



8-2014

Chemical Flux During Event Stormwater Flows in the Great Smoky Mountains National Park: Comparison of Two Streams Varying by Drainage Area and Elevation

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I am submitting herewith a thesis written by Matthew Williams Aplin entitled "Chemical Flux During Event Stormwater Flows in the Great Smoky Mountains National Park: Comparison of Two Streams Varying by Drainage Area and Elevation." I have examined the final electronic copy of this thesis for form and content and recommend that it be accepted in partial fulfillment of the requirements for the degree of Master of Science, with a major in Environmental Engineering.

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Chemical Flux During Event Stormwater Flows in the Great Smoky Mountains
National Park: Comparison of Two Streams Varying by Drainage Area and
Elevation

A Thesis Presented for the

Master of Science

Degree

The University of Tennessee, Knoxville

Matthew Williams Aplin

August 2014

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Abstract

Streams in the Great Smoky Mountains National Park in North Carolina and Tennessee have been impacted by acid deposition from anthropogenic sources for decades. Recent declines in acid deposition throughout the eastern U.S. appear to be initiating improvements in stream water quality. However, watershed recovery could take decades due to regional differences in the hydrologic and biogeochemical processes that influence chemical fate and transport. These processes have been extensively studied at longer time scales (i.e. seasonally, annually), by long-term annual ion budgets, and study designs based on grab samples. Less known are the acidification effects on streams through rapid ion transport during storm events. Of particular importance is advancing our understanding of ion transport at the storm-event scale with respect to soil sulfate desorption, nitrate saturation, and base cation depletion. In this study automated samplers allowed for continuous and time dependent stream sampling during stormflow events, which collected samples used to characterize event-based flux of stormwater chemistry. Two streams, one in a small, high elevation watershed and one in a larger, low elevation watershed were selected for study because of their distinct differences in hydrology. Eight events were sampled at each site (average of 23 samples per event) and analyzed for anions, cations, dissolved metals, pH, and acid neutralizing capacity. Samples were organized into three hydrograph categories (rising limb, peak, and falling limb). Throughfall samples were also utilized for an ion event-based input and output mass comparison. On average, sulfate desorption was not observed at either site because concentrations were not significantly different between hydrograph rising and falling limbs. Nitrate saturation and base cation depletion appears to govern the storm-based acidification response because of increased concentrations of nitrate and decreasing concentrations of base cations during events at the low elevation site. Although acid

deposition has declined, stream acidification was still observed with episodic drops in pH and ANC governed by the lack of base cations to buffer acid anions from inorganic nitrogen and possibly organic acids. Further study is needed on the influence of organic acids in the response to acidification in headwater streams.

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1. Introduction

The Great Smoky Mountains National Park (GRSM or “the Park”) has been impacted by acid deposition from anthropogenic sources of air pollution for decades such that aquatic species have been severely threatened, including the native brook trout (Flum and Novdin 1995, Robinson et al. 2008, Schwartz et al. 2014a). Significant declines in acid deposition in the eastern U.S. have been observed, but recent studies suggest that it could take decades for watersheds to recover from long-term deposition (Cai et al. 2011, Driscoll et al. 2003, Lehmann et al. 2007). There is a concern in the GRSM that episodic acidification will continue to occur due to prior long-term absorption of sulfate and the influence of acidic ions on natural processes such as cation weathering and export. Episodic or short-term acidification, which takes place during storm events or snowmelt has been shown to significantly disturb the chemical balance in streams and rivers (Deyton et al. 2008, Neff et al. 2013, Wellington and Driscoll 2004). The increase in sulfate and nitrate along with a decrease in pH are mostly associated with episodic acidification (Lawrence 2002, Wigington et al. 1996). However, different flowpaths, such as rapid interflow through upper layers of soils, also have an impact on storm chemistry and the ion flux through a watershed (Mulholland 1993). Previous studies involving acid deposition in the Park have investigated long-term baseflow trends with respect to ion flux in the Park or have used a single sample taken during a storm event to assess the effects of storm chemistry versus baseflow (Cai et al. 2011, Deyton et al. 2008). There is a need in the GRSM to monitor event-based flux of constituents such as sulfate, nitrate, calcium, and aluminum throughout a stormflow event to further understand the complex dynamics between hydrologic and biogeochemical processes, particularly in terms of retention and transport (Caissie et al. 1995, Neff et al. 2013).

Streams in the GRSM have remained acidified with acid neutralizing capacity measured below 50 $\mu\text{eq/L}$ in many locations (Robinson et al. 2008, Schwartz et al. 2014a, Weathers et al. 2006). Desorption of sulfate following long periods of adsorption, base-cation depletion, and nitrogen saturation within a watershed have all been linked to an insufficient recovery from acidification (Cai et al. 2011, Driscoll et al. 2003b, Gbondo-Tugbawa and Driscoll 2002, Jeffries et al. 2003). Soil desorption of sulfates and rapid transport during stormflows is a major concern in the GRSM as declines in anthropogenic deposition sources of sulfate stored in the soil could be released under conditions of higher pH and low sulfate concentrations in the soil water (Cai et al. 2010a). A greater capacity for soil absorption of sulfates in forested areas in the Southeast U.S. has been theorized as a cause for the lack of decline in stream sulfate as opposed to the Northeast where reductions in stream sulfate have been observed (Kahl et al. 2004). Cai et al. (2010a) showed soils in the GRSM still have the potential to absorb more sulfate and in one field-scale study found soil capacity with approximately 61% retained from throughfall. In another study by Cai et al. (2010b) the desorption of sulfates was found to occur after soil pH increased above 6.0 and sulfate concentration fell below 15 $\mu\text{mol/L}$ in a laboratory-controlled experiment. In that same study, elevated nitrate concentrations were linked to 96% of deposition ammonium being converted to nitrate due to nitrogen saturation. This nitrate then resides in the upper layers of soil and is then easily mobilized to streams during storm events (Cai et al. 2010c). Additional data with respect to sulfate and nitrate flux during storm events is needed to determine thresholds of soil sulfate desorption and nitrogen saturation processes, or a lack thereof, within the Park.

Different geologic and geographic properties can also alter the hydrological and chemical processes within a watershed (Billet and Cresser 1992, Likens and Buso 2006, Sullivan et al.

2006). Within the GRSM, these properties vary greatly including elevation, geologic formations, and soil characteristics (Neff et al. 2013). It is understood that higher elevation streams yield more acidic water than lower elevation streams as they receive larger amounts of precipitation and deposition and have poor acid buffering capacity, thinner and more depleted soil layers and steeper slopes with less contact time (Deviney et al. 2006, Neff et al. 2013, Silsbee and Larson 1982, Weathers et al. 2006). In the GRSM this is evident in baseflow sampling data throughout the Park as the lower elevation reaches have higher acid neutralizing capacity (ANC) and higher pH values (Robinson et al. 2008, Schwartz et al. 2014a). One exception in the GRSM is Rock Creek, a 3rd order stream that is a part of the Lower French Broad watershed. This stream is listed on Tennessee's 303d list as an impaired water body for low pH (TDEC 2010). Baseflow sampling has been conducted at Rock Creek from 1993 to the present showing an increasing trend in acidity but little is known about the processes related to acidification in this watershed. Nitrogen uptake in streams from periphyton occurs more in lower elevation watersheds, typically reducing inorganic nitrogen concentrations in lower elevation reaches (Mulholland et al. 2008). It is also known that long-term acid deposition may cause base cation depletion in soils resulting in a dilution effect that can result in more acidic stormflow (Cai et al. 2011, Fernandez et al. 2003). Differences in high and low elevations with respect to storm chemistry in the GRSM could help to explain the baseflow trends at Rock Creek.

Flowpath shifts in watersheds during stormflow events can also influence the episodic acidification process in streams (Suecker et al. 2000, Wellington and Driscoll 2004). During storm events high elevation streams receive little groundwater relative to the runoff moving quickly as interflow through the upper layers of soil with a short time of concentration (Wellington and Driscoll 2004). It has been shown that this process results in more acidic

stormflow as the upper layers contain higher amounts of protons from natural and anthropogenic deposition sources (Lawrence 2002, Neff et al. 2013, Wigington et al. 1996). Lower elevation streams receive more groundwater flow during events as infiltrating precipitation displaces soil water and is eventually routed into the stream (Mulholland 1993). This hydrologic process allows for prolonged contact with deeper soils and bedrock, resulting in an increase in base cations, greater buffering capacity, and higher pH (Schwartz et al. 2014a, Wellington and Driscoll 2004). Understanding how flowpaths influence stream chemistry in the GRSM can aid in explaining event-based ion flux.

Stormwater sampling in the GRSM has previously consisted of single samples within an event or using simple analyses to designate certain historic grab samples as stormflow per precipitation records (Neff et al. 2013, Schwartz et al. 2014b). Recent studies in the GRSM have shown that pH response during storm events was dependent on the magnitude of flow and the number of antecedent dry days (Deyton et al. 2008). While the change in pH and flow appeared to be highly correlated, the antecedent dry day correlation between watersheds varied. Long-term studies on historical data provided insight into the annual flux of storm chemistry but did not focus on the change within individual stormflow events. Monitoring concentrations of chemical constituents throughout an event hydrograph and transport analysis can provide information to better understand the interactions between watershed soils, geology, and hydrology (Tetzlaff et al. 2010).

