann-Kendall test revealed significantly increasing trends through all time for concentrations and mass flux of calcium ($p = 4.0 \times 10^{-5}$ and 0.004, respectively), sulfate ($p = 1.6 \times 10^{-4}$ and 2.1×10^{-1}, respectively), and bicarbonate ($p = 1.6 \times 10^{-4}$ and 2.1×10^{-1}, respectively) but not for

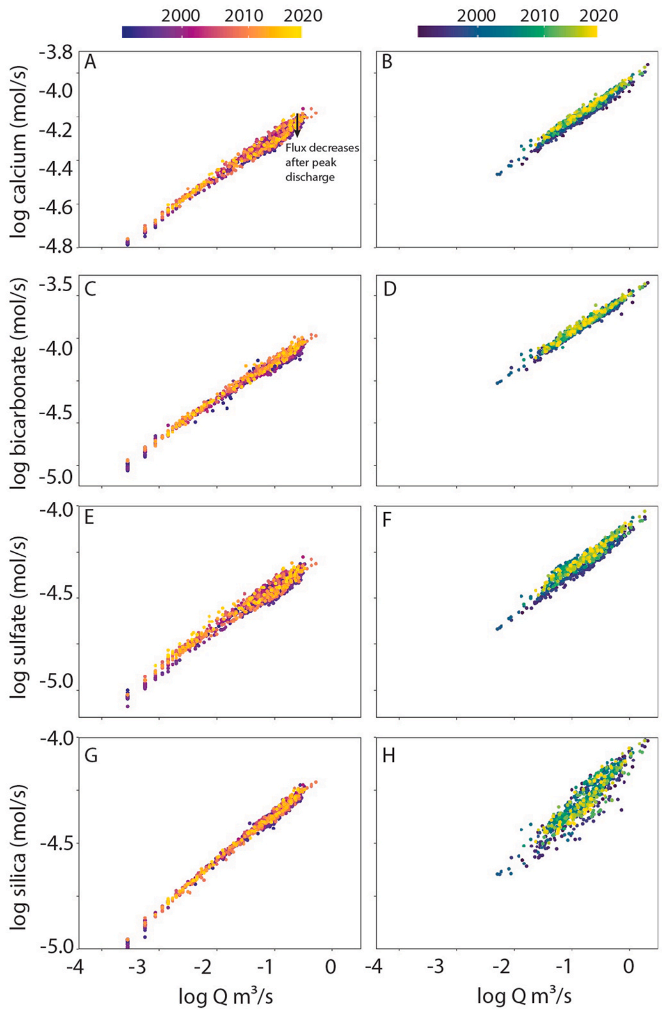

Fig. 5. F-Q, or mass flux plotted as a function of discharge, for log calcium (A, B), log bicarbonate (C,D), sulfate (E,F), and silica (G,H) for Andrews Creek (left side) and Albion Creek (right side) with data colored by year.

silica ($p = 0.26$ and 0.28, respectively; Table 1). Additionally, no overall increasing or decreasing trend in discharge through time exists at Albion Creek over the three-decade study period.

5. Discussion

5.1. Long-term trends in solute concentrations and mass flux

Concentrations of calcium, sulfate, and bicarbonate significantly increased through time at the outlets of both watersheds (Andrews Creek and Albion Creek), but silica concentrations did not change through time for either watershed. In contrast, mass flux of calcium, sulfate, and bicarbonate significantly increased through time at Albion Creek, but did not change through time at Andrews Creek. These different trends through time in mass flux but not concentration between the two sites point to different controlling processes through time, a surprising result given the overall similarities in the two watersheds. The differences may be in part related to differences in discharge trends through time, with decreasing discharge in Andrews Creek but not Albion Creek.

