

# Climate, Not Atmospheric Deposition, Drives the Biogeochemical Mass-Balance of a Mountain Watershed

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**Abstract** Watershed mass-balance methods are valuable tools for demonstrating impacts to water quality from atmospheric deposition and chemical weathering. Owen Bricker, a pioneer of the mass-balance method, began applying mass-balance modeling to small watersheds in the late 1960s and dedicated his career to expanding the literature and knowledge of complex watershed processes. We evaluated long-term trends in surface-water chemistry in the Loch Vale watershed, a 660-ha. alpine/subalpine catchment located in Rocky Mountain National Park, CO, USA. Many changes in surface-water chemistry correlated with multiple drivers, including summer or monthly temperature, snow water equivalent, and the runoff-to-precipitation ratio. Atmospheric deposition was not a significant causal agent for surface-water chemistry trends. We observed statistically significant increases in both concentrations and fluxes of weathering products including cations,  $\text{SiO}_2$ ,  $\text{SO}_4^{2-}$ , and ANC, and in inorganic N, with inorganic N being primarily of atmospheric origin. These changes are evident in the individual months June, July, and August, and also in the combined June, July, and August summer season. Increasingly warm summer temperatures are melting what was once permanent ice and this may release elements entrained in the ice, stimulate chemical weathering with enhanced moisture availability, and stimulate microbial nitrification. Weathering rates may also be enhanced by sustained water availability in high snowpack years. Rapid change in the flux of weathering products and inorganic N is the direct and indirect result of a changing climate from warming temperatures and thawing cryosphere.

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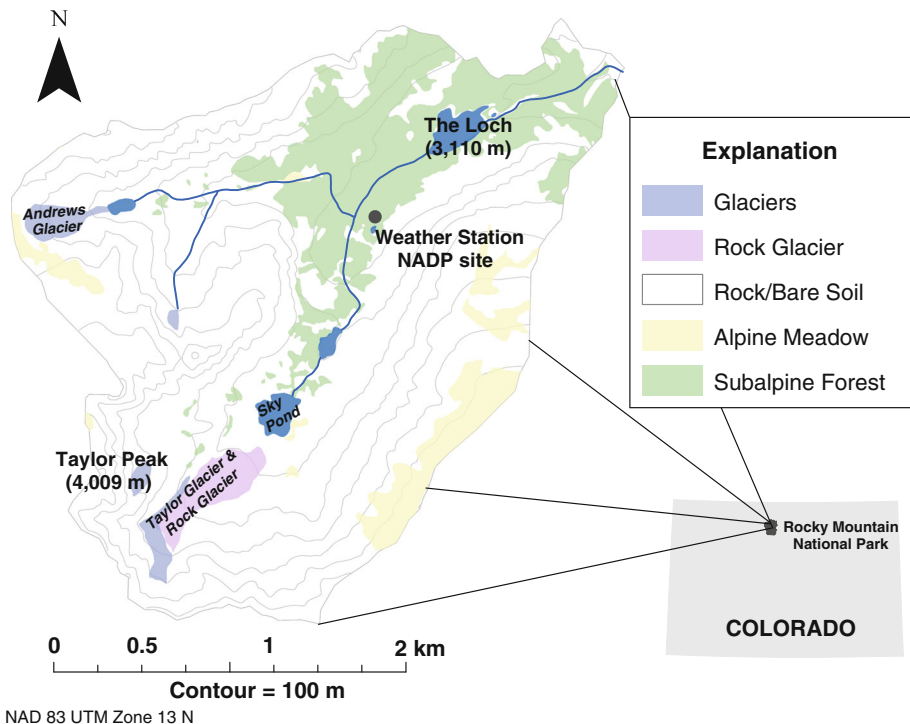
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## 1 Introduction

Watershed mass-balance calculations have developed as an important technique for estimating processes resulting from interactions of water with biota, soils, and bedrock. Owen Bricker, a pioneer of the method, began applying mass-balance modeling to small watersheds in the late 1960s and dedicated his career to expanding the literature and knowledge of complex watershed processes (Bricker et al. 1968; Cleaves et al. 1970; Katz et al. 1985; Baron and Bricker 1987; Simon et al. 2005). The mass-balance approach was developed to monitor the flux of water and associated dissolved and suspended chemicals from weathering and atmospheric deposition. Loch Vale Watershed (LVWS) in Rocky Mountain National Park, CO (Fig. 1), was instrumented in 1983 with Owen Bricker's help to address the response of an alpine and subalpine ecosystem to atmospheric deposition and climate (Baron 1992).