The purpose of this study is to characterize event-based chemistry during episodic stormflows to better understand biogeochemical controls on ion transport along different hydrologic flowpaths in two different watersheds, one small, high elevation watershed and the other a larger, low elevation watershed. The objectives of this research were to: 1) characterize

constituent flux of anions and base cations throughout multiple storm events at both sites through mean constituent deviations and hydrologic flowpaths; 2) investigate possible sulfate desorption, nitrogen saturation, and cation depletion at both sites; and 3) analyze differences between throughfall input and stream flow output in each watershed as an additional metric for evidence of retention and/or transport.

2. Methods

2.1 Study Area

The GRSM consists of over 2100 km² of protected forest located along the border of North Carolina and Tennessee (Figure 1). While the 3,000 km of streams in the GRSM are home to a diverse aquatic ecosystem and prominent trout fisheries, the Park also receives more acid deposition than any other national park (Baumgardner et al. 2003, Robinson et al. 2008, USEPA 1999) . An ongoing effort to monitor water quality in the Park began in 1993 with 185 monitoring sites and grew to 357 sites by 1995 (Schwartz et al. 2014b). Two study sites were selected within the collective group of Park-wide monitoring sites; upper Noland Creek and lower Rock Creek. One of these sites is a high elevation watershed consisting of two streams that merge to form Noland Creek at Noland Divide near Clingman's Dome (Figure 1). The Noland Divide Watershed (NDW) was chosen as the location for the high elevation stream to be compared with the low elevation Rock Creek (Figure 1).

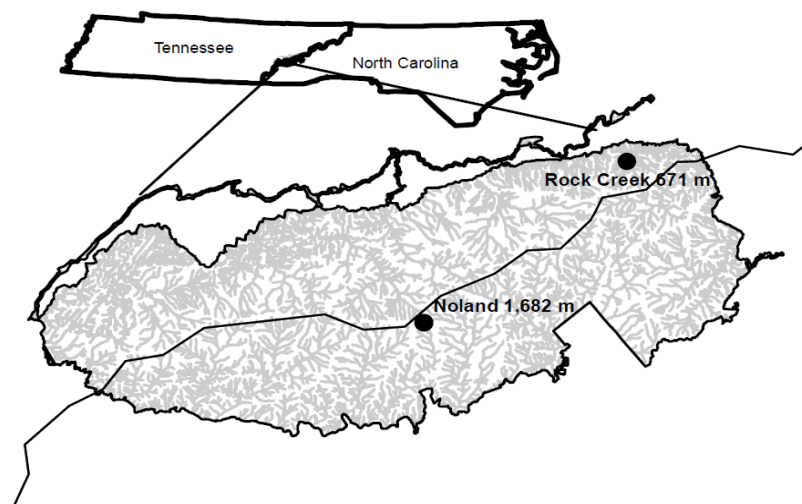


Figure 1: Auto-sampler locations and elevations

2.1.1 Noland Divide

NDW is a first order drainage system populated by red spruce, Fraser fir, and white yellow birch (Barker et al. 2002). NDW has not been subject to logging or fires like most of the GRSM, however an adelgid infestation is evident in the amount of dead Fraser fir basal (Barker et al. 2002). Soils are shallow in the NDW at less than 1 m in depth (Johnson and Lindberg 1992). Long-term sulfate flux trends were not evident in one study at the NDW, yet nitrate increases in throughfall and wet deposition were observed (Cai et al. 2010c). The lack of sulfate declines in the NDW was in contrast to other low-elevation sites in the GRSM which showed a reduction by $0.63 \mu\text{eq/L/yr}$ between 1984 and 2007 (Cai et al. 2010c, NADP 2010).

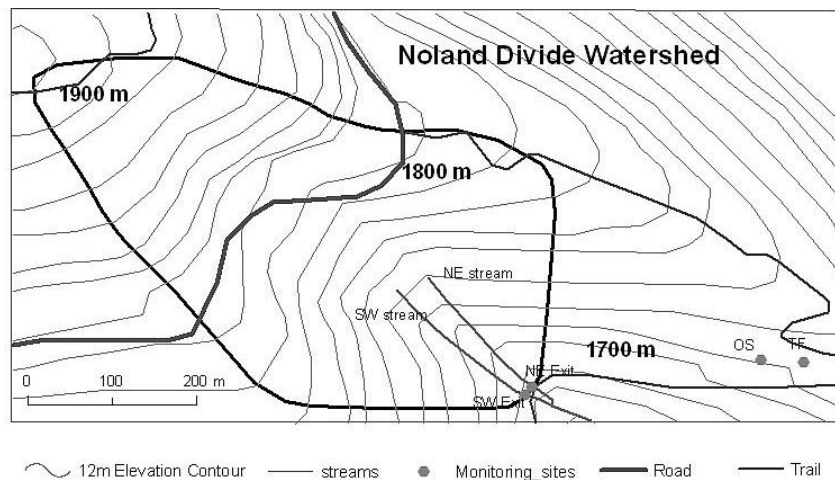


Figure 2: Map of the Noland Divide watershed showing water quality monitoring stations

NDW was selected based on its history as a study area for the effects of acid deposition dating back to the early 1990s. This site is continually monitored by the University of

Tennessee's Civil and Environmental Engineering (UT CEE) Department every two weeks for wet and dry deposition, throughfall, and soil water chemistry as well as stage, pH, conductivity, and temperature in two headwater streams (Figure 2). The Noland Creek Northeast (NE) stream is a first-order stream that drains an approximate area of 7 ha from a maximum basin elevation of 1,920 m to the sample location at 1,682 m (Figure 1). This small stream merges with another first order stream, Noland Creek Southwest (SW) stream, to form Noland Creek (Figure 2).

2.1.2 Rock Creek

The low-elevation collection site was placed at Rock Creek, a 3rd order stream, at an elevation of 671 m (Figure 1). The drainage area is approximately 362 ha with a maximum elevation of 1,768 m (Figure 3). Neff et al. (2013) lists specific characteristics of this watershed including a soil pH of 4.39, an effective soil cation exchange capacity of 5 meq/100g, a total soil depth of 80.9 cm, and an absence of Anakeesta rock. Vegetation is also listed in Neff et al. (2013) per maps from Madden et al. (2004) as consisting of 36.68% high and 35.40% low and mid-elevation mesic to sub-mesic forests with 18.07% subalpine woodlands and 9.53% shrub understory. Rock Creek was chosen because of its status on the 303-d list with 2.8 miles listed as impaired (TDEC 2010). Rock Creek is designated as a category 5, meaning one or more uses for this stream are threatened with 29 out of 66 data points collected not meeting set criteria (TDEC 2010).

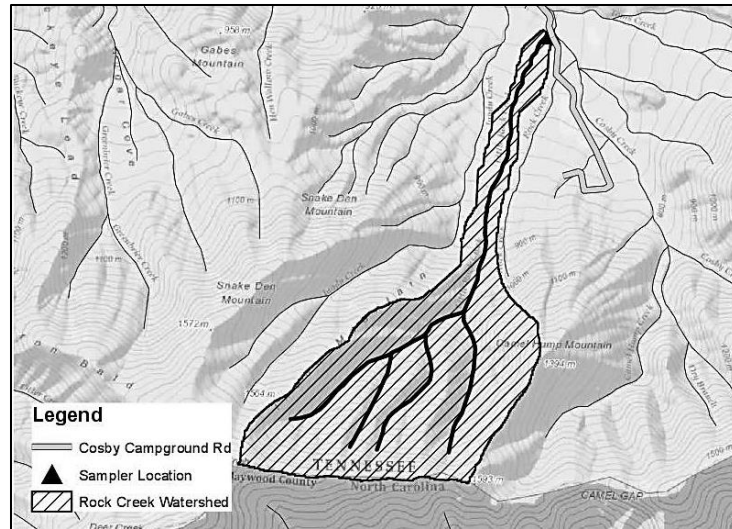


Figure 3: Map of Rock Creek Watershed

2.2 Water Monitoring/ Collection Equipment

Both sites were equipped with stage recording devices and an ISCO® 3700 auto-sampler. Both stage recording devices took measurements in 15 minute intervals. An existing three foot Tracom© H flume on the NE stream at NDW was used as the location for the auto-sampler in combination with a Global Water™ level logger stage recording device. The time was synced between the two devices to insure a correct stage reading at each sample taken. The stage level logger was also calibrated each visit using the staff gauge inside of the H flume for an accurate stream stage reading. Throughfall was collected in either two 5-gallon buckets lined with clean plastic bags (used in winter months due to freezing) or a series of funnels connected to one-gallon brown Nalgene jugs (used in spring and fall months). Throughfall volume was taken through weight (kg) calculations using a field scale and the unit weight of water.