In Andrews Creek, decreasing discharge with no change in mass flux driving increased solute concentrations is consistent with an interpretation of water chemistry driven by hydrologic fluctuations through time rather than changes in solute production or export. However, over the past two decades the dominant source of streamflow to Andrews Creek has shifted from snowmelt to talus groundwater (Foks et al., 2018). This change in balance of water sources could mask changes in geochemical processes that would lead to changes in solute mass flux without other changes in the watershed. The sensitivity of solute concentrations to hydrological fluctuations within Andrews Creek is further evident from the hysteresis of the C-Q relationship on an annual scale. For all analyzed solutes (calcium, silica, sulfate, and bicarbonate), the concentrations of solutes before peak discharge are greater than concentrations after peak discharge at similar values of discharge (e.g., calcium, Fig. 2). This pattern has been attributed to the flushing out of solutes due to spring snowmelt in Andrews Creek (Campbell et al., 1995). During low discharge in winter months, Andrews Creek exhibits chemostatic behavior (e.g., calcium, Fig. 4A). This chemostasis indicates possible decoupling of concentration and discharge where buildup and storage of solutes within a system effectively buffers the solute concentrations against changes in discharge or episodic inputs (Basu et al., 2010; Godsey et al., 2009; Musolff et al., 2017; Thompson et al., 2011). During spring and summer months at Andrews Creek, as the snowpack melts and discharge increases to peak discharge, concentrations decrease and dilution is evident in the C-Q relationship (defined as a negative slope, e.g., calcium in Fig. 3A) (Meybeck and Moatar, 2012; Shanley et al., 2011). During the winter, when discharge is low, solutes appear to build up within the subsurface, while in the spring and summer, when discharge is high due to snow melt, dilution is evident and most likely due to overland or shallow subsurface flow.

Mass flux data also show the importance of dilution and seasonality. After peak discharge the trend in mass flux is shifted downward in Andrews Creek (e.g., calcium, Fig. 2). This shift indicates a decrease in solute production at similar values of discharge and may be due to dilution from overland flow or the flushing out of solutes. Conversely, in

Table 2
Slopes and corresponding p-values for discharge and equivalence ratio trends through time at Andrews Creek and Albion Creek determined from a seasonal Mann-Kendall test.

	Discharge		Equivalence Ratio	
	Slope	p-value	Slope	p-value
Andrews Creek	−1.40E-04	0.007	-5×10^{-4}	0.06
Albion Creek	2.28E-05	0.97	-7×10^{-4}	0.002

Table 1
Slopes and corresponding p-values for concentration and mass flux trends through time at Andrews Creek and Albion Creek determined from seasonal Mann-Kendall test.

	Calcium		Bicarbonate		Sulfate		Silica	
	Slope	p-value	Slope	p-value	Slope	p-value	Slope	p-value
Concentrations								
Andrews Creek	0.015	7.1×10^{-4}	0.017	2.5×10^{-5}	0.026	4.1×10^{-4}	0.0069	0.06
Albion Creek	2.266	4.0×10^{-5}	0.6	1.6×10^{-4}	1.62	4.7×10^{-4}	0.2	0.26
Mass Flux								
Andrews Creek	3.1×10^{-5}	0.73	8.6×10^{-5}	0.42	9.4×10^{-5}	0.46	-1.5×10^{-4}	0.31
Albion Creek	0.303	0.004	0.08	2.1×10^{-1}	0.205	0.005	0.027	0.28

Albion Creek, increases in solute concentrations and mass flux with no change in discharge through time are consistent with an interpretation that changes in water chemistry are driven by geochemical processes that produce more solutes within the watershed that are then exported in the streamflow. At Albion Creek, C-Q relationships exhibit neither hysteresis nor chemostasis but rather a relatively linear decreasing trend in solute concentration with increasing discharge (e.g., calcium, Fig. 3B). This relationship between concentration and discharge at Albion Creek is still seasonally dependent, with dilution of these solutes from the spring to summer months and concentration of these solutes from the fall to winter months, but there does not appear to be the same flushing of solutes that is observed at Andrews Creek. Analyzing mass flux of these solutes in addition to concentration removes the effects of seasonality due to discharge and allows for better interpretation of the mechanisms driving temporal changes in solutes released from watersheds and the potential impact to downstream water quality.

