

Water Resources Research

RESEARCH ARTICLE

10.1002/2016WR019693

Special Section:

Concentration-Discharge Relations in the Critical Zone

Key Points:

Concentration-discharge relationships for streams in the Sierra Nevada are nearly chemostatic at streamflow rates higher than 50 L s^{-1} . Elevated levels of N, P, and S in streams indicate a “first flush” occurring during the first fall rains after the dry summer. Soil contents and stream concentration relationships are strong for Ca, Na, and P suggesting soil chemistry influences stream water chemistry. O-horizon interflow is a hydrologic pathway that should be considered for concentration-discharge relationships in Mediterranean forests.

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Citation:

Hunsaker, C. T., and D. W. Johnson (2017), Concentration-discharge relationships in headwater streams of the Sierra Nevada, California, *Water Resour. Res.*, 53, 7869–7884, doi:10.1002/2016WR019693.

Received 24 AUG 2016

Accepted 9 APR 2017

Accepted article online 25 APR 2017

Published online 14 SEP 2017

Concentration-discharge relationships in headwater streams of the Sierra Nevada, California

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Abstract We examined stream water concentration-discharge relationships for eight small, forest watersheds ranging in elevation from 1485 to 2465 m in the southern Sierra Nevada. These headwater streams revealed nearly chemostatic behavior by current definitions for K^+ , Ca^{2+} , Mg^{2+} , Na^+ , Cl^- , and SO_4^{2-} in most cases but not for NH_4^+ , NO_3^- , or ortho-P. The latter ions were somewhat enriched during high flows. All ions studied showed a dilution process at lower flows ($<50 \text{ L s}^{-1}$) with the concentration-discharge relationship being more chemostatic at higher flows. While previous studies in the Sierra Nevada have reported peak concentrations of NH_4^+ , NO_3^- , and SO_4^{2-} during snowmelt, the headwater systems of the Kings River Experimental Watersheds experience peak concentrations of these ions during the fall rains after the dry summer. These forested watersheds span the rain-snow transition zone, are 49–228 ha in size, and have soils derived from granite. A statistically significant relationship between soils and stream water concentrations for ortho-P, Ca^{2+} , and Na^+ strongly suggests that soil chemistry has a major influence on stream water chemistry. Factors controlling stream water NH_4^+ , NO_3^- , and SO_4^{2-} concentrations are less clear, but one possible source of spikes in these ions during storm events is input from O-horizon runoff where high concentrations were measured. Overall, stream water concentration-discharge relationships for these Sierran watersheds are similar to those found in other watershed systems (nearly chemostatic); however, the dominant processes controlling these relationships are probably localized because of different watershed characteristics like soil chemistry, vegetation cover, hydrologic flow paths, and weather patterns.

1. Introduction

Knowing more about the hydrological processes that control stream chemistry and the sources of chemical inputs is important for understanding how changing climate and future landscape conditions might change stream chemistry. Headwater streams (first to third order) make up a substantial proportion of the drainage network in mountain forests; Meyer *et al.* [2003] state that at least 80% of the nation's stream network is made up of small or headwater streams. Godsey *et al.* [2009] stated that chemical weathering of rock and solute transport are coupled with hydrology in watersheds and that this coupling is reflected in the relationships between solute concentrations and stream discharge. Scientists often study concentration-discharge relationships to better understand hydrological processes and chemical sources. Brooks *et al.* [2015] review our knowledge of how the amount, routing, and residence time of water in the subsurface is related to the biogeophysical structure of the critical zone and state that there is a “common knowledge gap” in how precipitation is partitioned in the critical zone. An examination of 59 geochemically diverse and undisturbed US watersheds of various sizes (8–5196 km^2) showed that their concentration-discharge relationships exhibit nearly chemostatic behavior for weathering products such as Ca, Mg, Na, and Si [Godsey *et al.*, 2009]. This behavior implies that solute concentrations in stream water are not determined by simple dilution of a fixed solute flux by a variable flux of water. In some studies more biologically active ions such as K^+ and NO_3^- have shown increased concentrations with increased flow; this has been attributed to several factors such as leaching from litter during higher flows, an artifact of limited sampling, or instrument changes on very dilute stream waters [Godsey *et al.*, 2009].

Several studies in the Sierra Nevada have investigated concentration-discharge relationships in stream waters. Williams and Melack [1991] investigated the effect of snowpack runoff on the chemical composition of streams in the Emerald Lake watershed in the southern Sierra Nevada. These authors noted pulses of NO_3^- , Cl^- , and SO_4^{2-} in stream waters during snowmelt that they attributed to pulses of these ions from

melting snowpack. They also noted a reduction in stream water base cations and acid neutralizing capacity (ANC) during snowmelt which was attributed to dilution. In a later paper, *Sickman et al.* [2003] reported that 50–70% of the NO_3^- pulses in streams during snowmelt at the Emerald Lake watershed originated from soils and talus, with the remainder coming from the snowpack. *Williams and Melack* [1997] reported significant, negative effects of discharge on concentrations of ANC and base cations (dilution) in streams draining mixed conifer forests (Tharp's Creek and Log Creek) in Sequoia National Park, California. These authors also noted positive relationships between discharge and SO_4^{2-} concentrations, but no consistent relationships between discharge and Cl^- , NO_3^- , NH_4^+ , or ortho-P. *Williams et al.* [2001] reported that soils and mineral weathering were important factors affecting Ca and K export in streams from small, rock-dominated subalpine catchments in Sequoia National Park, California. *Leonard et al.* [1979] reported that stream water NO_3^- concentrations peaked during snowmelt in Ward Creek in the Lake Tahoe Basin. *Coats and Goldman* [2001] reported that stream water NO_3^- peaked during the first phases of snowmelt and then later decreased during a "washout" phase later in the snowmelt period in both Ward and Blackwood creeks in the Tahoe Basin. A lot of variability in concentration-discharge relationships has been observed even within the Sierra Nevada.

Herndon et al. [2015] state that it remains difficult to develop generalized models for solute concentration-discharge behavior and recommend comparisons across catchments with the same lithology. In this paper, we examine concentration-discharge relationships for base cations and nitrogen, phosphorus, and sulfur (N, P, and S) in eight small watersheds of the southern Sierra Nevada, all with granite lithology, and compare them to the relationships found in relatively undisturbed streams of the Sierra Nevada and in select streams/rivers of the Hydrologic Benchmark Network in the United States [*Godsey et al.*, 2009]. We also compare solid soil content to stream water chemistry. Finally, we examine hypotheses for the observed differences in the concentration-discharge relationships for base cations, N, P, and S. These include (1) flow through the litter layer [*Johnson et al.*, 2011b; *Miller et al.*, 2005], (2) snowpack storage [*Sickman et al.*, 2003], and (3) relative contribution of different water sources to streamflow [*Liu et al.*, 2012].

2. Materials and Methods

2.1. Study Area

This research was performed on eight first and second-order perennial streams that make up the Kings River Experimental Watersheds (KREW) in the southern Sierra Nevada, California (Figure 1). KREW is a long-term research area established by the Forest Service, and the lower elevation portion includes part of the National Science Foundation's Southern Sierra Critical Zone Observatory. The Providence site (D102, P301, P303, and P304) ranges in elevation from 1485 to 2115 m and is at the rain-snow transition zone with 35–60% of precipitation in snow. Precipitation at the Bull site (B201, B203, B204, and T003) is dominated by snow (75–90%) and the elevation ranges from 2050 to 2490 m. On average over 90% of the total annual precipitation occurs between October and April in this Mediterranean climate, and the average annual precipitation is 123–139 cm across the elevations that we measure [*Safeeq and Hunsaker*, 2016].

KREW was designed by the authors as a replicated, paired-watershed study, thus the watersheds were chosen to be as similar as possible based on information available in 2000. The dominant forest cover is Sierran mixed-conifer, and all soils are derived from granite. None of this research area has had fire for over 100 years according to the records of the Sierra National Forest; thus, the organic or O-horizon (litter) layer was quite thick during the period studied. The watersheds range in size from 0.5 km² (P304 and B201) to 2.3 km² (T003). All of these watersheds have annual evapotranspiration exceeding precipitation as quantified by a runoff ratio of less than 50%. The characteristics that mainly control between-site differences are the lower temperatures at the higher elevations of the Bull site and consequently the dominant form of precipitation there is snow. While physically adjacent in their site groups (Figure 1) and similar in many landscape characteristics, there are some hydrologic and soil differences within each group (Table 1). The high elevation Cagwin soils have rapid permeability and a shallow rooting depth (50–120 cm) when compared to the Shaver soils in the Providence site which have moderately rapid permeability and a deeper rooting depth (102–203 cm) [*Giger and Schmitt*, 1983]. Perhaps the most striking difference is the low streamflow variability and high base flow index for P304 and somewhat for T003; this indicates a strong groundwater influence for these streams. Streamflow variability is highest for B203 and P303; this indicates quick flow