An ISCO® 3700 auto-sampler was also used for sample collection at Rock Creek. For stage recording purposes, an ISCO® 4230 bubbler stage recorder was connected to the 3700

auto-sampler to associate stage with the time that the sample was taken. Each visit to this site included a manual stage measurement to verify the reading on the 4230 stage recorder. A throughfall collection apparatus was also placed adjacent to the location of the auto-sampler consisting of a 6 inch (diameter) funnel connected to a one-gallon brown Nalgene jug. A throughfall sample was collected after each event and a volume measurement was taken. A volumetric flask was used to measure volume of water collected in the throughfall apparatus.

2.3 Stage-Discharge Relationship

A stage-discharge relationship was developed from flume manufacturer's standards at NDW and a widely used field measurement technique at Rock Creek in order to build a hydrograph for each storm event sampled. The stage-discharge for the NE streamlet at NDW was found using the following formula for a three foot Tracom© H flume with H = head in feet and Q = cubic feet per second:

$$Q = .000373 - .00046H^{0.5} + 1.877055H^{1.5} + 3.038756H^{2.5}$$

The velocity-area method (Buchanan and Somers 1976) was used to create a stage-discharge relationship for the site at Rock Creek. Velocity was measured along the same riffle at multiple stage heights using a Marsh McBirney Flo-Mate™ 2000. Three velocity and depth measurements were taken at one foot increments across the stream. An average velocity for each one-foot increment was used when calculating flow with Q = cubic feet per second, D = depth in feet, L = length in feet and V_{avg} = average velocity in feet per second in the following equation:

$$Q = \Sigma \left[\frac{1}{2} (D_i + D_{i+1}) * \frac{1}{2} (V_{avg_i} + V_{avg_{i+1}}) * (L_{i+1} - L_i) \right]$$

Each flow calculation was directly associated to the stage reading on the ISCO® 4230 at the time that the field measurements were taken. The relationship developed for Rock Creek is shown in (Figure 4).

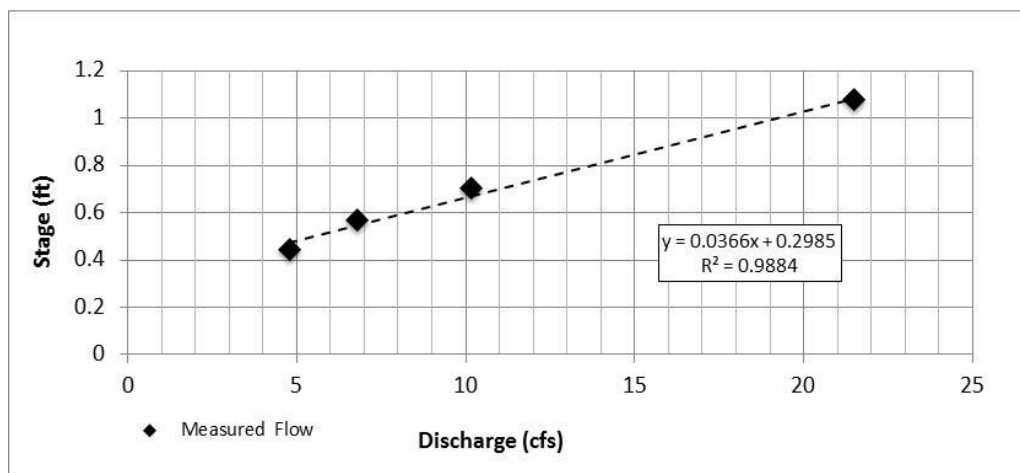


Figure 4: Stage-discharge relationship for Rock Creek.

2.4 Water Chemistry Analysis

Samples collected were transported to the University of Tennessee and analyzed for metals, cations, anions, metals, pH, conductivity, and acid neutralizing capacity (ANC). All samples were titrated to provide ANC values in addition to pH and conductivity measurements immediately after collection. All samples were tested at room temperature to standardize the results throughout the sampling period. Samples remained in refrigerated storage for further analysis. Conductivity, pH, and ANC values were found using a ManTech™ autotitrator, including gran titration analysis for ANC. Sulfate, nitrate, chloride, and ammonium values were

found using a Dionex™ ion chromatograph (IC). Standard solutions for IC analysis were prepared using high-grade reagents and deionized (DI) water. Total dissolved aluminum, calcium, potassium, magnesium, manganese, sodium, and silicon elements were found using a Thermo- Electron™ inductively coupled plasma spectrometer (ICP). All samples were processed and analyzed with quality assurance and quality control (QA/QC) checks such as field blanks, duplicate samples, and spike-splits. Round Robin samples provided by the United States Geological Survey (USGS) were also analyzed as a quality assurance test for the Civil and Environmental Engineering lab at UT. Procedures, equipment, and the corresponding method used for analysis can be found in Table 1.

Table 1: Procedures for sample chemistry analysis and associated methods.

Analysis	Procedure	Equipment	Method
pH	Potentiometric	PC-Titration Plus™	USEPA method 150.1
Conductivity (μS)	Potentiometric	PC-Titration Plus™	USEPA method 120.1
Acid Neutralizing Capacity (ANC)	Automated Titration	PC-Titration Plus™	Automated Gran titration for low ionic strength waters (Hillman et al. 1986)
Anions	Ion Chromatography	Dionex™	AWWA standard method 4110 (Eaton et al. 2005)
Cations, metals	Inductively coupled plasma spectrometry	Thermo-Elemental Ins Intrepid II™	USEPA method 6010B 6010C

2.5 Hydrograph Separation

Stream discharge consists of both baseflow (pre and post-events) and stormflow (during an interflow runoff event). To properly analyze stormflow chemistry, each hydrograph was separated graphically to determine which samples were taken during an event and which were

taken during baseflow conditions (Maidment 1992). Multiple methods exist for graphic separation of a hydrograph, including the straight-line, fixed-base, and variable-slope method. All of these methods are somewhat arbitrary and are not meant for predictive purposes. Yet when used in a consistent matter, they can provide adequate separation for constituent analysis. The watersheds analyzed in this study are small and the events sampled yielded typical, easily distinguishable hydrographs. Therefore, the straight-line method was chosen for this study. Each sample was then designated as being taken on the rising limb, peak, or falling limb of each hydrograph (Figure 5).

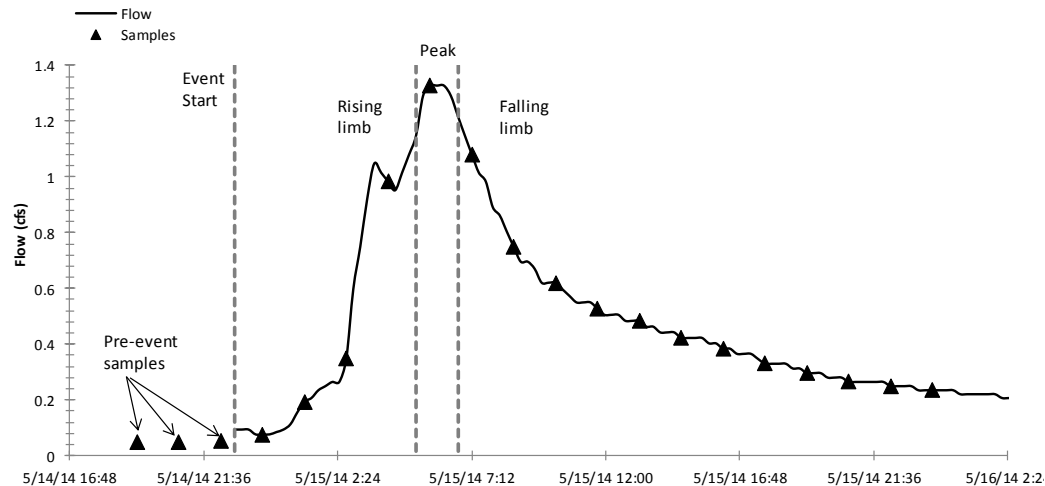


Figure 5: Sample designations for storm event number 8 (NST 8) at NDW

Krometis et al. (2007) used similar methods to perform an intra-storm analysis for variability in microbial partitioning. All samples collected outside of the hydrograph were considered baseflow samples and designated as pre-event or post-event.

2.6 Statistical Analysis

Using the statistical SAS Institute Inc. JMP platform, all constituent data for each site was analyzed for outliers and QA/QC. An analysis of means (ANOM) procedure was carried out using each section of the hydrograph (rising limb, peak, and falling limb) as the X factor and the constituent concentrations ($\mu\text{eq/L}$) as the Y response. Using an alpha value of 0.05, ANOM allows for statistically significant deviations from the mean to be evident if the p-value is less than 0.05. Upper and lower decision levels are representative of the sample power for each category (i.e. each section) and are shown as shaded areas in the output graphs. The decision level increases its bounds further for fewer samples within a category. The individual patterns of the mean comparisons can be further validated with sample events that continued through the entire hydrograph.

A student's t test was used to compare each constituent concentration ($\mu\text{eq/L}$) between NDW and Rock Creek. Constituent values for each hydrograph section at each site were compared between the two sites to test for significant differences in concentration. An alpha value of 0.05 was used with the JMP platform to provide p-values for each comparison with the hydrograph position as the X factor and each constituent as the Y response.