We note that water chemistry is not monitored continuously, or even at the same high-resolution sampling frequency as discharge. The frequency of water-chemistry sampling is often bi-monthly at most and often monthly or quarterly. Thus, the data require either analysis of single points of instantaneous concentrations or mass flux or some interpolation between samples. The analysis here focuses on temporal trends in instantaneous mass flux, which could miss some events (such as large rainstorms or peak snow melt runoff) that are important to calculating the cumulative mass flux through time and is not a perfect proxy for annual mass flux. However, the sampling frequency and pattern did not change through time at either watershed and samples were collected year-round at both locations. Thus, the differences in trends in instantaneous mass flux between the two watersheds are likely a representation of differences in trends in cumulative mass flux over annual or other varying time scales as well. The difference in temporal solute concentration, mass flux, and discharge trends between these two comparable alpine watersheds was not expected, so additional geochemical analyses, outlined below, were used to further explore these differences.

5.2. *Long-term trends in solute production by mineral weathering*

Enhanced mineral weathering has been invoked as a potential cause of increased sulfate and base-cation concentrations in other alpine systems (Gislason et al., 2009; Todd et al., 2012). Geochemical modeling of the stream water composition was performed using Geochemist's Workbench to evaluate possible changes in geochemical processes that could drive observed mass flux increases at Albion Creek but not Andrews Creek. Absence of significant trends in silica concentrations or mass flux over the study period for Albion Creek and Andrews Creek suggest that either silica mineral weathering is not increasing over the observation period or that silica concentrations are buffered in the watershed by vegetation uptake, precipitation of secondary minerals, or another process. Stream chemistry for the two watersheds plots within secondary mineral phases on K^+/H^+ to $SiO_{2(aq)}$ and Na^+/H^+ to $SiO_{2(aq)}$ activity plots (Fig. 6). Andrews Creek data plot in the kaolinite field on both diagrams, indicating potential Si buffering by precipitation of kaolinite. Albion Creek data plot on the boundary and into the gibbsite stability field in Albion Creek, suggesting potential buffering by mineral precipitation. Kaolinite has been observed in both watersheds (Mahaney and Fahey, 1980; Mast, 1992).

Calcite weathering is an important source of calcium in alpine watersheds, and with faster dissolution kinetics relative to most silicates, enhanced calcite weathering may respond to shorter-term changes in climate and hydrology more effectively than silicates. Calcite weathering was investigated as a potential mechanism for the increased mass flux of Ca out of Green Lakes Valley. In most cases, carbonic acid derived from atmospheric CO_2 is assumed to be the dominant weathering agent. However, in watersheds with even trace sulfides, like Andrews watershed (Mast et al., 1990) and Green Lakes Valley (Williams et al., 2006), the oxidation of pyrite

$$4FeS_2 + 15O_2 + 14H_2O \rightarrow 4Fe(OH)_3 + 8H_2SO_4 \tag{1}$$

Can be an important source of acid for weathering (e.g., Beaulieu et al., 2011). The high relative reactivity of sulfides and carbonates compared to silicates, combined with their widespread occurrence in alpine settings (Craig and Vokes, 1993), make them highly susceptible to natural and anthropogenic disturbances such as climate change-driving shifts in hydrological (e.g. groundwater elevation or dominant water sources) and landscape (increased mechanical weathering) changes. 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. The driving source of acid for calcite weathering is recorded in water chemistry. In a system where calcite dissolution is driven by carbonic acid, calcium and bicarbonate are the weathering products:

$$2CaCO_3 + 2CO_2 + 2H_2O \rightarrow 2Ca^{2+} + 4HCO_3^- \tag{2}$$

When sulfuric acid, derived from pyrite oxidation, is the dominant source of acid driving calcite weathering, sulfate is also a weathering product, in addition to calcium and bicarbonate:

$$2CaCO_3 + H_2SO_4 \rightarrow 2Ca^{2+} + 2HCO_3^- + SO_4^{2-} \tag{3}$$

Increased calcite dissolution tied to the production of sulfuric acid

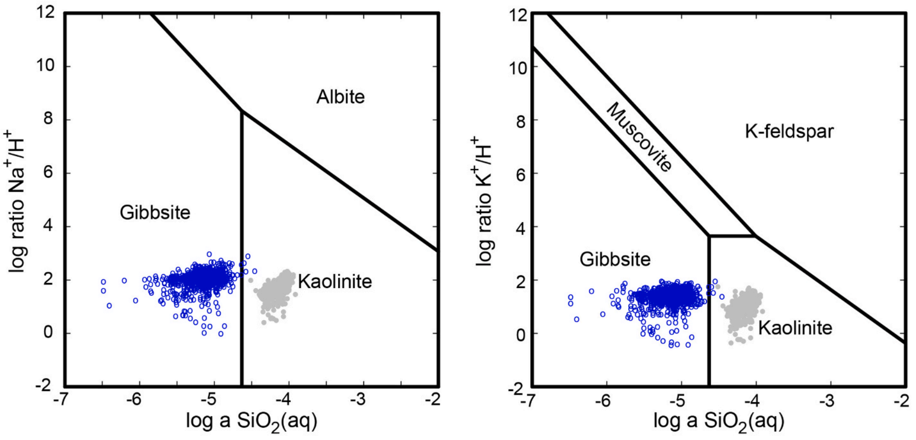

Fig. 6. Activity-activity diagrams for Andrews Creek (grey filled circles) and Albion Creek (blue open circles) for the Na^+-SiO_2-Al^{3+} system (left) and K^+-SiO_2-Al^{3+} system (right). Diagrams were constructed in Geochemist's Workbench using the thermo.tdat database at a temperature of 5C. Al^{3+} concentrations were set in equilibrium with the feldspar mineral. (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

from pyrite oxidation would therefore result in increased calcium and sulfate mass flux–but potentially not bicarbonate–leaving a watershed, which was observed at Albion Creek (Fig. 2F and Supplementary Figs. S3–S4) but not Andrews Creek (Fig. 2E and Supplementary Figs. S1–S2). Because of the difference in weathering products between carbonic- and sulfuric-acid-driven calcite dissolution, stoichiometric, or equivalence, ratios can be used to evaluate the dominant agent of calcite dissolution (Li et al., 2014) and provide insight into the processes driving increases in solute mass flux out of Albion Creek but not Andrews Creek. Equivalence ratios are based on equal charge of solutes. Carbonic-acid dissolution of calcite yields 2 mol of bicarbonate for every 1 mol of calcium with an equivalence ratio 1:1 bicarbonate to calcium (equivalence ratio of 1; equation (2)). On the other hand, sulfuric-acid dissolution of calcite yields 2 mol of bicarbonate for every 2 mol of calcium with an equivalence ratio 1:2 bicarbonate to calcium (equivalence ratio of 0.5; equation (3)). This ratio was calculated for the three decades of stream chemistry at Albion Creek and Andrews Creek (Fig. 7). At Andrews Creek (Fig. 7), equivalence ratios indicate sulfuric-acid-dominant weathering (equivalence ratio of 0.5) on an annual scale for much of the study period with no temporal trend ($p\text{-value} = 0.06$). There are periods within the record where the equivalence ratios trend toward carbonic-acid dominant (2011–2015), which may be a result of cyclic wet versus drier periods within the watershed. For Albion Creek (Fig. 7), equivalence ratios trended from carbonic-acid-dominant weathering to more sulfuric-acid-dominant weathering through time ($p\text{-value} = 0.002$), with similar increases in equivalence ratio during the 2011–2015 wet period as Andrews Creek. These equivalence ratios suggest that Andrews Creek watershed may be buffered against longer-term changes in weathering mechanisms due to a predominance of sulfuric-acid-dominated weathering; whereas weathering mechanisms may be changing in Green Lakes Valley through time as pyrite is oxidized to a greater extent and driving weathering.