Previous LVWS mass-balance studies have provided insight into mineral weathering sources and rates, the fate of atmospherically deposited solutes, and internal biogeochemical cycling. Base cations, silica, and alkalinity are derived from weathering of biotite gneiss that is composed of the minerals apatite, quartz, plagioclase, microcline, biotite, microcrystalline calcite, and sillimanite within the watershed (Baron and Bricker 1987;



**Fig. 1** Map of 660-hectare Loch Vale Watershed located in Rocky Mountain National Park, CO

Mast et al. 1990; Price et al. 2013). Price et al. (2013) found over their 24-year period of study that weathering of calcite accounts for 40–65 % of the contribution of  $\text{Ca}^{2+}$  to the watershed, while oligoclase and apatite account for 25 and 10–35 %, respectively. Wet deposition is a primary source for the relatively conservative species chloride ( $\text{Cl}^-$ ), sulfate ( $\text{SO}_4^{2-}$ ), and nitrate ( $\text{NO}_3^-$ ) (Baron et al. 1995; Clow and Drever 1996; Baron and Campbell 1997; Campbell et al. 2000). Isotopic analysis of dissolved  $\text{SO}_4^{2-}$  in LVWS also identified an internal mineral source (Mast et al. 1990; Kester et al. 2003). Ammonium ( $\text{NH}_4^+$ ) inputs from deposition exceed outputs and almost all  $\text{NH}_4^+$  is rapidly nitrified or consumed (Campbell et al. 1995, 2000; Williams et al. 1996).

Recent studies in LVWS suggest that changes in climate and atmospheric deposition are altering the mass balance of major dissolved elements (Baron et al. 2009). Trends in wet deposition reported by the National Atmospheric Deposition Program National Trends Network (NADP/NTN) show an increase in inorganic nitrogen (N) in precipitation throughout most of the United States since approximately 1980, while  $\text{SO}_4^{2-}$  has declined sharply (Lehmann et al. 2005). Increases in wet N deposition also occurred in the Rocky Mountains of the western United States, but there is no long-term (1984–2010) significant increase in wet N deposition in LVWS (Morris et al. 2012). The annual wet N deposition rate in LVWS exhibited high variability prior to 1995; from 1995 to 2010, wet N deposition was about  $3.0 \text{ kg N ha}^{-1} \text{ yr}^{-1}$  (Morris et al. 2012). In spite of steady wet N deposition inputs, annual N export from LVWS has increased since 2000, suggesting either an internal source of N or that the inputs and outputs are not in annual balance (Baron et al. 2009). Wet  $\text{SO}_4^{2-}$  deposition has decreased over time, but increasing  $\text{SO}_4^{2-}$  concentrations in LVWS surface waters imply increased mineral weathering (Mast et al. 1990; Kester et al. 2003; Baron et al. 2009).

The Rocky Mountain climate has changed in recent years (Ray et al. 2008). Summer and autumn temperatures in the Front Range of Colorado showed statistically significant warming trends from 1991 to 2006 and the increase in summer temperatures has been associated with increasing July temperatures (Baron et al. 2009; McGuire et al. 2013). Mean and minimum July temperatures in LVWS increased by 0.22 and 0.18  $^\circ\text{C yr}^{-1}$  from 1991 to 2006, respectively, and this trend was statistically significant (Baron et al. 2009). Warmer temperatures can increase weathering rates, influence the timing of snowmelt (Knowles et al. 2006), and alter the proportion of precipitation that falls as snow or rain (Stewart et al. 2005).

Glacier and other ice feature ablation rates increase as climate warms. Alpine glaciers are retreating worldwide in response to warming (Fountain et al. 2012). Alpine catchments occupied by active glaciers may yield weathering rates greater than the global mean (Anderson et al. 1997), and changes to the cryosphere can influence the flux of water, weathering products, nutrients, and organic matter in mountainous environments (Baron et al. 2009; Bogdal et al. 2009; Saros et al. 2010; Singer et al. 2012). We evaluated long-term trends in surface-water chemistry in LVWS to try to apportion the cause of changes in solute flux over time. We compared the long-term surface-water chemical time series with the time series of atmospheric deposition, air temperature, precipitation, and snow water equivalent (SWE). We also addressed the possible indirect climate effects from warming-induced ice ablation.

## 2 Site Description

Loch Vale watershed is a 660-hectare alpine/subalpine catchment in Rocky Mountain National Park, CO (Fig. 1), that was established to address the response of watershed-scale ecosystem processes to atmospheric deposition and climate change (Baron 1992; Baron et al. 2000; Campbell et al. 2000). It ranges in elevation from 4,009 m at the continental

divide to 3,110 m at the outlet of The Loch, the lowest elevation subalpine lake. Fully 80 % of LVWS is exposed rock and talus, and 3 % of talus may cover rock glaciers (Baron 1992; Clow et al. 2003). Other land cover includes 1 % permanent snow and ice, 11 % alpine, 6 % old-growth conifer forest, and 1 % wetlands. The climate is high-mountain continental with 105 cm of mean annual (1984–2012) precipitation, about 20 cm of which falls during the summer months. Mean annual (1984–2012) temperature is 1.4 °C and summer temperatures average 11.6 °C (<http://www.nrel.colostate.edu/projects/lvws/data.html>). Long-term Natural Resource Conservation Service Snow Telemetry (SNOTEL) data at Bear Lake, the nearest snow measurement site, show that average peak SWE of 50 cm occurred on April 25 for the period 1979–2010 (<http://www.wcc.nrcs.usda.gov/nwcc/site?sitenum=322&state=co>). Discharge from 1984 to 2010 measured at The Loch outlet averaged 79 cm yr<sup>-1</sup> (<http://www.nrel.colostate.edu/projects/lvws/data.html>).