A simple linear regression analysis was used to test significance of the relationship between flow and stream chemical concentrations for the rising and falling limbs separately. The JMP platform was used to perform a bivariate fit using the log base 10 of flow as the X factor and each constituent as the Y response. Slopes, r squared values, and p-values were found for each regression test, per hydrograph category.

2.7 Sulfate and nitrate mass flux calculations

Cumulative mass loading and transport throughout events was calculated for storm events that sampled throughout the entire hydrograph and for throughfall samples. The mass transported during the rising limb was compared to the mass transported during the falling limb at both sites as well as an individual storm mass flux between two sampled events occurring within the same day. Mass of each constituent was divided by the area (ha) of watershed to compare the large watershed's mass output against the small watershed. This provides a mass per unit area (M) of watershed (kg/ha) transported during each event. The following equation was used with C = concentration (kg/m³), Q = flow (cms), A = area of watershed (ha) and t = time (s) since the last sample: $M = \frac{C*Q*t}{A}$

3. Results

3.1 Storm Event Characteristics

A total of 16 storm events were used in this analysis. The precipitation, duration, and number of samples collected can be found in Table 2. The maximum precipitation depths (total for the duration of the storm event) were 2.21 inches at NDW and 2 inches at Rock Creek. Maximum duration for stormflows was 35.25 hours at NDW and 79.25 hours at Rock Creek. The naming convention used for each event in this study can also be found in Table 2. Event mean concentrations were used as a comparative analysis between events (inter-storm). Only the events that sampled throughout the entire hydrograph were used. Due to long draw down times at Rock Creek, fewer storms were captured throughout the entire hydrograph. All aluminum concentrations are shown in mg/L throughout this study due to the variation in the speciation of aluminum in streams (Driscoll et al. 1980).

Event mean pH was the highest during the shortest storm and the lowest during the longest storm at NDW (Table 2). Mean event ANC concentration was found to be higher in storms with less precipitation and lower in storms with more precipitation. Base cation and anion mean concentrations did not show much variance between events at NDW. Rock Creek mean pH showed similar patterns with duration as the lowest mean pH value was found in the storm with the longest duration. ANC was found to be the highest during the largest precipitation depth at Rock Creek, opposite to NDW (Table 2). Most ions concentrations did not change significantly between events although the largest standard deviations were found during the events with the longest duration.

Table 2: Individual storm event characteristics and event mean concentrations at Noland Divide (NDW) and Rock Creek

Location	Event # Std Dev	Start Date	Cum. Precip (in)	Duration (hrs)	pH	Event mean concentrations**											# BF* Samples	# SF* Samples	Total samples collected
						ANC (µeq/L)	K ⁺ (µeq/L)	Mg ²⁺ (µeq/L)	Na ⁺ (µeq/L)	Ca ⁺ (µeq/L)	Cl ⁻ (µeq/L)	NO3 ⁻ (µeq/L)	SO4 ²⁻ (µeq/L)	Al (mg/L)	ΣBC ξ -ΣAA				
NDW	NST 1	9/13/2013	1.45	30	----	----	----	----	----	----	----	----	----	----		0	14	14	
	NST 2	11/26/2013	1.62	17.25	----	----	----	----	----	----	----	----	----	----		3	20	23	
	NST 3	2/21/2014	0.83	8.5	----	----	----	----	----	----	----	----	----	----		20	2	23	
	NST 4	3/3/2014	0.45	19.5	5.53	6.12	9.26	16.85	21.54	41.32	12.59	24.01	42.95	0.24	9.41	6	15	21	
	SD				0.39	1.34	0.74	0.43	0.34	2.10	0.47	0.28	0.60	48.53					
	NST 5	4/7/2014	2.21	16	5.53	5.60	8.76	17.13	19.01	43.45	11.06	23.57	41.41	0.09	12.32	13	8	21	
	SD				0.52	1.57	0.19	0.52	1.14	1.21	0.70	0.94	2.14	2.81					
	NST 6	4/14/2014	0.46	18.5	5.58	7.11	9.00	16.66	20.72	40.22	12.69	21.67	49.01	0.10	3.23	6	17	23	
	SD				0.41	1.98	0.39	0.54	1.43	1.42	1.21	1.04	21.80	4.35					
	NST 7	4/28/2014	0.61	9	5.62	8.01	8.87	17.24	22.10	43.48	11.45	21.18	50.06	0.08	9.01	13	8	21	
	SD				0.32	3.35	0.31	0.69	4.18	1.59	0.69	1.16	12.62	3.19					
	NST 8	5/14/2014	1.5	35.25	5.52	6.53	8.98	17.04	18.42	45.56	11.29	20.39	43.60	0.12	14.72	3	17	20	
SD				0.67	2.71	0.23	0.37	2.24	2.19	0.88	1.40	2.89	6.80						
Rock Creek	RST 1	11/18/2014	0.53	65	----	----	----	----	----	----	----	----	----	----		0	23	23	
	RST 2	2/4/2014	0.23	12.25	----	----	----	----	----	----	----	----	----	----		14	9	23	
	RST 3	2/21/2014	0.81	32.25	----	----	----	----	----	----	----	----	----	----		1	23	24	
	RST 4	3/2/2014	0.79	33.75	5.66	10.51	9.44	22.10	25.83	44.98	10.19	39.69	40.52	0.05	11.94	4	19	23	
	SD				0.31	1.17	0.68	0.97	2.36	1.75	0.18	1.04	1.54	0.02					
	RST 5	3/16/2014	2	152	5.68	11.88	9.83	23.63	26.85	49.11	9.72	40.72	41.91	0.04	17.07	10	14	24	
	SD				0.33	2.73	0.24	0.88	0.73	2.55	0.26	1.25	1.29	0.05					
	RST 6	3/28/2014	0.8	45.5	----	----	----	----	----	----	----	----	----	----		16	8	24	
	RST 7	4/7/2014	1.28	79.25	5.55	7.16	11.00	24.96	22.50	55.75	9.06	45.97	42.35	0.06	16.84	3	21	24	
	SD				0.39	2.05	0.78	2.25	1.78	5.18	0.64	4.87	8.83	0.03					
	RST 8	5/14/2014	0.38	33.25	5.60	9.64	11.71	23.92	23.32	52.07	9.06	42.60	39.96	0.10	19.39	3	21	24	
	SD				0.49	3.64	0.97	1.67	1.56	3.76	0.93	5.00	2.69	0.04					
Σ																115	239	355	
*BF = baseflow; SF = stormflow																			

*BF = baseflow; SF = stormflow

** Only events that sampled throughout the entire hydrograph were used for event mean concentrations

ξ Sum of the base cations - sum of the acidic anions

3.1 Analysis of Means

The analysis of means was carried out using standard box plots in addition to the ANOM output in JMP. Uniform scaling on the boxplots provides an analysis for concentration differences and dominating ions while the JMP output provides an individual and statistically significant analysis on separate scales. Samples from all 16 storms were utilized within each hydrograph category.

3.1.1 NDW

A total of 8 storm events were captured at the Noland NE stream with a total of 166 samples analyzed. Increases in proton concentration as derived from pH were observed during the rising limb followed by drop during peak flows (Figure 7). Shaded boxes in Figures 7, 8, 11, and 12 indicate the upper and lower decision levels based on the number of data points in each category. Any points outside of the shaded region are statistically significant deviations from the mean ($\alpha=0.05$). Stream pH averaged 5.44 in post-event samples, slightly lower than pre-event samples (5.68) (Table 3). Sulfate was found to have the highest concentrations among the chemical parameters examined with the exception of calcium which was similar in concentration to sulfate (Figure 9). Mean sulfate concentration between hydrograph categories was not found to increase or decrease with statistical significance ($p<0.05$) throughout stormflow events in the ANOM analysis (Figure 8). Maximum concentrations of sulfate, nitrate, and chloride were found to be 54.04, 35.72, and 34.20 $\mu\text{eq/L}$ respectively (Table 3). Nitrate and chloride anion concentrations increased during the rising limb (Figure 9). Both pre-baseflow and post-baseflow sulfate

concentrations ($\mu\text{eq/L}$) were approximately the same while chloride and potassium concentrations decreased significantly during the falling limb and in post-event samples and Mg^{2+} and Ca^{2+} concentrations ($\mu\text{eq/L}$) returned to near pre-event levels after increases in peak flows. Base cations, chloride, and proton concentration all increased with respect to each other during the rising limb and peak flows. ANC showed a steady decrease in mean values throughout storm events with post-event ANC remaining lower than pre-event levels (Figure 6).