The significant increase in calcium- and sulfate-mass flux, but not bicarbonate (Fig. 5 B,D,F), coupled with significant decrease in bicarbonate to calcium equivalence ratios through time at Albion Creek (Fig. 7) is consistent with increased sulfuric-acid-driven dissolution of calcite (bicarbonate to calcium equivalence ratio of 0.5) relative to weathering by carbonic acid (bicarbonate to calcium equivalence ratio of 1). In a previous study in the Green Lakes Valley, Williams et al. (2006) analyzed the outflow from the rock glacier upstream from the Albion Creek sampling site and discovered a similar enrichment of sulfate and calcium during late summer months, and they proposed a similar geochemical conceptual model with dissolution of pyrite and calcite best explaining elevated concentrations at the glacier outflow. The trends in Albion Creek contrast with no change in calcium- and sulfate-mass flux and no consistent trend in equivalence ratios at Andrews Creek, suggesting that either changes in hydrology that drive significantly decreasing discharge through time masks long-term shifts in dominant-weathering agent or other mechanisms are limiting enhanced pyrite weathering through time.

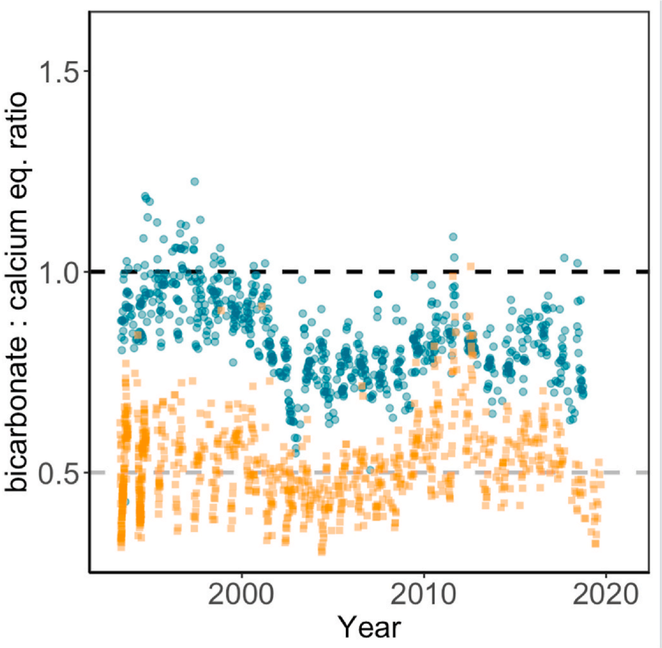

Fig. 7. Bicarbonate to calcium equivalence ratios for Andrews Creek (orange squares) and Albion Creek (blue circles) through time. The black dashed line denotes an equivalence ratio of 1 where carbonic acid is the dominant calcite weathering agent while the grey dashed line denotes an equivalence ratio of 0.5 where sulfuric acid is the dominant calcite weathering agent. (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

This variable response between watersheds in calcium and sulfate exports through time (Fig. 5, A and E compared to B and F) is consistent with previous studies that have documented changes in calcium and sulfate in alpine streams and lakes across the globe (Crawford et al., 2019; Gislason et al., 2009; Mast et al., 2011; Salerno et al., 2016; Sommaruga-Wögrath et al., 1997; Thies et al., 2007; Todd et al., 2012; Williams et al., 2006). Mast et al. (2011) observed that calcium and sulfate concentrations increased in some alpine watersheds in Colorado but not in others. For example, in the Weminuche lakes, sulfate and calcium concentrations increased and were attributed to increases in weathering of pyrite and subsequent strong-acid weathering of calcite, while in Mount Zirkel and Flat Tops Lakes, sulfate concentration decreased and was attributed to decreasing atmospheric deposition. The additional mass-flux analysis in this study highlights the importance of analyzing total-mass export in addition to concentrations through time. In Andrews Creek, significantly increasing concentrations might lead to an interpretation of increased weathering; however, mass flux does not increase and discharge decreases, providing evidence of changes in hydrology dominating the temporal trends in calcium and sulfate concentrations. In Albion Creek, increases in calcium and sulfate concentration were concomitant with increases in mass flux and no change in discharge, revealing geochemical processes responsible for the increased concentration.