### 3 Methods

We compared trends in surface-water chemical concentrations and fluxes with trends in air temperature, precipitation amount, SWE, and wet deposition chemistry. Seasonal water sampling with weekly summer sample collection began in 1983. Weekly year-round sampling of surface waters at The Loch outlet began in 1991 and continues to present. Annual trends are presented from 1991 to 2010. We used the longer (1983–2010) record for June, July, and August and summer (combined June, July, and August). Since no trends were observed for other months or seasons, these results are not reported. All data were reported for water years (WY) October 1 through September 30.

Surface-water samples collected at The Loch outlet were analyzed following standard procedures (<http://www.nrel.colostate.edu/projects/lvws/data.html>). Data quality assurance procedures included field blanks, field duplicates, charge balance calculations, and comparisons between theoretical conductance and measured conductance (Allstott et al. 1999; Botte and Baron 2004; Richer and Baron 2011). Export was calculated by multiplying weekly concentrations of individual solutes by weekly discharge. Weekly export loads were summed for the year, summer, and June, July, and August to yield watershed outputs in kilograms per hectare per year (kg ha<sup>-1</sup> yr<sup>-1</sup>). Data reported here include the sum of base cations (Ca<sup>2+</sup>, Mg<sup>2+</sup>, Na<sup>+</sup>, K<sup>+</sup>), SO<sub>4</sub><sup>2-</sup>, inorganic N, Cl<sup>-</sup>, acid-neutralizing capacity (ANC), and dissolved silica (SiO<sub>2</sub>).

Precipitation chemistry and amount have been measured at the National Atmospheric Deposition Program/National Trends Network (NADP/NTN) CO98 Loch Vale site (<http://nadp.sws.uiuc.edu/sites/siteinfo.asp?id=CO98&net=NTN>) located at an elevation of 3,159 m since 1983. Data reported in this study included precipitation amount, the sum of base cations, SO<sub>4</sub><sup>2-</sup>, inorganic N, and Cl<sup>-</sup>.

Daily temperature was measured at the Loch Vale Main Weather Station (<http://co.water.usgs.gov/lochvale/data.html>). Snow water equivalent was taken from the Bear Lake SNOTEL site (<http://www.wcc.nrcs.usda.gov/nwcc/site?sitenum=322&state=co>). Runoff-to-precipitation ratios (R:P) were calculated from measured discharge at The Loch outlet (<http://www.nrel.colostate.edu/projects/lvws/data.html>) and measured NADP precipitation at the CO98 site (<http://nadp.sws.uiuc.edu/sites/siteinfo.asp?id=CO98&net=NTN>). We assumed inter-annual comparability in catch efficiency. Precipitation measurements in snow-dominated mountain environments are always subject to uncertainty, but the analysis of overall error of NADP measurements from colocated samplers, including several

mountainous sites, concluded the magnitude of error in sample volume is of minor environmental significance to data users (Wetherbee et al. 2005).

### 3.1 Trends in Long-Term Data

The Mann–Kendall test (MKT) was used to evaluate trends in wet deposition and surface-water chemical fluxes and concentrations. The MKT was performed using annual, summer, and June, July, and August data using a statistical package from Helsel et al. (2006). Statistical significance was determined to the 95 % confidence interval ( $p \leq 0.05$ ) and noted with an asterisk in tables and figures. In the “Results” and “Discussion” sections below, significance is used to denote statistical significance with 95 % confidence.

### 3.2 Kendall Rank Correlation Test

The Kendall rank correlation test was used to determine the statistical significance of correlations between climatic variables, including temperature, runoff-to-precipitation ratio (R:P), and peak SWE, with observed trends in water chemistry at The Loch outlet. Kendall’s tau measures the monotonic strength of association between two independent nonparametric variables that exhibit skewness around a general trend (Helsel and Hirsch 2002). Correlations can either be described as positively correlated when Kendall’s tau is positive, negatively correlated when Kendall’s tau is negative, or no correlation when Kendall’s tau is zero. Statistical significance was determined to the 95 % confidence interval ( $p \leq 0.05$ ) and noted with an asterisk in tables and figures.

## 4 Results

### 4.1 Wet Deposition Trends

Analysis of 1991–2010 annual wet deposition showed no significant temporal trends for cations or inorganic N (Table 1). There was, however, a significant decline of  $\text{SO}_4^{2-}$ ,  $\text{H}^+$ , and  $\text{Cl}^-$  (Table 1). Annual  $\text{SO}_4^{2-}$  deposition decreased by  $0.12 \text{ kg ha}^{-1} \text{ yr}^{-1}$ , annual  $\text{H}^+$

**Table 1** Annual wet deposition and water chemistry flux trends from Mann–Kendall trend test results for WY1991–2010 in LVWS, Rocky Mountain National Park, CO

Solute	Wet deposition			Loch outlet flux		
	Trend ( $\text{kg ha}^{-1} \text{ yr}^{-1}$ )	<i>P</i> value	Trend	Trend ( $\text{kg ha}^{-1} \text{ yr}^{-1}$ )	<i>P</i> value	Trend
Cations	0.08	0.098	Increasing	0.17	0.284	Increasing
Inorg. N	0.00	0.897	No trend	0.03	0.330	Increasing
$\text{SO}_4^{2-}$	−0.12	0.003	Decreasing*	0.16	0.098	Increasing
$\text{H}^+$	−2.79E−03	0.008	Decreasing*	−1.84E−04	0.002	Decreasing*
$\text{Cl}^-$	−0.02	0.007	Decreasing*	0.02	0.153	Increasing
$\text{SiO}_2$	n/a	n/a	n/a	0.15	0.284	Increasing
ANC	n/a	n/a	n/a	0.23	0.183	Increasing