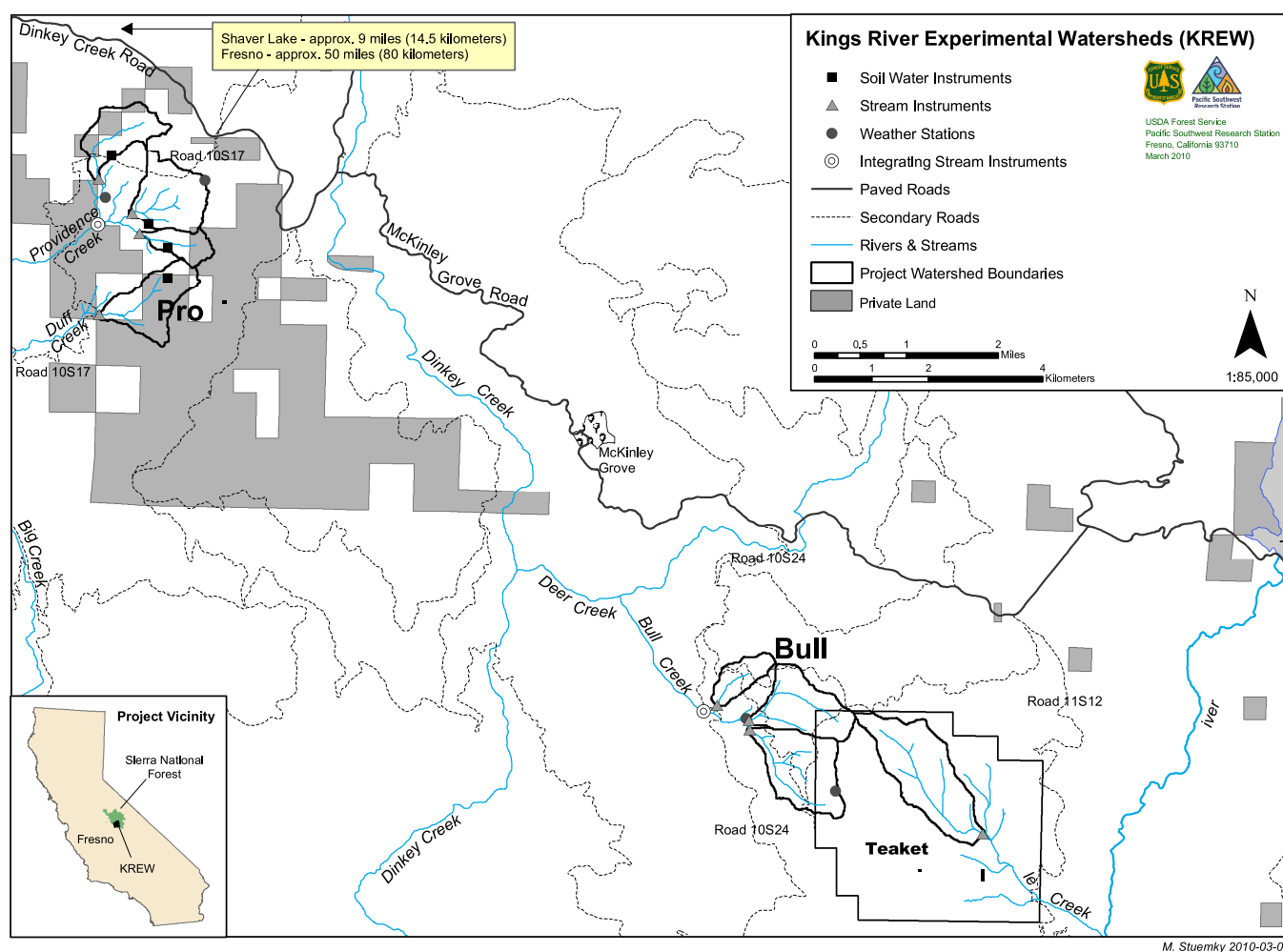


Figure 1. The Kings River Experimental Watersheds study area (map centroid Lat 36°57'55" Lon 119°3'2") is comprised of two sites, Providence and Bull, each with a group of four watersheds. Watershed codes from the top left to the bottom right are P301, P303, P304, and D102 in Providence site and B201, B203, B204, and T003 in Bull site. Stream and weather instrument locations are shown.

Table 1. Watershed Physical Characteristics and Stream Hydrologic Characteristics [Safaeq and Hunsaker, 2016; Hunsaker et al., 2012; Hunsaker and Neary, 2012; Johnson et al., 2011a]^a

Characteristic (Unit)	Bull Site				Providence Site			
	T003	B204	B203	B201	P303	D102	P301	P304
Watershed area in km ² (ha)	2.3 (228)	1.7 (167)	1.4 (138)	0.5 (53)	1.3 (132)	1.2 (121)	1.0 (99)	0.5 (49)
Mean elevation (m)	2289	2365	2373	2257	1905	1782	1979	1899
Elevation range (m)	2050–2465	2195–2490	2185–2490	2145–2380	1730–1990	1485–1980	1790–2115	1760–1980
Average slope (%)	24	17	18	18	20	27	19	22
Drainage density (km/km ²)	5.5	5.0	4.6	6.0	7.4	10.1	7.4	6.9
Channel length (km)	3.1	2.2	2.2	0.8	0.8	1.4	1.5	0.9
Dominant soil type (% of area)	Cagwin 94%	Cagwin 98%	Cagwin 80%	Cagwin 67%	Shaver 66%	Shaver 48%	Gerle-Cagwin 62%	Shaver 55%
Q _{min} (mm/d)	0.19	0.11	0.08	0.12	0.03	0.06	0.03	0.36
Q _{max} (mm/d)	8.46	11.95	14.26	9.13	8.22	10.09	10.04	6.63
Q _{mean} (mm/d)	1.40	1.50	1.80	1.19	0.77	0.81	1.11	1.12
Streamflow variability or slope of the flow duration curve	–2.58	–3.25	–4.04	–2.29	–3.71	–3.33	–3.69	–1.85
Base flow index (%)	76.1	68.1	68.2	73.3	74.3	76.0	71.6	88.1
Recession constant or k (day)	0.027	0.031	0.037	0.033	0.031	0.027	0.036	0.014
Runoff ratio (%)	33.4	35.8	42.9	28.4	17.7	19.7	25.9	29.4

^aThe largest value for a characteristic within each site is shown in bold and the smallest in italics.

and a flashy hydrograph. *Hunsaker et al.* [2012] and *Safeeq and Hunsaker* [2016] describe the hydrology and meteorology characteristics of the study area; *Johnson et al.* [2011a] describe the soil characteristics in detail.

2.2. Data

We analyzed data for 8 years from 2004 through 2011. Stream water grab samples were collected by hand on a regular schedule every 2 weeks. Stream water samples were also collected by automated ISCOTM samplers during high-flow events. Streamflow varies substantially during the year; thus, a “high-flow event” is relative to stream discharge because the field technician may change the magnitude required for a sampling event in the sampler program based on the discharge observed during the previous 2 week period. For example, a flow of at least 10 mm above the previous daily maximum stage must be maintained for 30 min before a sample is taken; once this criteria is met a sample is taken every 30 min, as long as the flow remains above the sample enable criteria, until all 20 bottles are filled. At a minimum, an event sample for chemistry analyses was ideally collected on the rising side, the falling side, and the peak of the event hydrograph. Water samples were kept cool while in the field and frozen the same day they were collected (samples were not filtered or acidified prior to freezing). ISCOTM samplers were not run from July through September because there are almost no summer rain events and nutrients would not be stable at the summer temperatures inside the instrument sheds. All chemistry analyses were performed by the Forest Service’s Riverside Fire Sciences Laboratory, Riverside, California. Calcium, Mg, K, Na, SO_4^{2-} , NO_3^- , and Cl^- were analyzed by Ion Chromatography (EPA Method 300.1) and ammonium and ortho-P were analyzed by automated colorimetric analysis (EPA Methods 365.1 and 350.1, respectively). Samples that were reported as below detection limits ($\text{Ca}^{2+} = 1.25 \mu\text{mol L}^{-1}$, $\text{Mg}^{2+} = 2.06 \mu\text{mol L}^{-1}$, $\text{K}^+ = 1.28 \mu\text{mol L}^{-1}$, $\text{Na}^+ = 2.13 \mu\text{mol L}^{-1}$, $\text{SO}_4^{2-} = 0.52 \mu\text{mol L}^{-1}$, $\text{NO}_3^- = 0.81 \mu\text{mol L}^{-1}$, $\text{Cl}^- = 1.41 \mu\text{mol L}^{-1}$, $\text{NH}_4^+ = 2.78 \mu\text{mol L}^{-1}$, and ortho-P = $0.53 \mu\text{mol L}^{-1}$) were converted to half the value between 0 and the detection limit for the purposes of averaging and plotting.

Volume-weighted average annual stream concentrations were calculated as described by *Williams and Melack* [1997],

$$C_w = \frac{\sum_{i=1}^n C_i V_i}{\sum_{i=1}^n V_i}, \quad (1)$$

where C_w = weighted average concentration, C_i = concentration in sample i , and V_i = volume of water in discharge in sample i . Discharge was measured on a 15 min basis whereas concentrations were measured either closely spaced during an event or approximately biweekly for grab samples. Thus, each concentration sample was applied to the cumulative discharge values over the intervals between midpoints in time between concentration sample collections [*Williams and Melack*, 1997]. Student’s t tests were conducted using Microsoft Excel[®] software. Regression analyses were performed using DataDesk 7[®] software.

Soil nutrient contents reported in this paper were taken from *Johnson et al.* [2011a]. A total of 87 quantitative soil pits were dug over the Bull and Providence watersheds and sampled for bulk density, coarse fragment content, and nutrient concentrations. From this data, soil mass and nutrient contents (kg ha^{-1}) were calculated.

3. Results

3.1. Concentration-Discharge Relationships

Figure 2 shows plots of discharge versus concentration for the eight watersheds monitored in this study. The solid symbols indicate watersheds within the Providence site, the open symbols indicate those within the Bull site. In each case, the data show strong decreasing concentrations with discharge up to approximately 50 L s^{-1} (1.9–8.8 mm/d depending on watershed size) of discharge, after which concentrations tend to level off with some outliers of high concentration in the cases of NH_4^+ , NO_3^- , and ortho-P.