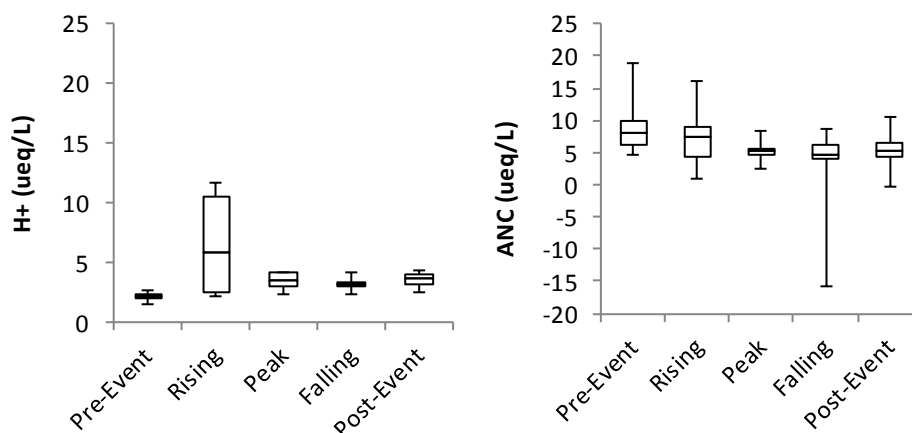


Figure 6: Boxplots of proton and ANC concentrations (ueq/L) throughout events at NDW

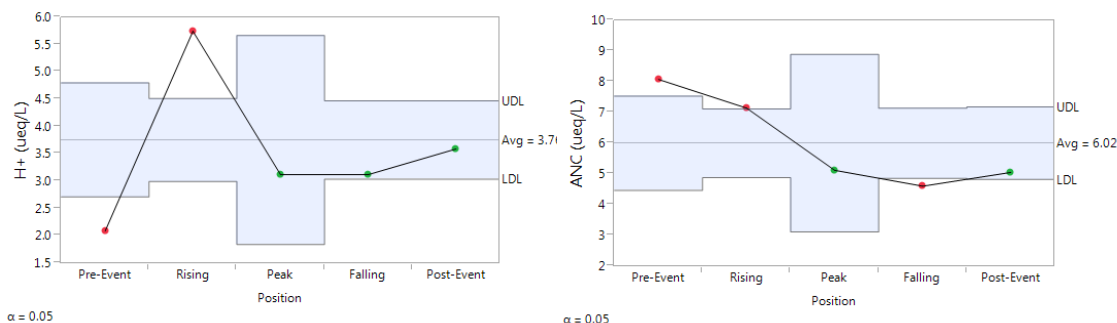


Figure 7: ANOM results for proton and ANC concentrations ($\mu\text{eq/L}$) at NDW

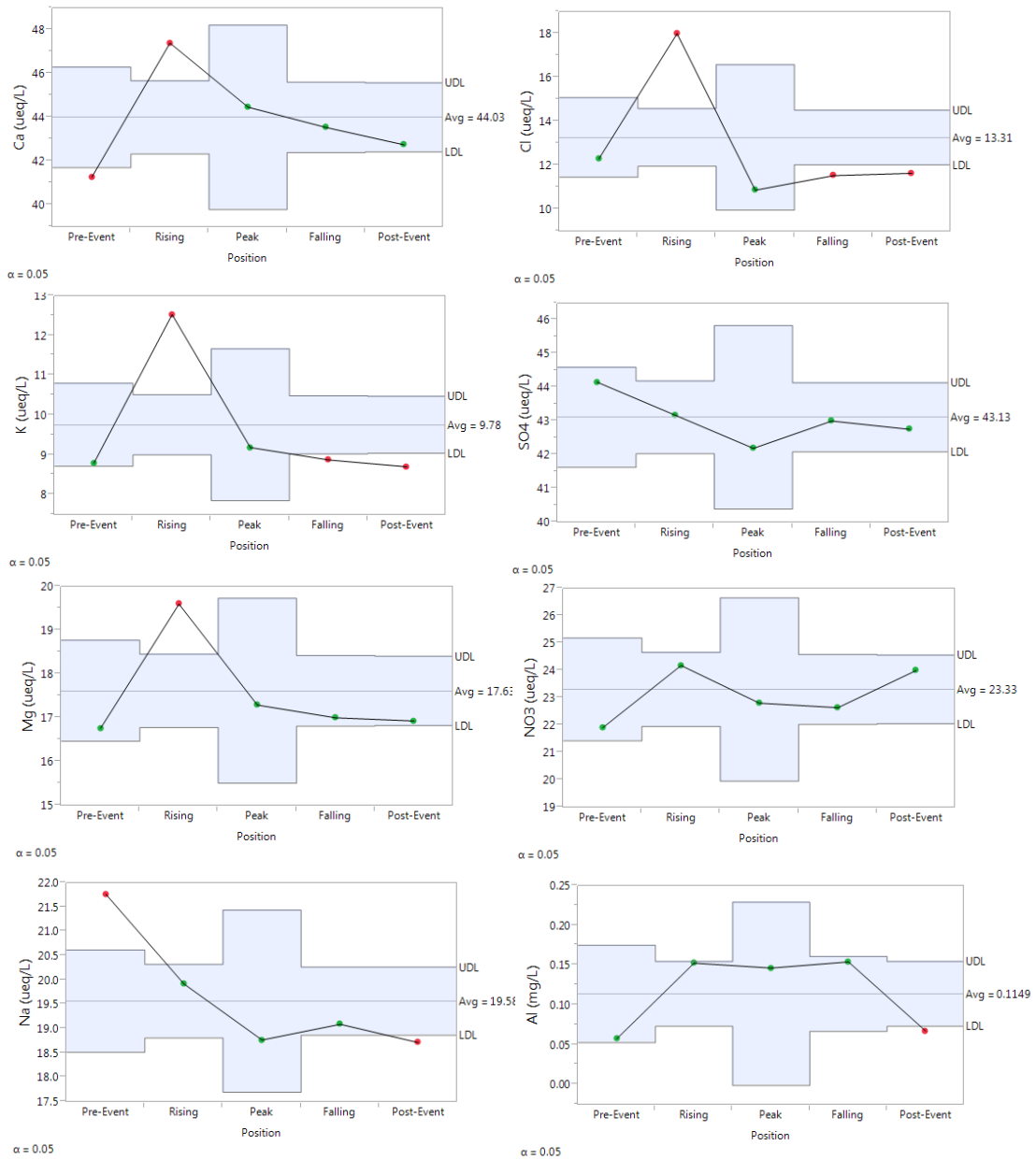


Figure 8: ANOM results for ion concentrations (µeq/L) throughout events at NDW

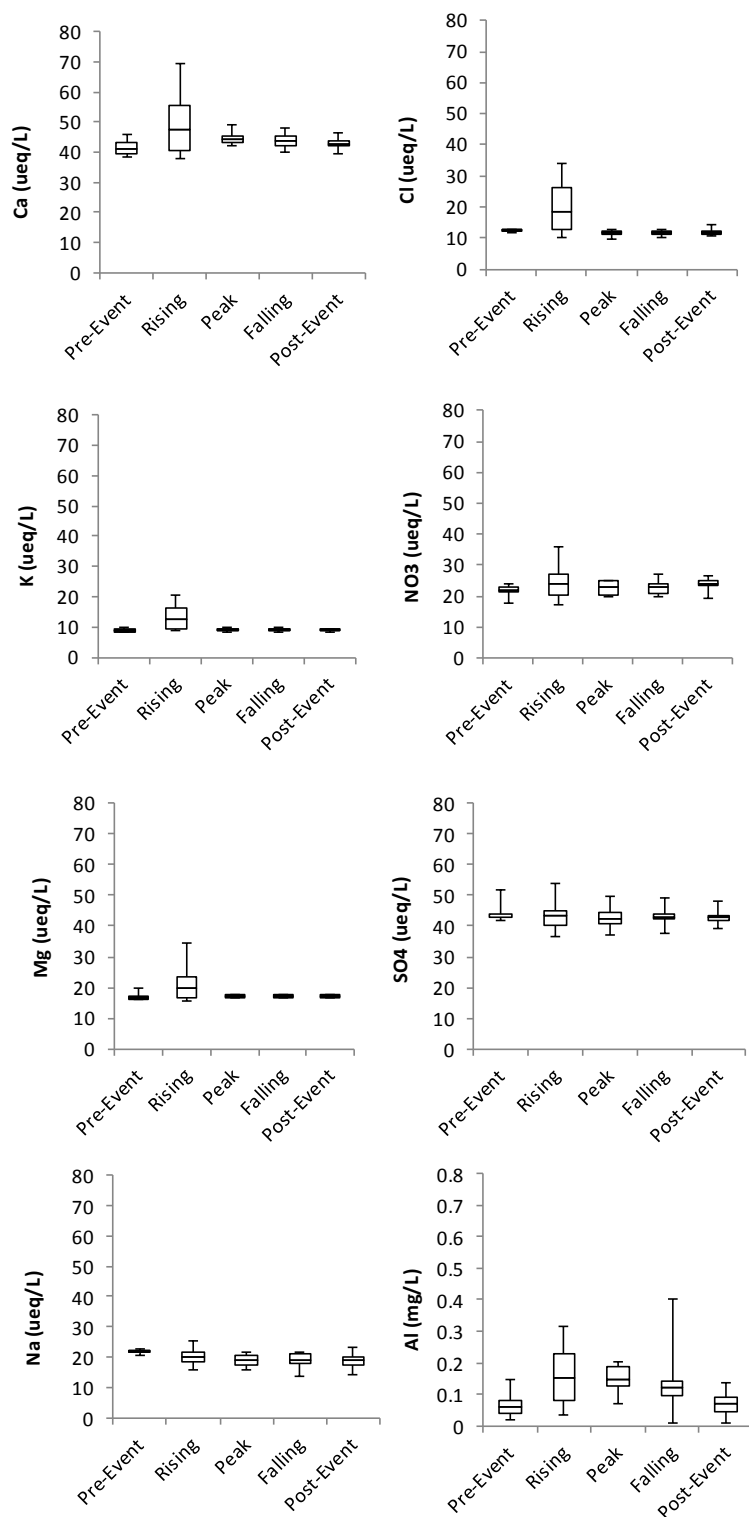


Figure 9: Boxplots of chemical constituent concentrations ($\mu\text{eq/L}$) throughout events at NDW

Samples yielded a maximum ANC of 18.93 $\mu\text{eq/L}$ and a minimum of -15.76 $\mu\text{eq/L}$ (Table 3) with large drops in the falling limb (Table 6). Base cation surplus (BCS, sum of the base cations – sum of acidic anions) did not vary much but was found to be the lowest during the falling and post-event categories. Compared to the titrated ANC concentrations however, the differences are variable with negative ANC values and positive BCS (Table 3).