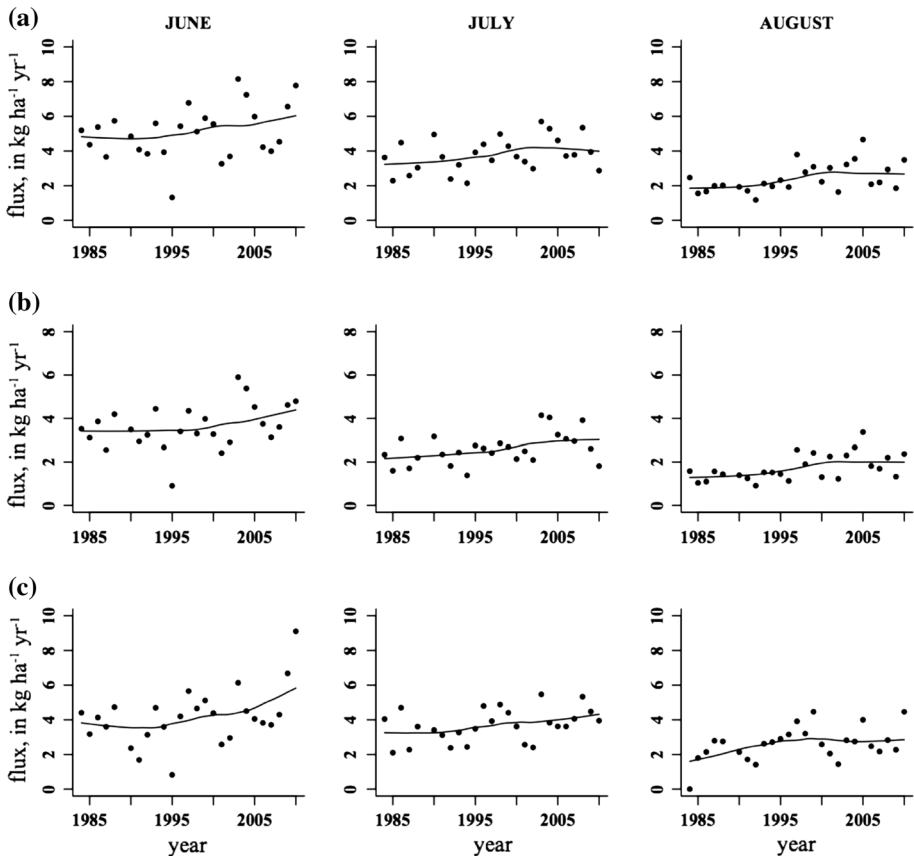
Statistically significant trends ( $p \leq 0.05$ ) are noted with an asterisk. Silica and ANC are not measured in wet deposition

deposition decreased by  $2.79 \times 10^{-3} \text{ kg ha}^{-1} \text{ yr}^{-1}$ , and annual  $\text{Cl}^-$  deposition decreased by  $0.02 \text{ kg ha}^{-1} \text{ yr}^{-1}$  (Table 1).

#### 4.2 Surface-Water Chemistry Trends

Using annual resolution, there was no significant trend over time in the 1991–2010 fluxes of weathering materials or inorganic N, except for  $\text{H}^+$ , which decreased by  $1.84 \times 10^{-4} \text{ kg ha}^{-1} \text{ yr}^{-1}$  (Table 1). The fluxes of all solutes increased during the summer months from 1984 to 2010, however, some significantly (Fig. 2). The greatest flux increase was observed in June for the cations,  $\text{SO}_4^{2-}$ , and ANC.

Not all trends were significant. Cation flux trends were not significant for June and July, in spite of an increase in summer flux (Table 2). The summer total cation flux was driven primarily by an August increase of  $0.05 \text{ kg ha}^{-1} \text{ yr}^{-1}$  (Fig. 2a; Table 2). The change in  $\text{SO}_4^{2-}$  flux was insignificant in July, but strong and significant increases of 0.11 and  $0.04 \text{ kg ha}^{-1} \text{ yr}^{-1}$  in June and August, respectively, provided a significant summer trend (Fig. 2b; Table 2). Acid-neutralizing capacity increased over time, with a summer increase



**Fig. 2** June, July, and August water chemistry flux in LVWS, Rocky Mountain National Park, CO, from 1984 to 2010 with smooth curve fitted by loess (locally weighted polynomial regression) for **a** cations, **b**  $\text{SO}_4^{2-}$ , and **c** ANC

**Table 2** Summer, June, July, and August water chemistry flux and concentration trends from Mann–Kendall test results for WY1984–2010 from LVWS, Rocky Mountain National Park, CO