Godsey et al. [2009] suggested plotting log concentrations ($\log[C]$) against log discharge ($\log[Q]$) and using the slope (m) as an indicator of “nearly chemostatic behavior.” Figure 3 shows plots of log concentration against log discharge for our data, and Table 2 provides slopes and coefficients of determination (r^2 values), with a notation when the probability values for the slopes were different from zero ($P < 0.05$). A slope of

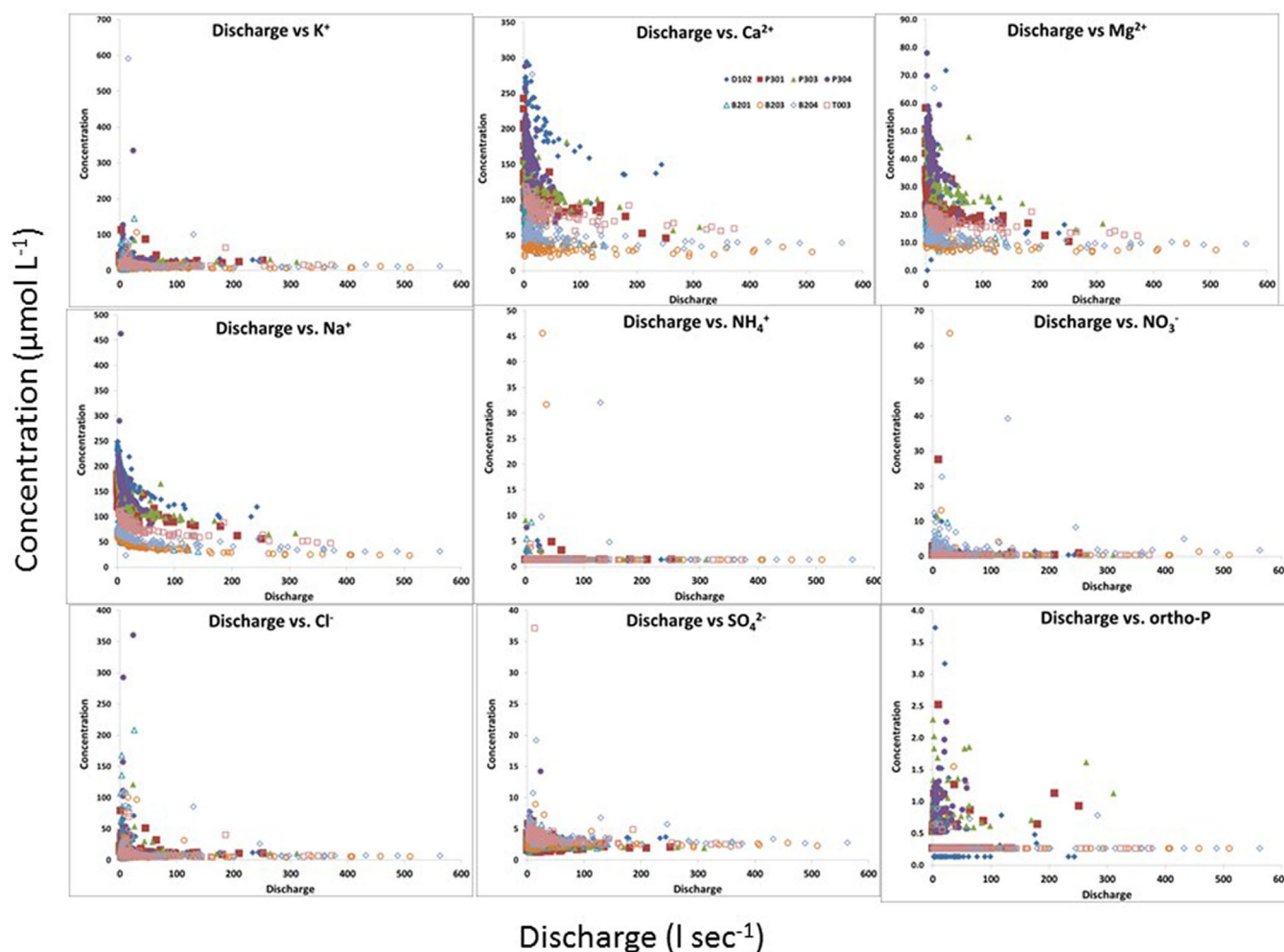


Figure 2. Concentration-discharge relationships for potassium, calcium, magnesium, sodium, ammonium, nitrate, chloride, sulfate, and ortho-phosphate.

zero would indicate that the watershed behaves chemostatically, meaning the system keeps concentrations constant as discharge varies [Godsey *et al.*, 2009]. Conversely, a slope of -1 would indicate that concentrations vary inversely with discharge and that dilution was functioning as the dominant process controlling concentrations. The slopes from our regression analyses were negative, close to zero, and almost always highly significant (different from a zero slope) according to traditional P values ($P < 0.05$) for all eight watersheds for Ca^{2+} , Mg^{2+} , K^{+} , Na^{+} , and Cl^{-} (Table 2). Thus according to the criteria given by Godsey *et al.* [2009], our headwater systems exhibited “nearly chemostatic” behavior for base cations, as well as Cl^{-} and SO_4^{2-} . Despite statistical significance, however, the r^2 values for the regressions were low (<0.20) in many cases for Ca^{2+} and Mg^{2+} , and in all cases for K^{+} and Cl^{-} . Only in the case of Na^{+} did both statistical significance and r^2 values suggest a strong relationship between discharge and concentration. For ortho-P and SO_4^{2-} , half or less of the slopes were statistically significant (different from a zero slope) and r^2 values were low (<0.20) in most cases. For NH_4^{+} and NO_3^{-} , the slopes were sometimes positive and sometimes negative, r^2 values were all less than 0.02, and while still close to zero, the slopes were seldom statistically significant from zero ($P < 0.05$). Positive slopes indicate enrichment for these ions in the streams at high flows.

Herndon *et al.* [2015] defined the limits of chemostatic behavior as $-0.1 < m < 0$ for these C to Q regressions, but they did not specify whether m should be statistically significant or not. Thus, at face value and regardless of statistical significance, for their definition four watersheds were chemostatic for Ca^{2+} , four for Mg^{2+} (all at Bull), all eight watersheds for K^{+} , one for Na^{+} , seven for Cl^{-} , four for ortho-P, six for SO_4^{2-} , three for NH_4^{+} , and five for NO_3^{-} (Table 2). If only statistically significant m values are included, three watersheds

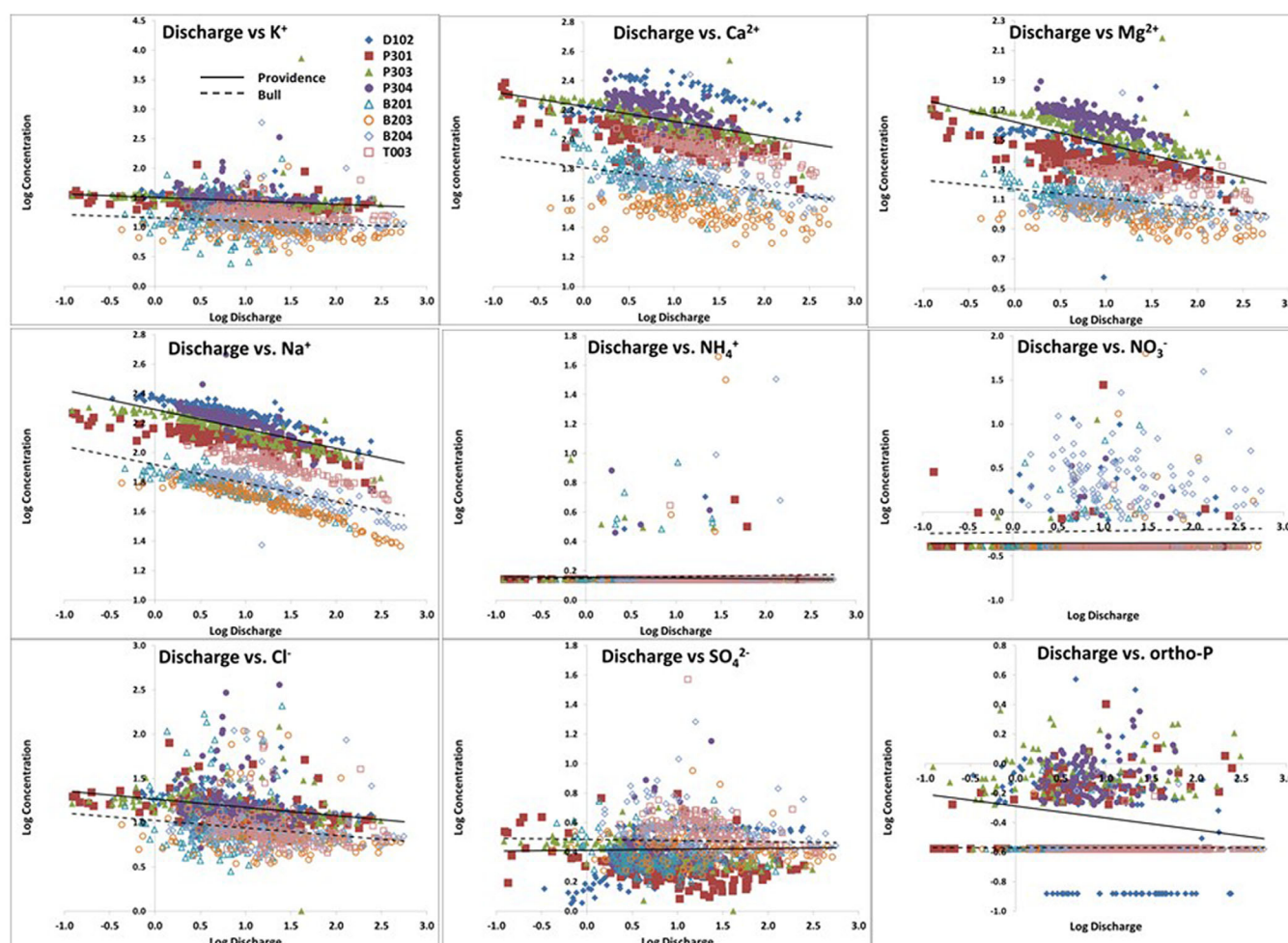


Figure 3. Log [concentration] – Log [discharge] plots show relationships for potassium, calcium, magnesium, sodium, ammonium, nitrate, chloride, sulfate, and ortho-phosphate. Open symbols show Bull watersheds, solid symbols show Providence watersheds. Regression lines for all data at Bull and all data at Providence watersheds are shown separately.

are chemostatic for Ca^{2+} , four for Mg^{2+} (all at Bull), five for K^{+} , one for Na^{+} , six for Cl^{-} , none for ortho-P, three for SO_4^{2-} , none for NH_4^{+} , and none for NO_3^{-} .