3.1.2 Rock Creek

A total of 8 storm events were captured at the Rock Creek with 189 samples analyzed. Stream pH values declined steady through events as proton concentrations increased and remained slightly higher during the falling limb than in pre-event samples (Figure 11). Storm samples averaged a pH of 5.54 with a minimum of 4.70 and a maximum of 5.80 (Table 4). Baseflow samples yielded an average pH of 5.55, a minimum of 5.42, and a maximum of 5.80 (Table 4). ANC showed a steady decline with a lower decision level exceedance during the falling limb (Figure 12). ANC values ranged from a max of 22.25 $\mu\text{eq/L}$ to a minimum of -14.41 $\mu\text{eq/L}$ although mean concentrations did not fluctuate substantially throughout an event. Nitrate concentrations decreased during the rising limb but continued to increase past pre-event levels throughout the event (Figure 12). Sulfate concentrations ($\mu\text{eq/L}$) remained relatively flat throughout events with the exception of a few samples that yielded high values during peak flows and throughout the falling limb yielding a slight mean value increase with statistical significance ($p < 0.05$) in the falling limb (Figure 12). Nitrate concentrations were high, although calcium concentrations were the highest throughout events. Base cations concentrations for calcium and magnesium ($\mu\text{eq/L}$) showed significant decreases during the rising limb though

concentrations in the falling limb were higher than in pre-event samples. A lack of post-event samples (n=1) due to very long draw down times at Rock Creek provides a very rough estimate of post-event concentrations. BCS was found to be the lowest during the falling limb (minimum of -3.89) indicating base cation depletion may be occurring during events at Rock Creek (Table 4).

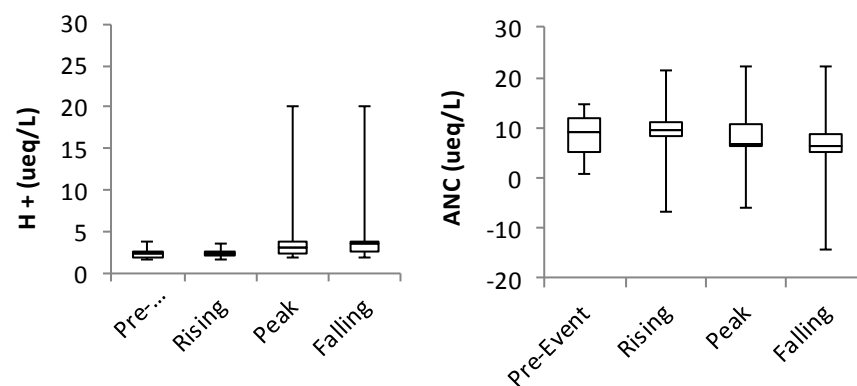


Figure 10: Boxplots of proton and ANC concentrations ($\mu\text{eq/L}$) throughout events at Rock Creek

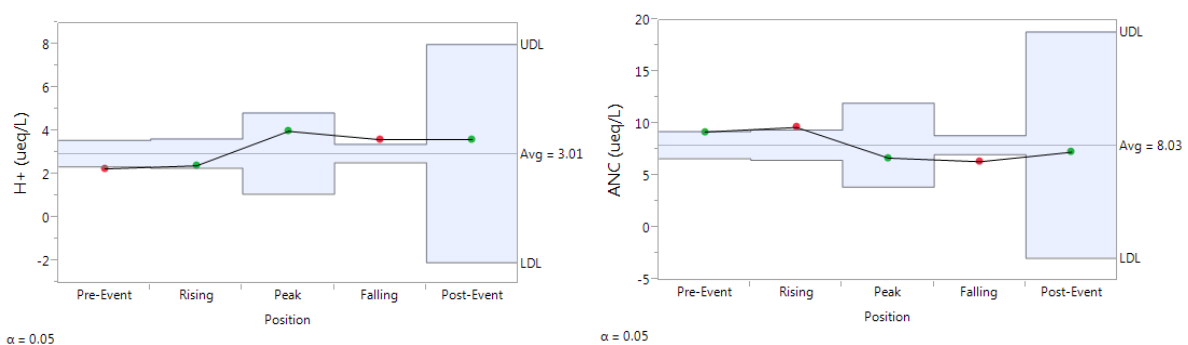


Figure 11: ANOM results for proton and ANC concentrations ($\mu\text{eq/L}$) throughout events at Rock Creek