Solute	Time period	Flux			Concentration		
		Trend (kg ha <sup>-1</sup> yr <sup>-1</sup> )	<i>P</i> value	Trend	Trend (mg l <sup>-1</sup> yr <sup>-1</sup> )	<i>P</i> value	Trend
Cations	Summer	0.13	0.028	Increasing*	0.02	0.005	Increasing*
	June	0.05	0.146	Increasing	0.02	0.004	Increasing*
	July	0.04	0.086	Increasing	0.02	0.004	Increasing*
	August	0.05	0.018	Increasing*	0.06	0.022	Increasing*
SO <sub>4</sub> <sup>2-</sup>	Summer	0.02	0.017	Increasing*	0.02	0.017	Increasing*
	June	0.11	0.012	Increasing*	0.02	0.028	Increasing*
	July	0.04	0.058	Increasing	0.02	0.007	Increasing*
	August	0.04	0.016	Increasing*	0.04	0.016	Increasing*
ANC	Summer	0.13	0.087	Increasing	0.02	0.004	Increasing*
	June	0.07	0.113	Increasing	0.02	0.001	Increasing*
	July	0.04	0.028	Increasing*	0.02	0.003	Increasing*
	August	0.03	0.103	Increasing	0.02	0.006	Increasing*
SiO <sub>2</sub>	Summer	0.20	0.015	Increasing*	0.01	0.033	Increasing*
	June	0.09	0.086	Increasing	0.02	0.007	Increasing*
	July	0.02	0.402	Increasing	0.01	0.134	Increasing
	August	0.03	0.156	Increasing	0.03	0.156	Increasing
Inorg. N	Summer	0.02	0.058	Increasing	3.27E–03	0.086	Increasing
	June	4.53E–03	0.428	Increasing	2.58E–03	0.103	Increasing
	July	6.17E–03	0.158	Increasing	3.20E–03	0.04	Increasing*
	August	7.64E–03	0.009	Increasing*	0.01	0.009	Increasing*
Cl <sup>-</sup>	Summer	0.01	0.052	Increasing	0.00	0.108	No trend
	June	4.68E–03	0.158	Increasing	1.50E–03	0.134	Increasing
	July	3.14E–03	0.086	Increasing	1.08E–03	0.139	Increasing
	August	2.56E–03	0.104	Increasing	2.56E–03	0.104	Increasing

Statistically significant trends ( $p \leq 0.05$ ) are noted with an asterisk

of 0.13 kg ha<sup>-1</sup> yr<sup>-1</sup>, but the only significant flux trend occurred in July (Table 2). The summer increase in SiO<sub>2</sub> flux of 0.20 kg ha<sup>-1</sup> yr<sup>-1</sup> was significant, but the trends were not significant for any individual month (Table 2). Finally, even though there was an increase in the amount of inorganic N and Cl<sup>-</sup> flux over time, the only significant increase was for inorganic N in August (Table 2).

The concentrations of nearly all solutes increased significantly in all summer months from 1984 to 2010 (Table 2). The exceptions were SiO<sub>2</sub>, inorganic N, and Cl<sup>-</sup>, whose trends were significant in some, but not all, months. A significant summer increase in SiO<sub>2</sub> concentration was driven by June values. Concentrations of inorganic N increased in all months, but the rate of increase, which was slight, was only significant in July and August. The increase in Cl<sup>-</sup> concentrations over time was very small and insignificant (Table 2).

We compared the solute flux with environmental drivers to get an idea of causes for increasing flux over time from LVWS. All solute fluxes for all time periods were positively

correlated with average maximum July temperature, R:P, and peak SWE at The Loch outlet (except for annual  $\text{Cl}^-$  flux, August  $\text{SO}_4^{2-}$  flux, and all inorganic N flux with peak SWE), but not all correlations were significant (Table 3). The flux of different solutes displayed almost unique responses to different drivers. The annual cation flux correlated significantly with R:P, while June and July cation fluxes correlated significantly with peak SWE. August cation flux was significantly related to average maximum July temperatures. Annual  $\text{SO}_4^{2-}$  flux correlated positively with average maximum July temperatures and R:P. Acid-neutralizing capacity and  $\text{SiO}_2$  fluxes were significantly correlated with peak SWE annually and for June and July. July  $\text{SiO}_2$  flux was also significantly correlated with R:P. Annual, June, and July inorganic N fluxes were significantly correlated with R:P, while the August inorganic N flux was most strongly correlated with maximum July temperatures. Chloride fluxes were not significantly related to any driver. None of the solutes showed a significant correlation with wet deposition (Table 3).

**Table 3** Correlations of annual, June, July, and August solute fluxes with average maximum July temperatures, runoff-to-precipitation ratios (R:P), peak snow water equivalent (SWE), and wet deposition using Kendall rank correlations for WY1991–2010

Solute flux	Season	Avg. Max July Temp.	R:P	Peak SWE	Wet deposition
Cations	Annual	+	+*	+	–
	June	N/A	+	+*	
	July	+	+	+*	
	August	+*	+	+	
$\text{SO}_4^{2-}$	Annual	+*	+*	+	–
	June	N/A	+	+	
	July	+	+	+	
	August	+	+	0	
ANC	Annual	+	+	+*	N/A
	June	N/A	+	+*	
	July	+	+	+*	
	August	+	+	+	
$\text{SiO}_2$	Annual	+	+	+*	N/A
	June	N/A	+	+*	
	July	+	+*	+*	
	August	+	+	+	
Inorg. N	Annual	+*	+*	+	+
	June	N/A	+*	+	
	July	+	+*	+	
	August	+*	+	–	
$\text{Cl}^-$	Annual	+	+	0	–
	June	N/A	+	+	
	July	+	+	+	
	August	+	+	+	