A more general way to examine concentration-discharge relationships is to plot data on a monthly basis. Figures 4 and 5 show box plots of data from water years 2004 through 2011 for discharge and concentrations for all watersheds within the Bull and Providence sites. For the Bull site, most high discharge values occur in late spring (May and June) during snowmelt with occasional outliers in February (a midwinter thaw) and October (likely a large rainstorm before snow starts) (Figure 4A). For the Providence site, the pattern is more even: snowmelt discharge values are lower than at Bull and there are a significant number of outliers in midwinter (December and January), reflecting the less constant snowpack and frequent midwinter thaws at this rain-snow transition site (Figure 4B). Most high nitrate and ammonium values occur in October at Bull (Figures 4C and 4E) and July at Providence (Figures 4D and 4F), probably reflecting a flush of nitrate after the dry summers. No particular seasonal pattern for ortho-P is evident at Bull (Figure 4G), but values are lower than at Providence for reasons that will be discussed below. Peak ortho-P values at Providence tend to occur in October (Figure 4H) probably because of the first flush after dry summers. Peak values for sulfate at both Bull and Providence occur mostly in October as well (Figures 4I and 4J).

For the more “nearly chemostatic” ions such as calcium, magnesium, and sodium, seasonal patterns exist (lower values in spring snowmelt, higher in summer and autumn), and there are fewer outliers than for nitrate, ammonium, ortho-P, and sulfate (Figure 5). Potassium and chloride patterns more resemble the

Table 2. Slope, Standard Error of Slope, and r^2 Values for Regressions of Log [Concentration] and Log [Discharge]^a

	Ca ²⁺		Mg ²⁺		K ⁺		Na ⁺		Cl ⁻	
	Slope	r ²	Slope	r ²	Slope	r ²	Slope	r ²	Slope	r ²
<i>Bull</i>										
B201	-0.180 ± 0.014*	0.54	-0.097 ± 0.012*	0.31	-0.064 ± 0.043	0.01	-0.158 ± 0.008*	0.72	-0.098 ± 0.056	0.01
B203	-0.051 ± 0.012*	0.11	-0.071 ± 0.010*	0.24	-0.083 ± 0.027*	0.06	-0.165 ± 0.007*	0.81	-0.093 ± 0.034*	0.04
B204	-0.075 ± 0.013*	0.19	-0.053 ± 0.012*	0.11	-0.056 ± 0.032	0.01	-0.144 ± 0.077*	0.74	-0.077 ± 0.034*	0.03
T003	-0.113 ± 0.008*	0.63	-0.098 ± 0.008*	0.59	-0.091 ± 0.021*	0.14	-0.150 ± 0.006*	0.84	-0.094 ± 0.044*	0.03
All data	-0.079 ± 0.012*	0.20	-0.060 ± 0.008*	0.29	-0.054 ± 0.016*	0.02	-0.125 ± 0.007*	0.32	-0.085 ± 0.019*	0.05
<i>Providence</i>										
D102	-0.019 ± 0.018	0.01	-0.133 ± 0.015*	0.36	-0.051 ± 0.010*	0.14	-0.129 ± 0.004*	0.86	-0.098 ± 0.019*	0.15
P301	-0.098 ± 0.009*	0.41	-0.113 ± 0.008*	0.54	-0.063 ± 0.013*	0.13	-0.099 ± 0.005*	0.72	-0.102 ± 0.018*	0.17
P303	-0.135 ± 0.007*	0.61	-0.132 ± 0.009*	0.56	-0.051 ± 0.025*	0.02	-0.132 ± 0.006*	0.25	-0.088 ± 0.016*	0.04
P304	-0.172 ± 0.017*	0.39	-0.180 ± 0.012*	0.59	-0.034 ± 0.033	0.00	-0.176 ± 0.012*	0.59	-0.038 ± 0.063	0.00
All data	-0.101 ± 0.008*	0.08	-0.144 ± 0.009*	0.09	-0.057 ± 0.010*	0.05	-0.119 ± 0.007*	0.34	-0.081 ± 0.015*	0.03
	Ortho-P		SO ₄ ²⁻		NH ₄ ⁺		NO ₃ ⁻			
	Slope	r ²	Slope	r ²	Slope	r ²	Slope	r ²		
<i>Bull</i>										
B201	+0.003 ± 0.012	0.00	-0.045 ± 0.016*	0.05	+0.0026 ± 0.0180	0.00	+0.0360 ± 0.0150	0.01		
B203	-0.004 ± 0.009	0.00	-0.020 ± 0.013	0.00	+0.0088 ± 0.0228	0.00	+0.0312 ± 0.0351	0.00		
B204	+0.007 ± 0.010	0.00	-0.070 ± 0.016*	0.11	+0.0330 ± 0.0189	0.01	-0.0978 ± 0.0570	0.01		
T003	-0.005 ± 0.011	0.00	-0.126 ± 0.023*	0.21	-0.0088 ± 0.0094	0.00	-0.0090 ± 0.0157	0.00		
All data	-15.7e⁻⁶ ± 0.005	0.01	-0.008 ± 0.010	0.00	-0.0084 ± 0.0091	0.00	+0.0155 ± 0.0258	0.00		
<i>Providence</i>										
D102	-0.183 ± 0.046*	0.09	0.167 ± 0.018*	0.39	<0.0001	0.00	-0.0099 ± 0.0379	0.00		
P301	-0.009 ± 0.026	0.00	-0.070 ± 0.013*	0.17	+0.0099 ± 0.0061	0.01	-0.0161 ± 0.0219	0.00		
P303	-0.099 ± 0.031*	0.02	-0.032 ± 0.029	0.00	-0.0159 ± 0.0103	0.00	-0.0071 ± 0.0158	0.00		
P304	+0.133 ± 0.060*	0.03	-0.006 ± 0.028	0.00	-0.0195 ± 0.0189	0.00	+0.0703 ± 0.0400	0.01		
All data	-0.068 ± 0.023*	0.00	-8.0e⁻⁶ ± 0.012	0.00	-0.0101 ± 0.0124	0.00	+0.0038 ± 0.0142	0.00		

^aAsterisks indicates slope is significantly different from 0, $P < 0.05$. Slopes with values less than 0 but greater than -0.1 are highlighted in bold as per Herndon et al. [2015] definition of chemostatic.

latter ions, however, with peak values in October associated with first flushes after dry summers (Figures 5C, 5D, 5I, and 5J).

3.2. Concentration Changes During Events

Nitrate, NH_4^+ , ortho-P, and SO_4^{2-} concentrations in the KREW streams were very low as expected for watersheds without recent land disturbance or pollution point sources (Figure 6). However, it is of interest to know when pulses of solutes occur and compare our results to those of previous studies in the Sierra Nevada [Coats and Goldman, 2001; Leonard et al., 1979; Sickman et al., 2003; Williams and Melack, 1991, 1997].

A high-flow event can occur at KREW when there is a substantial rain event, a rain-on-snow event, or during snowmelt. The regular stream grab samples were collected every 2 weeks and are likely biased toward base flows. The automated ISCOTM samplers collected only during high-flow events. We graph the mean of all chemistry samples taken from 2004 through 2011 by type, grab, or ISCOTM (Figure 6). The chemistry concentrations in the event samples taken by the ISCOTM were always higher for Cl^- , K^+ , NH_4^+ , NO_3^- , ortho-P, and SO_4^{2-} . Usually, they were significantly different ($P < 0.05$, Student's t test). This pattern was true for both the snow dominated watersheds at Bull and the rain-on-snow watersheds at Providence.

Figures 7 and 8 show box plots of discharge and ion concentrations for the ISCOTM (high-flow event) samples. The seasonal patterns for ISCOTM samples are similar to those for the grab samples: most high discharge values during these events occur in spring during snowmelt whereas most high concentrations of nitrate, ortho-P, and sulfate occur in the fall first flush (Figure 7). As with the grab samples, seasonal patterns for ammonium are unclear. Seasonal patterns for calcium, magnesium, and sodium in the ISCOTM samples are similar to those for the grab samples, with a decrease during spring snowmelt, and an increase during the fall (Figure 8). Seasonal patterns for potassium and chloride in the ISCOTM samples are also similar to those in the grab samples with peaks in the autumn.