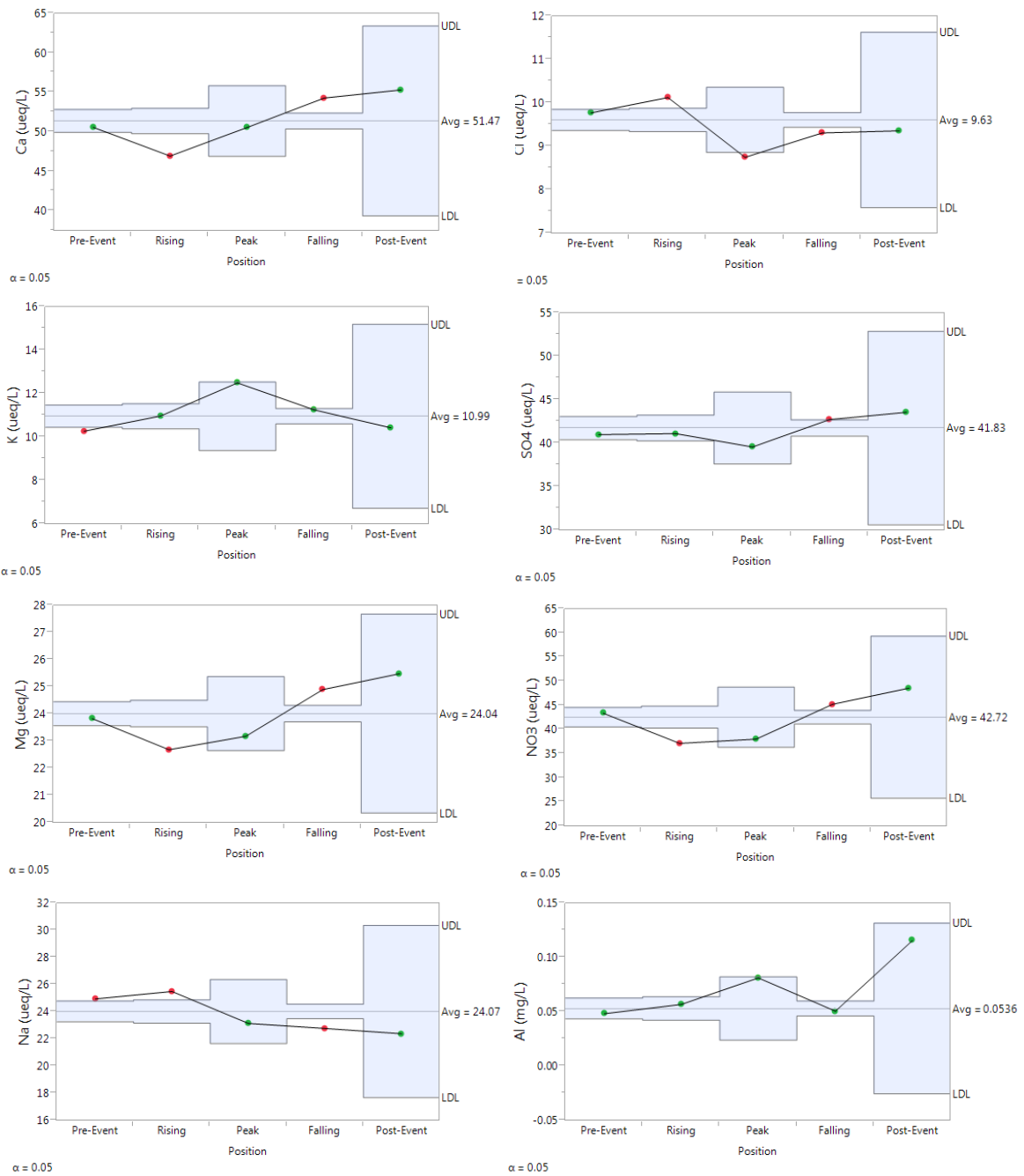


Figure 12: ANOM results for ion concentrations throughout events at Rock Creek

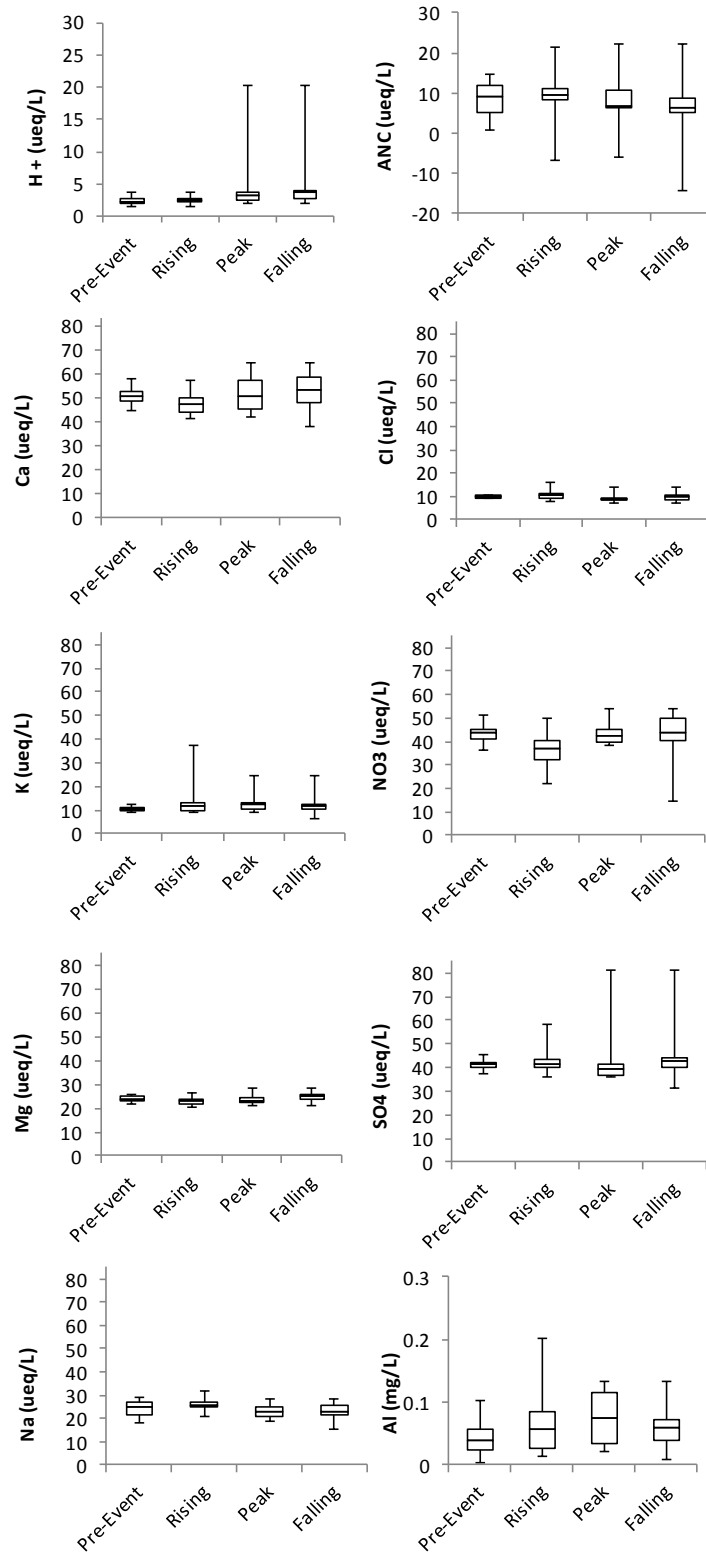


Figure 13: Boxplots of ion concentrations ($\mu\text{eq/L}$) throughout events at Rock Creek

Table 3: NDW sample concentration mean, max, and min values

		pH			ANC (μeq/L)			K ⁺ (μeq/L)			Mg ²⁺ (μeq/L)			Na ⁺ (μeq/L)					
	n	Min	Mean	Max	Min	Mean	Max	Min	Mean	Max	Min	Mean	Max	Min	Mean	Max			
Pre-Event	21	5.59	5.68	5.84	4.56	8.10	18.93	8.34	8.81	9.71	16.06	16.78	19.76	20.44	21.78	22.69			
Rising	34	4.93	5.23	5.68	0.88	7.34	16.19	8.65	12.65	20.61	15.69	19.71	34.25	15.99	19.94	25.23			
Peak	7	5.40	5.50	5.62	2.41	5.14	8.31	8.58	9.21	10.18	16.72	17.31	17.67	15.88	18.78	21.88			
Falling	38	5.38	5.50	5.65	-15.76	4.63	8.68	8.28	8.89	9.88	16.69	17.02	17.51	13.51	19.11	21.62			
Post-Event	38	5.36	5.44	5.62	-0.24	5.36	10.64	8.39	8.72	9.12	16.50	16.94	17.80	14.39	18.73	23.31			
		Ca ⁺ (μeq/L)			Cl ⁻ (μeq/L)			NO3 ⁻ (μeq/L)			SO4 ²⁻ (μeq/L)			Al (mg/L)			ΣBC-ΣAA*		
	n	Min	Mean	Max	Min	Mean	Max	Min	Mean	Max	Min	Mean	Max	Min	Mean	Max	Min	Mean	Max
Pre-Event	21	38.28	41.31	45.72	11.50	12.33	12.91	17.72	21.91	23.94	41.65	44.18	51.95	0.01	0.12	0.40	9.08	10.25	12.25
Rising	34	38.00	47.65	69.40	10.17	18.19	34.20	17.12	24.21	35.72	36.66	43.18	54.04	0.07	0.15	0.20	14.37	14.38	25.52
Peak	7	42.15	44.50	49.10	9.60	10.90	12.83	20.00	22.83	24.43	36.92	42.21	49.87	0.01	0.07	0.11	11.70	13.85	16.81
Falling	38	39.96	43.57	48.26	10.06	11.57	12.86	19.70	22.71	26.88	37.79	43.02	49.16	0.02	0.06	0.15	8.37	10.89	11.28
Post-Event	38	39.43	42.77	46.44	10.45	11.67	14.23	19.30	24.03	26.38	39.13	42.78	47.90	0.03	0.15	0.32	8.15	8.69	9.83

*ΣBC-ΣAA = sum of the base cations - sum of the acidic anions

Table 4: Rock Creek sample concentration mean, max, and min values

		pH			ANC (ueq/L)			K ⁺ (μeq/L)			Mg ²⁺ (μeq/L)			Na ⁺ (μeq/L)					
	n	Min	Mean	Max	Min	Mean	Max	Min	Mean	Max	Min	Mean	Max	Min	Mean	Max			
Pre-Event	50	5.42	5.65	5.80	0.83	9.30	14.70	9.26	10.30	12.53	21.51	25.50	25.50	17.87	24.99	29.09			
Rising	45	4.93	5.60	5.80	-6.68	9.39	21.42	9.34	11.61	37.04	20.07	26.66	26.66	20.85	25.69	31.74			
Peak	7	5.30	5.52	5.71	-5.93	6.79	11.68	9.40	12.53	19.87	20.75	25.29	25.29	18.97	23.19	28.38			
Falling	84	4.70	5.49	5.70	-14.41	6.46	22.25	6.47	11.88	24.89	20.87	28.33	28.33	15.36	23.09	28.17			
Post-Event	1	5.44	5.44	5.44	7.36	7.36	7.36	10.46	10.46	10.46	25.51	25.51	25.51	22.43	22.43	22.43			
		Ca ⁺ (μeq/L)			Cl ⁻ (μeq/L)			NO3 ⁻ (μeq/L)			SO4 ²⁻ (μeq/L)			Al (mg/L)			ΣBC-ΣAA*		
	n	Min	Mean	Max	Min	Mean	Max	Min	Mean	Max	Min	Mean	Max	Min	Mean	Max	Min	Mean	Max
Pre-Event	50	44.57	50.67	58.21	8.97	9.79	10.37	36.54	43.54	51.46	37.50	41.08	45.52	0.00	0.04	0.11	10.21	17.06	17.99
Rising	45	41.31	47.03	57.53	7.95	10.27	15.92	22.14	36.99	49.75	36.11	41.58	58.41	0.01	0.06	0.22	22.15	25.37	28.90
Peak	7	42.11	50.65	58.22	7.01	8.76	10.12	38.63	42.45	46.26	36.11	39.65	44.62	0.02	0.08	0.16	9.47	20.79	30.75
Falling	84	37.96	53.60	64.69	7.24	9.58	14.33	14.34	44.08	54.24	31.33	43.07	81.40	0.01	0.06	0.15	-3.89	20.17	27.75
Post-Event	1	55.41	55.41	55.41	9.38	9.38	9.38	48.73	48.73	48.73	43.65	43.65	43.65	0.03	0.03	0.03	12.06	12.06	12.06

*ΣBC-ΣAA = sum of the base cations - sum of the acidic anions

3.2 Rock Creek and Noland Comparison: student's t test

The student's t test results showed Rock Creek with significantly higher concentrations in most hydrologic categories compared with NDW (Table 5). Due to a lack of sample power in the post-event category at Rock Creek, the student's t test was only carried out for pre-event, rising limb, peak, and falling limb samples. Rock Creek showed higher amounts of nitrate than NDW throughout an event although NDW did control in sulfate concentrations for pre-event, rising, peak, and falling limb. Rock Creek controlled significantly for most base cations throughout an event while NDW statistically showed much higher levels of aluminum in pre-event, rising, and peak samples.