June flux values were not compared with July temperatures. Positive correlations are noted with a plus sign (+); negative correlations are noted with a minus sign (–); and no correlation is noted with a zero (0). Statistically significant trends ( $p \leq 0.05$ ) are noted with an asterisk



### 4.3 Comparison of Flux in Extreme Years

We calculated the mean annual flux for all solutes for the warmest and coolest Julys, highest and lowest R:P years, and wettest (highest SWE) and driest (lowest SWE) years in order to gain insight into causal agents of change. Extremes were defined as the five lowest and five highest years for average maximum July temperatures, R:P, and peak SWE (Fig. 3; Table 4). The Mann–Whitney  $U$  test was used to determine whether the two extremes (lowest and highest) came from the same distribution.

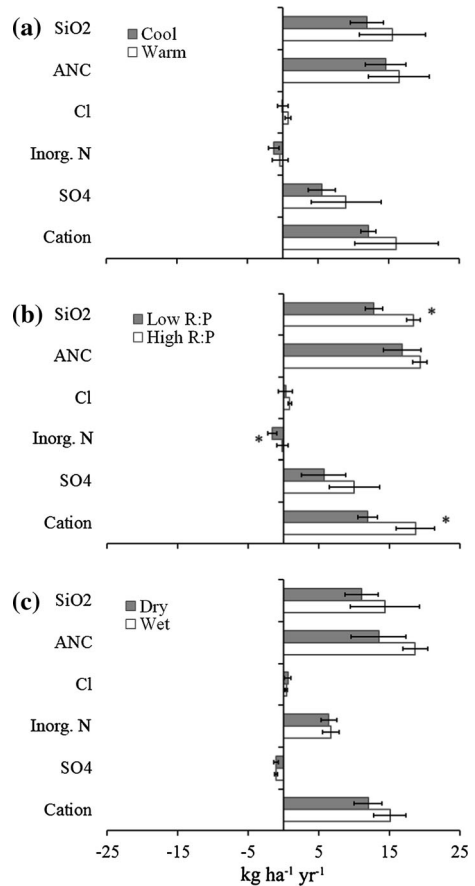
There were greater annual fluxes of  $\text{SiO}_2$ , ANC,  $\text{SO}_4^{2-}$ , and cations in LVWS in years with the warmest July temperatures, but the increases were not statistically significant (Fig. 3a; Table 4). Years with the highest R:P produced more  $\text{SiO}_2$ , ANC,  $\text{Cl}^-$ ,  $\text{SO}_4^{2-}$ , and cations compared to years with the lowest R:P, and the difference was significant for  $\text{SiO}_2$  and cations (Fig. 3b). Years with the highest R:P had an average annual production of 18.67 (SD = 2.69) kg cations  $\text{ha}^{-1} \text{yr}^{-1}$  and 18.37 (SD = 0.97) kg  $\text{SiO}_2 \text{ha}^{-1} \text{yr}^{-1}$ . The years with the lowest R:P had an annual average production of 11.91 (SD = 1.38) kg cations  $\text{ha}^{-1} \text{yr}^{-1}$  and 12.79 (SD = 1.24) kg  $\text{SiO}_2 \text{ha}^{-1} \text{yr}^{-1}$  (Table 4b). In high R:P years, significantly less inorganic N was retained (0.20 (SD = 0.82) kg N  $\text{ha}^{-1} \text{yr}^{-1}$ ) in the watershed than years when the R:P was low (1.61 (SD = 0.67) kg N  $\text{ha}^{-1} \text{yr}^{-1}$ ). Years with the highest peak SWE resulted in greater net flux of cations, inorganic N, ANC, and  $\text{SiO}_2$  in LVWS compared to years with the lowest peak SWE, but the differences were not statistically significant (Fig. 3c; Table 4).

The R:P ratio is related to July maximum temperatures (Fig. 4). The average R:P was 0.77 from 1984 to 2010, suggesting slightly more than 23 % of precipitation was evaporated, transpired, or sublimated. Runoff approached or exceeded precipitation with R:P of 0.90, 0.89, 1.00, 1.16, 0.88, and 0.95, respectively, in water years 1998, 1999, 2000, 2003, 2005, and 2006 (Fig. 4a). Average maximum July temperatures were significantly and positively correlated with annual R:P ( $p = 0.034$ ), suggesting that July temperatures influence the amount of discharge. In most years when the R:P was greater than average, the autumn (September, October, November) discharge was also greater than average (Fig. 4b).