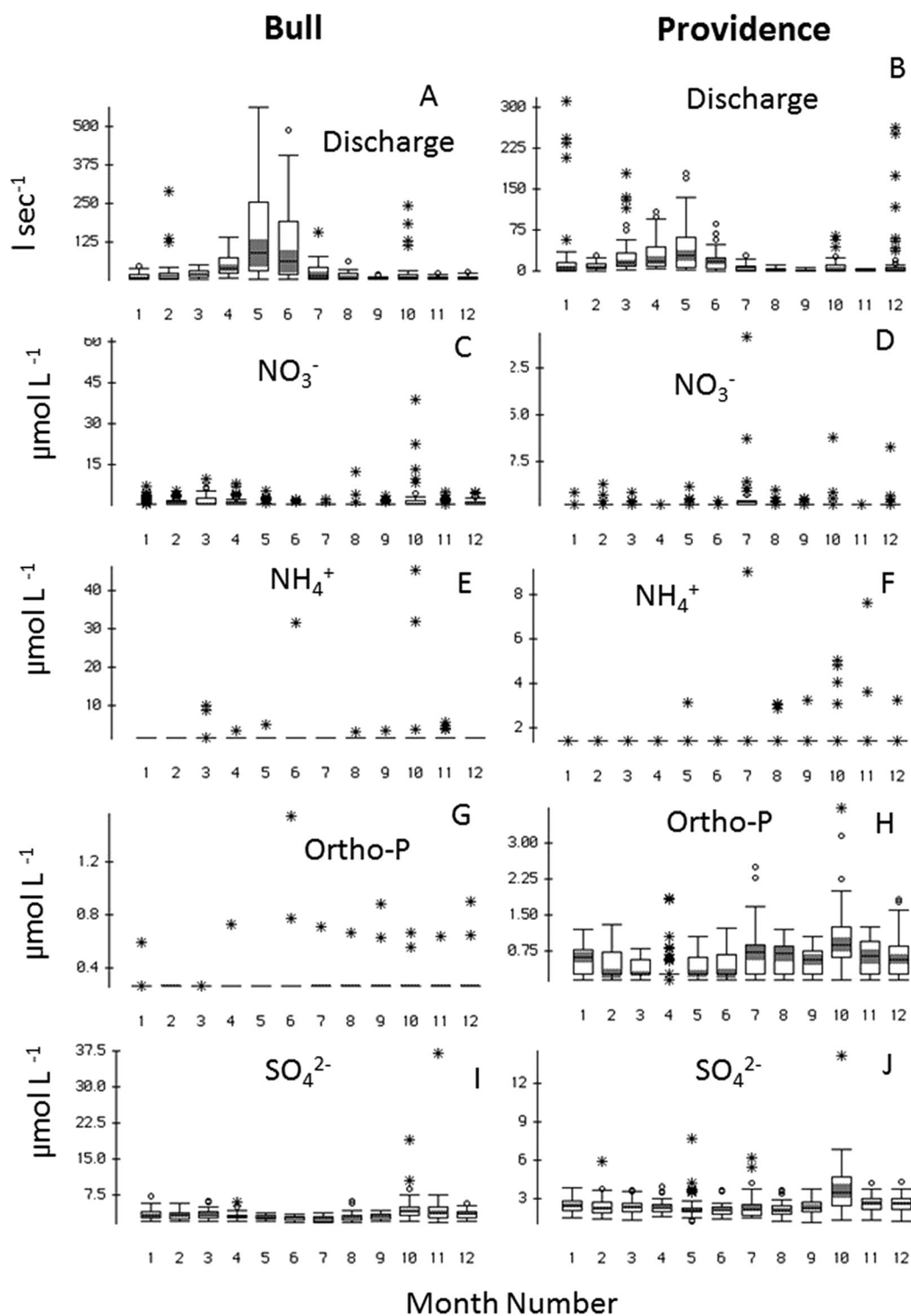


Figure 4. Box plots of stream discharge, nitrate, ammonium, ortho-P, and sulfate concentrations in grab samples by month. The horizontal middle line indicates the median; the lower and upper edges of the box indicate the 25 and 75% points, respectively; the whiskers indicate the main body of the data (not including outliers), shaded intervals are for comparing medians and defined by ± 1.58 (high hinge - low hinge)/ $\sqrt{n}$, circles indicate outliers and stars indicate extreme outliers.

3.3. Relationships Between Soil Contents and Stream Concentrations

As noted previously [Johnson *et al.*, 2011a], there are significant differences in soil concentrations (mg kg^{-1}) and contents (kg ha^{-1}) between the Bull and Providence watersheds. Specifically, the higher-elevation Bull

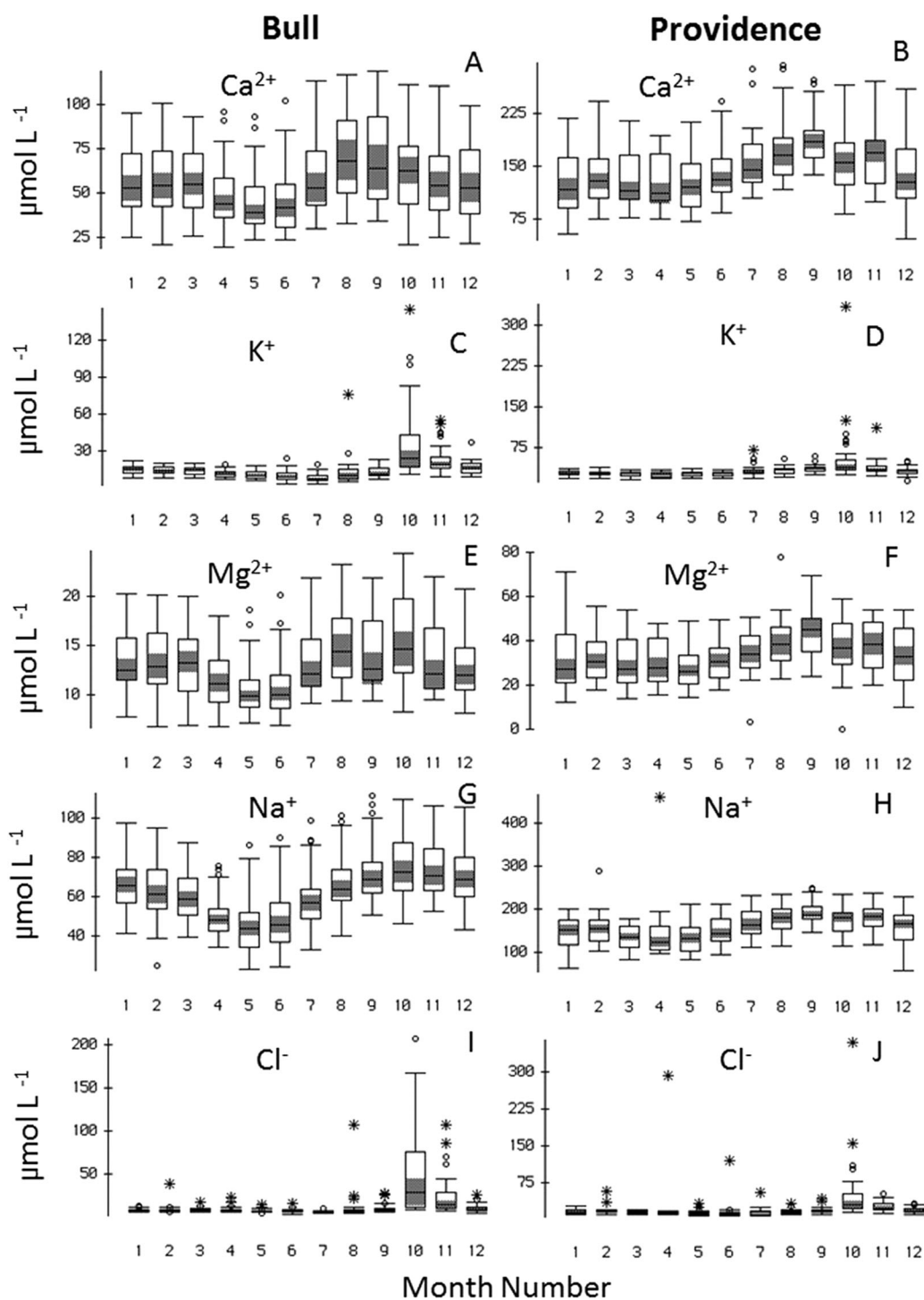


Figure 5. Box plots of calcium, potassium, magnesium, sodium, and chloride concentrations in grab samples by month. The horizontal middle line indicates the median; the lower and upper edges of the box indicate the 25 and 75% points, respectively; the whiskers indicate the main body of the data (not including outliers), shaded intervals are for comparing medians and defined by ± 1.58 (high hinge – low hinge)/ $\sqrt{n}$, circles indicate outliers and stars indicate extreme outliers.

watersheds have significantly lower ($P < 0.01$) extractable P (both Bray No. 1 and bicarbonate), Ca²⁺, Mg²⁺, and Na⁺ contents than the Providence watersheds (Table 3). Differences in soil contents for NH₄⁺-N, NO₃⁻-N, total N, and SO₄²⁻-S between the sites were not significant. The patterns in weighted average annual stream water concentrations match differences in soil content quite closely: concentrations of ortho-P, Ca²⁺, Mg²⁺,