It is still unclear why these two watersheds have different weathering behavior and exhibit differences in temporal trends in solute mass flux. In other studies, increases in sulfate and base-cation concentrations have been attributed to enhanced weathering, increased biological activity, or melting of ice features caused by increasing air temperatures (Baron et al., 2009; Hill, 2008; Mosello et al., 2002; Rogora et al., 2003; Sommaruga-Wögrath et al., 1997; Tait and Thaler, 2000; Thies et al., 2007; Williams et al., 2006). However, the similarities in the elevation, lithology, and geomorphology of these watersheds suggest that other watershed characteristics or processes are responsible for the difference in temporal trends. Albion Creek drains the Green Lakes watershed and is larger than the Andrews Creek watershed, which has only one surface water feature, a wetland. Larger watershed area and more surface water could lead to more mixing and buffer against changes through time, but water chemistry in Albion Creek changes more than Andrews Creek. However, if pyrite weathering is the primary driver of the change in solute mass flux, it is possible that pyrite weathering in Andrews Creek has been driven by seasonal variations in water-table elevation over the length of the record. In contrast, it is possible that groundwater elevations are decreasing after a period of stability in the Green Lakes Valley watershed. This would expose pyrite to oxygenated, infiltrating waters and shift the weathering mechanism causing increased solute mass flux. This untested hypothesis would require data that are not available and motivates the importance of long-term groundwater records in remote sites, which are hard to come by.

6. Conclusions

The results of this study suggest different long-term chemical and hydrological changes in two similar alpine catchments as observed from the comparison of solute-concentration and mass-flux data sets. The combination of both mass flux and concentration analysis allows for identification of concentration changes due to changes in mass flux compared to those caused by changes in discharge, either seasonally or due to longer-term droughts or climate change. At Andrews Creek, overall calcium, sulfate, and bicarbonate concentrations increased significantly over the three-decade record with a concurrent significant overall decreasing trend in discharge. However, solute mass flux did not increase at Andrews Creek. At Albion Creek, calcium, sulfate, and bicarbonate concentrations and mass flux significantly increased over the three-decade record but with no overall significant trend in discharge.

Differences in equivalence ratios between the two sites indicate a shift in weathering mechanism with increased pyrite oxidation at Albion Creek but not at Andrews Creek, despite increased calcium and sulfate concentrations through time at Andrews Creek. Results from the analysis of Andrews Creek and Albion Creek, as well as for other high-elevation systems, suggest broad-scale shifts in dominant-weathering behavior (e.g., increased sulfide weathering) and water sources (e.g., snowmelt versus talus groundwater). Additionally, the differences in behavior between Andrews Creek and Albion Creek, two similar alpine watersheds located 28 km from each other, highlights the variability in stream chemistry that can occur with modest differences in characteristics of a watershed, which control its ability to buffer against fluctuations in water sources or sources of solutes. The ratios of carbonic-acid-derived and sulfuric-acid-derived weathering products in the watersheds through time suggest potential differences in weathering drivers between the watersheds, which could cause differences in solute mass flux trends through time. One possible difference is relative stability of groundwater elevation. If groundwater levels are more dynamic in Andrews Creek, pyrite weathering could be driven by seasonal or other short-term water-table fluctuations, keeping pyrite oxidation as the primary weathering mechanism. In contrast, if the groundwater table elevation in Green Lakes Valley is lowering after a period of stability due to climate change, this would expose pyrite to oxygenated, infiltrating fluids and increase solute mass flux as observed.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data is available through open data portals.

Acknowledgments

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.apgeochem.2022.105402.

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