**Table 4** Comparison of the mean and standard deviation annual flux, in kg  $\text{ha}^{-1} \text{yr}^{-1}$ , for the five coolest versus warmest years, lowest runoff-to-precipitation ratio (R:P) versus highest R:P years, and driest (low peak SWE) versus wettest years (high peak SWE)

a)	Warmest maximum July temperatures						Coldest maximum July temperatures					
	Cations	$\text{SO}_4^{2-}$	Inorg.N	$\text{Cl}^-$	ANC	$\text{SiO}_2$	Cations	$\text{SO}_4^{2-}$	Inorg.N	$\text{Cl}^-$	ANC	$\text{SiO}_2$
Average	16.08	8.96	-0.42	0.71	16.45	15.56	12.16	5.47	-1.29	-0.03	14.57	11.94
SD	5.89	4.97	1.11	0.44	4.29	4.67	1.06	1.92	0.76	0.73	2.87	2.34
b)	High R:P						Low R:P					
	Cations	$\text{SO}_4^{2-}$	Inorg.N	$\text{Cl}^-$	ANC	$\text{SiO}_2$	Cations	$\text{SO}_4^{2-}$	Inorg.N	$\text{Cl}^-$	ANC	$\text{SiO}_2$
Average	18.67	10.00	-0.20	0.88	19.30	18.37	11.91	5.69	-1.61	0.28	16.81	12.79
SD	2.69	3.57	0.82	0.25	1.05	0.97	1.38	3.13	0.67	1.01	2.62	1.24
c)	High peak SWE						Low peak SWE					
	Cations	$\text{SO}_4^{2-}$	Inorg.N	$\text{Cl}^-$	ANC	$\text{SiO}_2$	Cations	$\text{SO}_4^{2-}$	Inorg.N	$\text{Cl}^-$	ANC	$\text{SiO}_2$
Average	15.05	-1.09	6.69	0.36	18.64	14.37	11.97	-1.10	6.41	0.57	13.49	11.03
SD	2.30	0.26	1.20	0.19	1.78	4.93	2.00	0.34	1.10	0.48	3.88	2.36

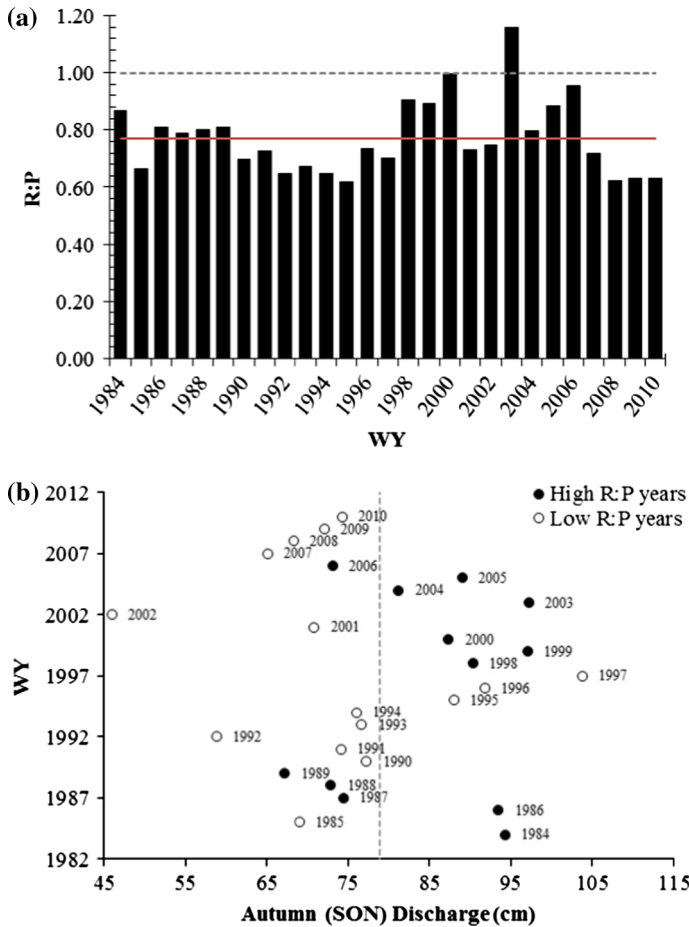
**Fig. 3** Comparison of means for the five most extreme years: **a** coolest versus warmest maximum July temperatures; **b** lowest R:P (runoff-to-precipitation ratio) versus highest R:P; and **c** driest (low peak SWE) versus wettest (high peak SWE). Error bars depict standard deviation



## 5 Discussion

Surface-water chemistry in LVWS is changing significantly during the summer months. This was not apparent using an annual time step, but is obvious in strong summer increases in weathering products and inorganic N. Annual fluxes in LVWS, as in other high-mountain watersheds with seasonal snowpacks, are dominated by snowmelt. Snowmelt drives the annual hydrograph and annual flux values, and while it may indirectly influence weathering rates, as discussed below, our observed changes in summer flux are too small to influence the annual totals.

There were significant increases in the summer fluxes and concentrations of cations, SiO<sub>2</sub>, SO<sub>4</sub><sup>2-</sup>, and ANC, and in inorganic N over time. Surprisingly, none of the trends were statistically correlated with wet atmospheric deposition. Instead, LVWS solute concentrations and flux were correlated with average maximum July temperature, R:P, and SWE. The greatest increases over time in concentrations and fluxes at The Loch outlet occurred in July and August. Hydrologically, this is commensurate with the receding hydrograph and return to base flow, as has been shown for other alpine catchments (e.g., Williams and Melack 1991). Late summer is also the time of maximum cryosphere thaw. We observed this with LVWS R:P ratios in warm years, and it matches theoretical constructs posed by



**Fig. 4** Time-series column plot of **a** the annual runoff-to-precipitation ratio (R:P) in LVWS for water years (WY) 1984 to 2010. The red line depicts the average annual R:P, while the *black dashed line* represents when runoff equals precipitation inputs; and **b** Autumn cumulative discharge for above average R:P years (*solid circles*) and below average R:P years (*hollow circles*). The *gray dashed line* represents average autumn discharge for LVWS

Clow et al. (2003) and Williams et al. (2006), which suggest increasing contributions of glacier, rock glacier, and permafrost melt to mountain streams as the 0 °C isotherm increases in elevation.