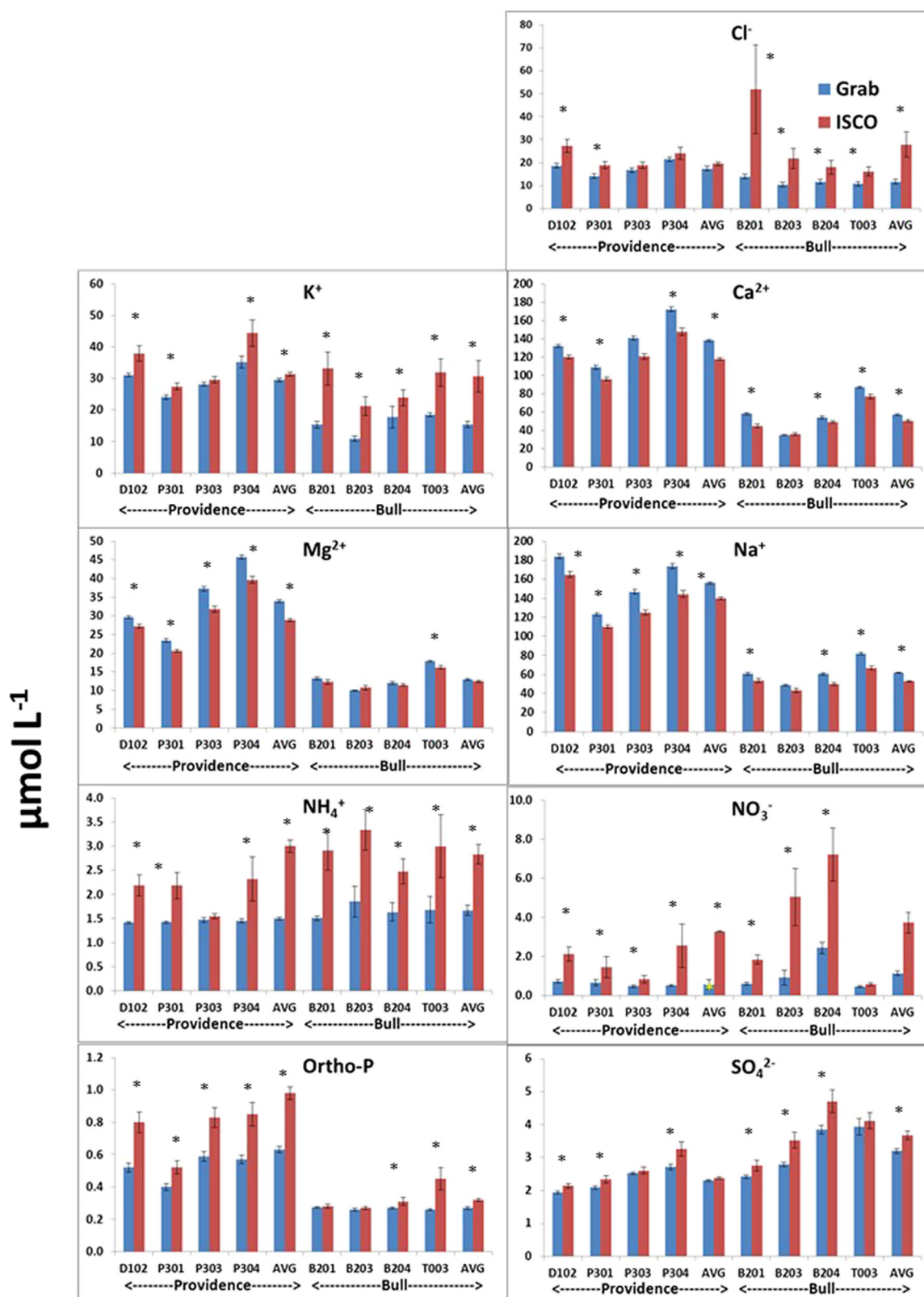


Figure 6. Chemistry concentrations in stream grab samples, collected by hand every 2 weeks, compared to samples taken by automated samplers during high-flow events. The mean (with 1 standard error) by watershed is shown for 8 years of data (2004–2011). An * indicates statistically significant differences between grab and event samples, Student's t test, $P < 0.05$.

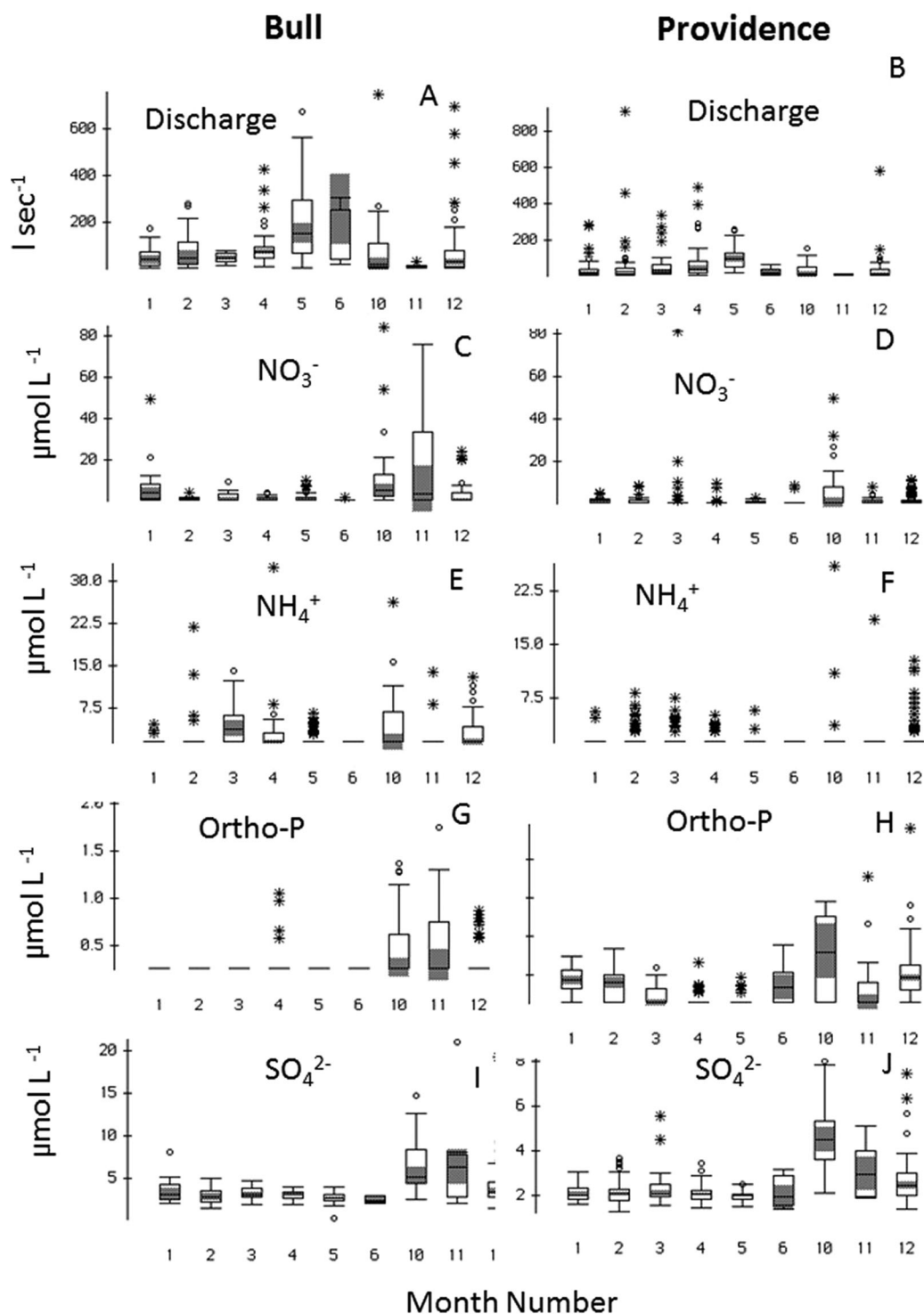


Figure 7. Box plots of stream discharge, nitrate, ammonium, ortho-P, and sulfate concentrations in ISCO™ samples by month. The horizontal middle line indicates the median; the bottom and top edges of the box indicate the 25 and 75% points, respectively; the whiskers indicate the main body of the data (not including outliers), shaded intervals are for comparing medians and defined by ± 1.58 (high hinge - low hinge)/n, circles indicate outliers and stars indicate extreme outliers. ISCO™ samplers were not operated in summer base flow months (July–September).

and Na^+ were significantly lower in the Bull than in the Providence watersheds (Table 3). Weighted average annual stream water concentrations of K^+ were also lower in the Bull watersheds, as were exchangeable K^+ contents in soils, but the soil contents differed by much less (18% lower at Bull) than the stream

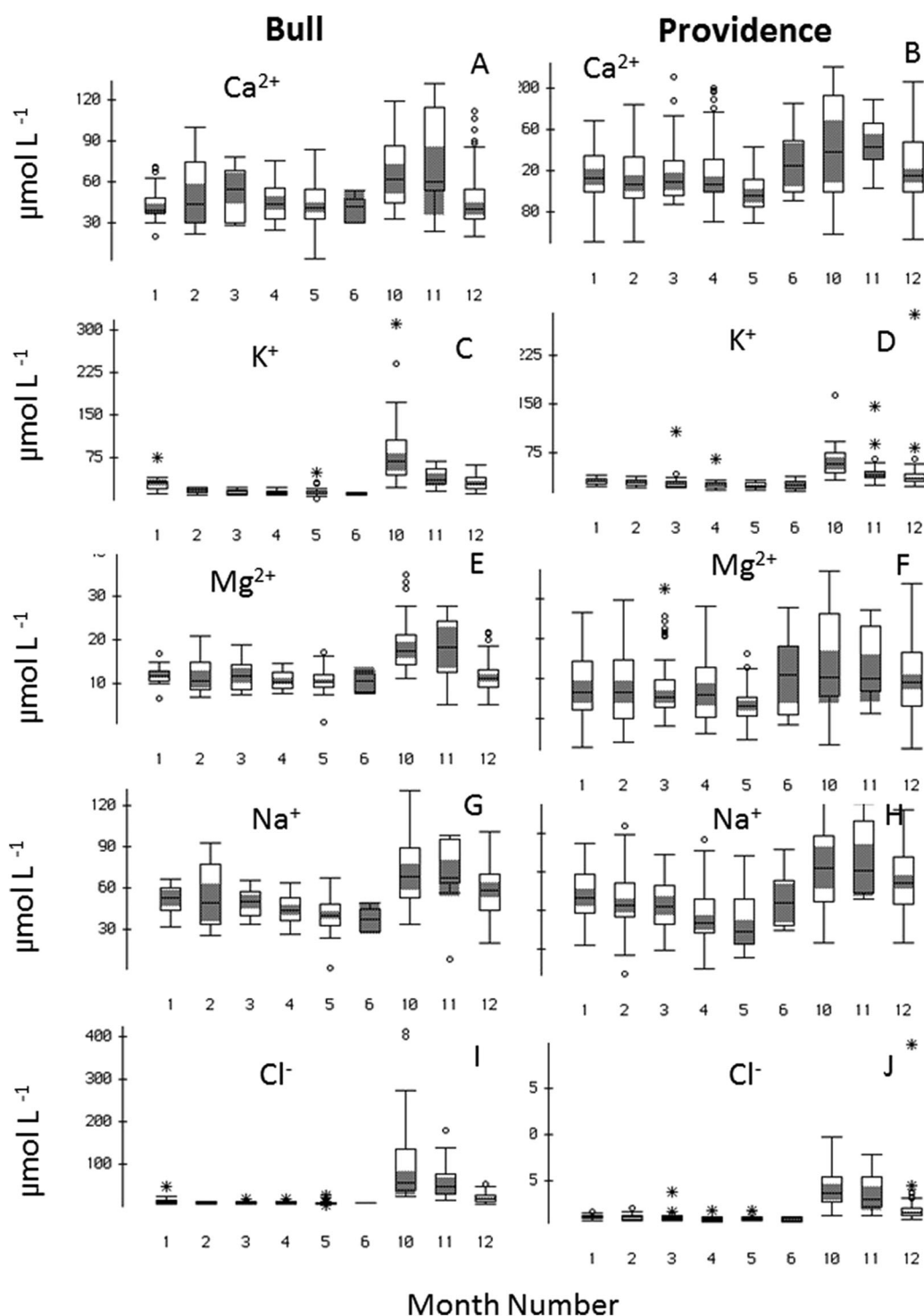


Figure 8. Box plots of calcium, potassium, magnesium, sodium, and chloride concentrations in ISCO™ samples by month. The horizontal middle line indicates the median; the bottom and top edges of the box indicate the 25 and 75% points, respectively; the whiskers indicate the main body of the data (not including outliers), shaded intervals are for comparing medians and defined by ± 1.58 (high hinge - low hinge)/ $\sqrt{n}$, circles indicate outliers and stars indicate extreme outliers. ISCO™ samplers were not operated in summer base flow months (July-September).

concentrations (52% lower at Bull), and the soil differences were not significant even at the $P < 0.05$ level. There were no significant differences in stream water NH_4^+ -N, NO_3^- -N, or inorganic N between the Bull and Providence watersheds, as was also the case for soils (Table 3).

Table 3. Average Contents (kg ha^{-1}) in Soils and Volume-Weighted Average Stream Water Concentrations ($\mu\text{mol L}^{-1}$) From the Bull and Providence Watersheds^a

	Bull	Providence	P
Soils	kg ha^{-1}		
Ca^{2+}	1172 ± 129	3165 ± 319	<0.01
K^+	513 ± 45	622 ± 69	0.09
Mg^{2+}	123 ± 10	230 ± 28	<0.01
Na^+	46 ± 3	81 ± 8	<0.01
$\text{SO}_4^{2-}\text{-S}$	71 ± 10	88 ± 15	0.18
$\text{NH}_4^+\text{-N}$	242 ± 21	218 ± 22	0.20
$\text{NO}_3^-\text{-N}$	18 ± 2	18 ± 3	0.18
Inorganic N	260 ± 22	236 ± 24	0.23
Total N	6644 ± 402	5804 ± 396	0.07
Bray P	114 ± 11	273 ± 26	<0.01
Bicarbonate P	92 ± 9	145 ± 15	<0.01
Streams	$\mu\text{mol L}^{-1}$		
Ca^{2+}	49 ± 10	124 ± 14	<0.01
K^+	14 ± 2	29 ± 4	0.01
Mg^{2+}	12 ± 2	29 ± 5	0.01
Na^+	52 ± 7	136 ± 14	<0.01
$\text{SO}_4^{2-}\text{-S}$	2.95 ± 0.26	2.41 ± 0.2	0.08
$\text{NH}_4^+\text{-N}$	1.73 ± 0.17	1.46 ± 0.02	0.11
$\text{NO}_3^-\text{-N}$	1.09 ± 0.47	0.52 ± 0.07	0.16
Inorganic N	2.81 ± 0.62	1.98 ± 0.07	0.14
Ortho-P	0.28 ± 0.004	0.56 ± 0.07	0.01

^ap values indicate probabilities of differences between Bull and Providence watersheds, Student's *t* test. Soils data from Johnson *et al.* [2011a].

Figure 9 shows plots of soil contents against weighted average stream concentrations for the individual watersheds and the regression coefficients. The Bull watersheds are identified as nonfilled symbols and the Providence watersheds as filled symbols. The slopes of the regressions for Ca^{2+} , Na^+ , Bray P, and bicarbonate P are significant at the $P < 0.05$ level. The P values for K^+ and Mg^{2+} are 0.13 in each case. The R^2 values for NH_4^+ , NO_3^- , inorganic N, and SO_4^{2-} were all less than 0.05 and P values > 0.60 (not shown).

4. Discussion and Conclusions

Although the KREW watersheds show negative, near zero slopes (m) for $\log[Q]$ versus $\log[C]$ for Ca^{2+} , Mg^{2+} , K^+ , Na^+ , and Cl^- suggesting “nearly chemostatic” behavior, most of these slopes are significantly different from zero according to traditionally accepted P values ($P < 0.05$), indicating some dilution. Dilution is particularly strong at discharge values less than 50 L s^{-1} . On the other hand, with the exception of Na^+ , many of the r^2 values for the regressions were quite low indicating a weak relationship between $\log[Q]$ and $\log[C]$ despite the fact that the slopes were statistically significant.

The criteria for judging whether the KREW watersheds exhibit chemostatic or “near-chemostatic” behavior provide inconsistent answers for many of the ions measured. In the general sense that C varies much less than Q over time, the KREW watersheds could be called “near-chemostatic” for all measured ions. The problem of definition comes in defining boundaries. For example, if the Herndon *et al.* [2015] seemingly arbitrary criteria of $-0.1 < Q < 0$ were changed to $-0.2 < Q < 0$, all eight of the KREW watersheds would be defined as chemostatic for Na^+ , the ion that has the highest r^2 values and high statistical significance for m.

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The close relationship between soils and stream water concentrations for ortho-P, Ca^{2+} , and Na^+ (weaker for Mg^{2+} and K^+) strongly suggests that soil chemistry has a major influence on stream water chemistry in these systems for those ions. This in turn is consistent with the near-chemostatic nature of these ions in stream water, as the soil pools of these ions are orders of magnitude greater than preliminary estimates of annual fluxes via streamflow. The lower base cation status and extractable P status of the Bull watersheds probably reflects greater acidification pressure at these higher elevation sites (average soil pH is 5.4 at Bull and 5.8 at Providence from Johnson *et al.* [2011a]). The contributions of primary mineral weathering to stream water chemical composition in the KREW watersheds are unknown, but may be relevant to the degree of weathering and differences in base cation and extractable P pools. Liu *et al.* [2012] used KREW water chemistry from 2004–2007 in end-member mixing analysis and mixing models to determine that stream discharge was dominated by subsurface flow (about 60%) while less than 40% was from snowmelt runoff and less than 7% was from fall storm runoff. They suggested that subsurface flow moves through preferential pathways in the soil-bedrock interface thus enabling chemical fluxes from this zone.

Factors controlling stream water NH_4^+ , NO_3^- , and SO_4^{2-} concentrations are less clear. In contrast to many other studies that have shown peak concentrations during snowmelt [Coats and Goldman, 2001; Denning *et al.*, 1991; Leonard *et al.*, 1979; Piatek *et al.*, 2005; Stohlgren *et al.*, 1991; Williams and Melack, 1991; Williams *et al.*, 2001], we find that peak NO_3^- concentrations occur mostly during the first autumn rains, usually in October. This is true for both grab samples and high-flow event samples. We hypothesize that this is due to a combination of factors, including the first flush after the normal summer drought of a Mediterranean climate, and the occurrence of