The increase in runoff in higher R:P years is much greater than can be accounted for entirely by glacial melt from small headwater glacial remnants. While some runoff may come from melting ice, high R:P may be more related to the snowmelt rate, with warm summer temperatures leading to more rapid melt and thus more runoff export instead of subsurface storage. The presence of liquid water in talus and block fields, or in newly thawed substrates, may enhance chemical weathering of calcite and apatite that are exposed by mechanical weathering (Mast et al. 1990, 1992; Price et al. 2013). Hall et al. (2002) suggested chemical weathering in cold environments is limited by moisture availability rather than temperature. Under this framework, it is possible that warm Julys increase the water available for mineral dissolution by thawing glacial ice or seasonal snow. In years of high SWE, seasonal snow

persists longer into the summer, providing meltwater later in the summer season. Anderson et al. (1997) found chemical weathering in glacial environments to be relatively high, as have others in more recent studies (Williams et al. 2006; Saros et al. 2010; Caine 2010). Cation,  $\text{SiO}_2$ , and ANC fluxes were positively correlated with peak SWE during June and July, the months that often correspond with spring snowmelt, suggesting a relationship between years with high snowfall and water chemical composition.

The source of some solutes coming from the cryosphere could include dry deposition in the form of dust or enhanced chemical weathering caused by prolonged moisture contact with rock as described above. Bulk snowpack chemistry data from the USGS Rocky Mountain Snowpack Chemistry Network ([http://co.water.usgs.gov/projects/RM\\_snowpack/index.html](http://co.water.usgs.gov/projects/RM_snowpack/index.html)) reveal cation concentrations in the LVWS snowpack have been increasing since 1993. A 2006 dust event covered much of the Rocky Mountains, including LVWS, resulting in a 10-fold increase in  $\text{Ca}^{2+}$  and 100-fold increase in ANC compared to early- and late-season snow (Rhoades et al. 2010). The concentration of cations in the LVWS snowpack in 2006 was  $24.2 \text{ meq L}^{-1}$ , while a similar dust event in 2008 resulted in a concentration of  $26.6 \text{ meq L}^{-1}$ . Neff et al. (2008) suggested that dust loads increased by 500 % following western settlement of the United States during the nineteenth century. In recent decades, the San Juan Mountains in southern Colorado experience up to seven large dust deposition events every year. Based on these studies, there is no doubt that episodic dust events add minerals to the snowpack and that the occurrence of these events is increasing. However, the importance of these events on LVWS water quality is unknown.

We previously hypothesized that increased late summer inorganic N flux could be the result of some combination of N released from melting ice and enhanced microbial nitrification rates (Baron et al. 2009). Recent research suggests both mechanisms are plausible. Saros et al. (2010) found higher concentrations of nitrate ( $\text{NO}_3^-$ ) in glacial meltwater compared to seasonal snow meltwater in the central and northern Rocky Mountains, and ice samples from two Front Range glaciers in 2012 contained considerable inorganic N (J.S. Baron, unpublished data). Even a small input of melting ice may affect water chemistry in warm years when rapid snowmelt leads to more runoff and export. Microbial nitrification also occurs in periglacial environments (Wynn et al. 2007; Saros et al. 2010; Osborne 2012). As with weathering rates, it appears moisture, not temperature, may govern microbial activity in cold environments. Additional evidence of microbial nitrification comes from comparison of isotopes in  $\text{NO}_3^-$  in snowpack, snowmelt, rainfall, and surface water. During snowmelt and throughout the summer, much of the inorganic N in stream water bears the signature of microbial nitrification, even at the highest elevations directly below ice (Campbell et al. 2000; E.K. Hall personal communication).

## 6 Conclusions

Watershed mass-balance methods have been valuable tools for demonstrating impacts to water quality from atmospheric deposition, leading to air quality policies that have greatly improved the ecological condition of US surface waters (Likens et al. 2001; Greaver et al. 2012). Mass-balance studies have also been fundamental to our understanding the role of mineral weathering on water quality (Bricker 1986; Price et al. 2013). By exploring the change in mass balances over time in LVWS, we have discovered a change in summer water chemistry and export in response to warming summer temperatures and SWE. The connection between these drivers and the flux of weathering products and inorganic N is not necessarily direct. Warm summer temperatures and high SWE may stimulate mineral

weathering with enhanced moisture availability, and warm summer temperatures may melt what was once permanent ice to release elements entrained therein. Moisture availability also appears to increase microbial nitrification, and all these processes likely contribute to summer season increases in LVWS chemical fluxes. There is an unknown but increasing influence of dust inputs. While long-term monitoring in instrumented watersheds has been criticized as unscientific, wasteful, and expensive, it is empirical studies such as these that increase our ability to understand and quantify cause and effect in times of rapid environmental change.

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