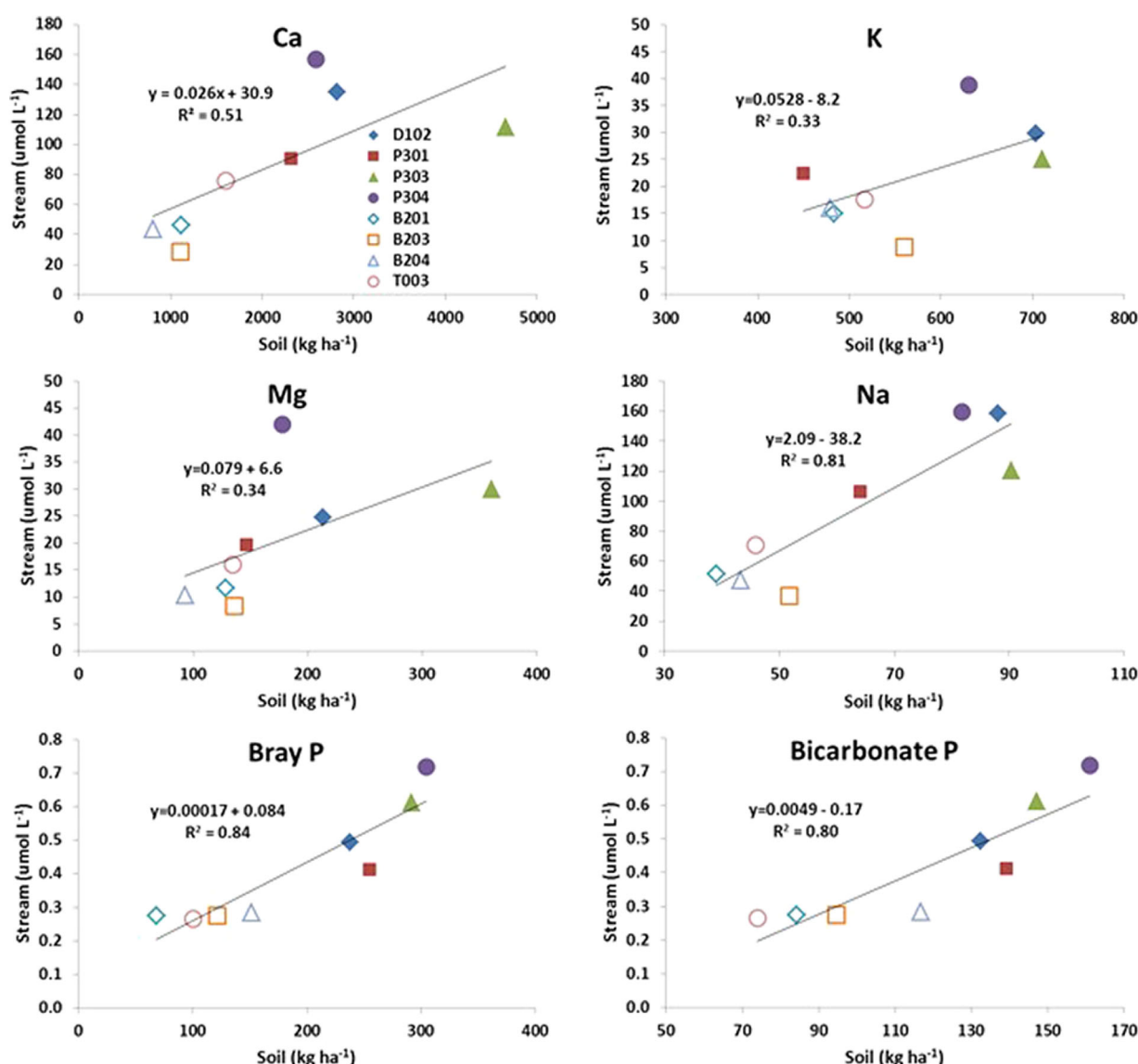


Figure 9. Regression equations and r-square values for soil contents of Ca^{2+} , K^+ , Mg^{2+} , Na^+ , Bray P, and bicarbonate P as plotted against weighted average stream concentrations for the individual watersheds. Note: soil values are for solid soils, not soil water.

interflow within the organic horizon (O-horizon) at this time. Because of the lack of rooting in the O-horizons of these systems (due to extreme summer drought), decomposition/nutrient mineralization and vegetation uptake processes are spatially decoupled, and the intense competition for N between roots and decomposers that characterizes more humid forest soils is absent [Stark, 1973; Johnson *et al.*, 2009]. Because of this vertical decoupling, nutrients released during decomposition in O-horizons are not immediately taken up by plants and are solubilized by rain or snowmelt, creating solutions with very high inorganic N and P concentrations, which presumably infiltrate the soil at preferential flow paths. Studies by W. Miller and colleagues [Gergens *et al.*, 2013; Loupe *et al.*, 2009; Miller *et al.*, 2005, 2006] have found that because Sierran soils become hydrophobic during dry summers, runoff through the O-horizon overlying mineral soils occurs during summer rainfall or early fall rains preceding the first major snowfall. This O-horizon runoff is often highly enriched in nutrients, especially NH_4^+ and NO_3^- [Miller *et al.*, 2005, 2006]. We have installed O-horizon interflow collectors of the design described by Miller *et al.* [2005] in the upper watershed of P301 and found NO_3^- concentrations averaging 188 and as high as 500 $\mu\text{mol L}^{-1}$ [Johnson *et al.*, 2011b]. Should any runoff waters of this type enter streams, an autumnal peak in stream water NO_3^- could be expected. A strong first flush of NH_4^+ and NO_3^- in O-horizons and soils at P301 have also been measured using resin-based collectors [Johnson *et al.*, 2014; Woodward *et al.*, 2013].

The comparisons of grab and ISCOTM high-flow samples suggest that Ca^{2+} , Mg^{2+} , and Na^{+} concentrations are slightly diluted during most storm events. The increases during storm events in K^{+} , NH_4^{+} , NO_3^{-} , ortho-P, and SO_4^{2-} concentrations suggests a source of these nutrients from sites in the system not normally accessed during base flow. O-horizon interflow is one possible source of spikes in these ion concentrations during storm events. O-horizon runoff concentrations of K^{+} , NH_4^{+} , NO_3^{-} , ortho-P, and SO_4^{2-} at the upland P301 site averaged 311, 37, 118, 21, and 14 $\mu\text{mol L}^{-1}$, respectively, values which greatly exceed those in streamflow, mostly by an order of magnitude or more (29, 1.5, 0.5, 0.6, and 2.4 $\mu\text{mol L}^{-1}$, respectively; Table 3). On the other hand, average concentrations of Ca^{2+} and Mg^{2+} in O-horizon runoff (137 and 46 $\mu\text{mol L}^{-1}$, respectively) were of the same order of magnitude as in streams (124 and 29 $\mu\text{mol L}^{-1}$, respectively) and would not be expected to cause pulses of these solutes if O-horizon interflow was the source.

Average Na^{+} concentrations in O-horizon interflow (42 $\mu\text{mol L}^{-1}$) were considerably lower than in streams (136 $\mu\text{mol L}^{-1}$) perhaps reflecting a bedrock source of this solute in streams.

Brooks *et al.* [2015] discuss the well-known ability of watersheds to release stored water and solutes during high stream discharge, but they also emphasize a knowledge gap about how precipitation is stored and routed with respect to a watershed's characteristics such as regolith depth and structure, soil properties, vegetation, hydrologic signatures, meteorology, etc. Herndon *et al.* [2015] recommend comparisons across watersheds with the same lithology to help develop generalized models for concentration-discharge behavior. Our research meets this need because it compares concentration-discharge relationships for nine ions in eight headwater systems with the same lithology and similar landscape characteristics. A lot of variability has been observed for concentration-discharge relationships within the Sierra Nevada, and our research findings have some patterns that are similar and some that are different to those previously published. All ions at KREW showed a dilution process at lower flows ($<50 \text{ L s}^{-1}$) with the concentration-discharge relationship being more chemostatic at higher flows; thus, we conclude that many ions are "nearly chemostatic" except for ortho-P, NH_4^{+} , and NO_3^{-} which are enriched for some watersheds. The dilution behavior at low flow for some ions could be explained by a lack of stream connection to the nutrient-rich O-horizon during dry periods when low flows usually occur. Also of note is that despite the difference in precipitation type (snow-dominated and rain-snow transition) among the watersheds studied, and thus the timing of stream discharge, the concentration-discharge patterns are similar.

Within the Sierra Nevada literature on concentration-discharge relationships, the findings of Williams and Melack [1997] in Sequoia National Park are for a location most similar to the landscape characteristics at KREW, although one of the two streams is not perennial. Their streams, like ours, exhibited dilution for Na^{+} , Ca^{2+} , and Mg^{2+} , but their reported discharge did not exceed the 50 L s^{-1} transition point we identified. Sulfate in the Sequoia watersheds behaved the same as in the KREW watersheds. For N, P, and S our systems exhibit a "first flush" occurring during the first fall rains after the dry summer; this is a different behavior from the flux during snowmelt observed in other parts of the Sierra Nevada. However, the snowmelt flux was observed in watersheds with some differences in landscape characteristics, i.e., volcanic soils in Tahoe [Leonard *et al.*, 1979; Coats and Goldman, 2001] and shallow soils with little vegetation at Emerald Lake watershed [Williams and Melack, 1991; Sickman *et al.*, 2003]. We observed some concentration-discharge differences both between and within sites at KREW even with the watersheds close proximity to each other. Although there are some differences in hydrologic signatures (Table 1), especially for the P304 and T003 with high groundwater input, we did not see these two watersheds expressing substantially different or more consistent concentration-discharge relationships. Different concentration-discharge relationships have been documented in the Sierra Nevada, and this is likely because the dominant processes controlling these relationships are a function of various watershed characteristics such as soil depth and chemistry, bedrock geology, vegetation type and cover, organic matter, hydrologic flow paths, and meteorological patterns.

Appendix A: Database Acknowledgments

The data used in this publication can be accessed from the Forest Service Research Data Archive and referenced as Hunsaker and Safeeq [2017] and Hunsaker and Padgett [2017].

Acknowledgments

We wish to especially thank Pamela Padgett and David Jones of the Pacific Southwest Research Station for performing all of the water chemistry analyses at Riverside, California. The stream discharge data are a product of the work of hydrologists Sean Eagan and Thomas Whitaker, hydrologic technician Kevin Mazzocco, and many field assistants over the years. KREW was established with USDA Forest Service funding from the National Fire Plan and consistently supported by the Pacific Southwest Research Station. We received support from California's State Water Resources Control Board, through Proposition 50 (Water Security Clean Drinking Water, Coastal, and Beach Protection Act of 2002). Some support since 2007 also has been provided through the Southern Sierra Critical Zone Observatory (National Science Foundation EAR-0725097). Use of firm or trade names is for reader information only and does not imply endorsement of any product or service by the U.S. Government. Data are available upon request from the USDA Forest Service, Research & Development data archive (<https://doi.org/10.2737/RDS>).

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