Table 5: Student's t test results for ion concentrations between Rock Creek (RC) and Noland Divide Watershed (NDW) noting the stream with the greater mean concentration and the t test significance level.

	Pre-Event	Rising	Peak	Falling	Post-Event
Na ⁺	RC (<.0001)	RC (<.0001)	RC (0.0007)	RC (0.1522)	RC (<.0001)
K ⁺	RC (<.0001)	NDW (0.1101)	RC (0.5116)	RC (0.0219)	RC (0.1907)
Mg ²⁺	RC (<.0001)	RC (<.0001)	RC (<.0001)	RC (<.0001)	RC (0.0308)
Ca ⁺	RC (0.0074)	RC (<.0001)	RC (<.0001)	RC (0.012)	NDW (0.5387)
Al	NDW (0.0022)	NDW (0.0012)	NDW (0.0005)	NDW (0.6242)	NDW (0.4757)
Cl ⁻	RC (<.0001)	RC (<.0001)	RC (0.0002)	RC (0.3911)	RC (0.0001)
NO ₃ ⁻	RC (<.0001)	RC (<.0001)	RC (<.0001)	RC (<.0001)	RC (0.0002)
SO ₄ ²⁻	NDW (0.0039)	NDW (0.2306)	NDW (0.3082)	RC (0.2611)	RC (0.9119)
Controlling Site (p-value)					

3.3 Flow-Concentration Correlations

The stream base cations, K⁺, Ca²⁺, and Mg²⁺ concentrations and flow correlate with one another at NDW with greater significance during the rising limb than the falling limb (Figure

14). The differences in base cation concentration ($\mu\text{eq/L}$) flux between the two watersheds can be seen in the bivariate regression results. Magnesium and calcium both showed negative slopes on the rising limb at Rock Creek versus positive slopes at NDW (Table 6). There is a much stronger correlation with calcium and flow than sulfate at NDW, which essentially remains constant although the sulfate regression analysis yielded a negative slope for both the rising limb and falling limb (Table 6). Sulfate remained flat at Rock Creek during the rising limb and trended upward during the falling limb. Nitrate tended to increase with flow at NDW with a slope of 5.18 while Rock Creek showed strong decreasing trends in the rising limb followed by increasing trends in the falling limb. Sodium showed a more declining slope at NDW than Rock Creek and aluminum was highly variable although showing an overall correlation with flow at NDW.

Table 6: Bivariate regression slope, R^2 , and p-value results per hydrograph category for NDW and Rock Creek

Ion	Position	NDW			Rock Creek		
		Slope	R^2	p-value	Slope	R^2	p-value
H^+	Rising	5.1	0.84	<.0001	1.03	0.19	0.0038
	Falling	0.32	0.1	0.0532	2.13	0.33	<.0001
ANC	Rising	-2.7	0.41	<.0001	-4.1	0.07	<.0001
	Falling	-1.71	0.14	0.022	-6.12	0.15	0.0005
K^+	Rising	4.74	0.72	<.0001	0.18	0.6	<.0001
	Falling	-0.36	0.12	0.0345	0.1	0.15	<.0001
Mg^{2+}	Rising	4.87	0.628	<.0001	-1	0.02	0.3496
	Falling	-0.036	0.01	0.72	6.14	0.5	<.0001
Na^+	Rising	-0.5	0.25	<.0001	-0.12	0.15	0.0162
	Falling	-2.42	0.24	<.0001	-0.231	0.44	<.0001
Ca^+	Rising	9.63	0.7	<.0001	-3.45	0.03	0.2758
	Falling	3.72	0.39	<.0001	23.88	0.61	<.0001
Cl^-	Rising	7.51	0.6	<.0001	2.57	0.2	0.0023
	Falling	-1.84	0.74	<.0001	-2.23	0.23	<.0001
NO_3^-	Rising	5.75	0.42	<.0001	-15.55	0.21	0.0019
	Falling	-0.1	0	0.92	18.33	0.21	<.0001
SO_4^{2-}	Rising	-1.64	0.08	<.0001	0.27	0	0.8977
	Falling	-3.17	0.23	0.0021	4.25	0.02	<.0001
Al	Rising	0.03	0.49	<.0001	0.01	0.24	0.0041
	Falling	-0.01	0	<.0001	0	0.03	0.2658

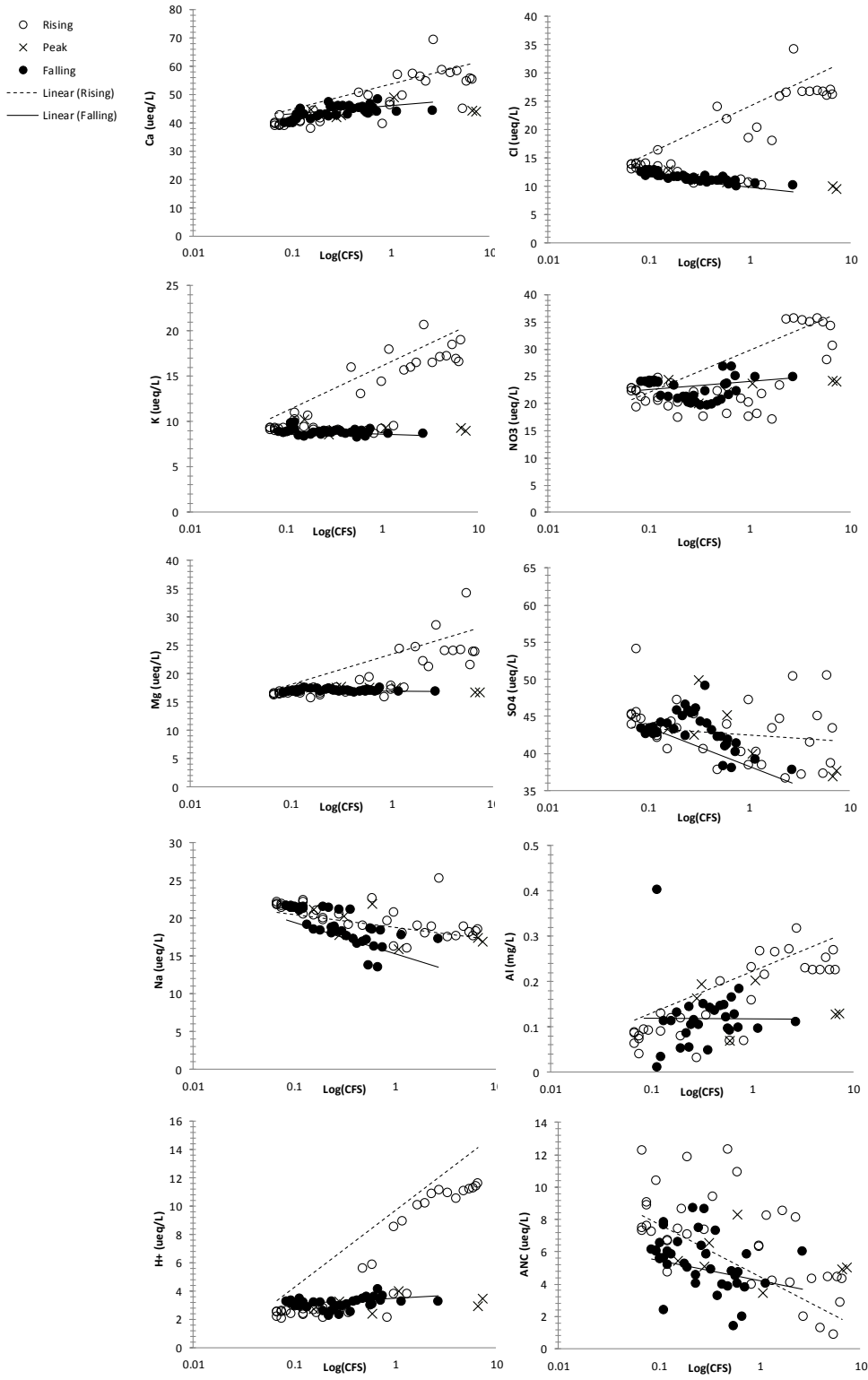


Figure 14: Ion concentration vs $\log(\text{flow CFS})$ correlation at NDW

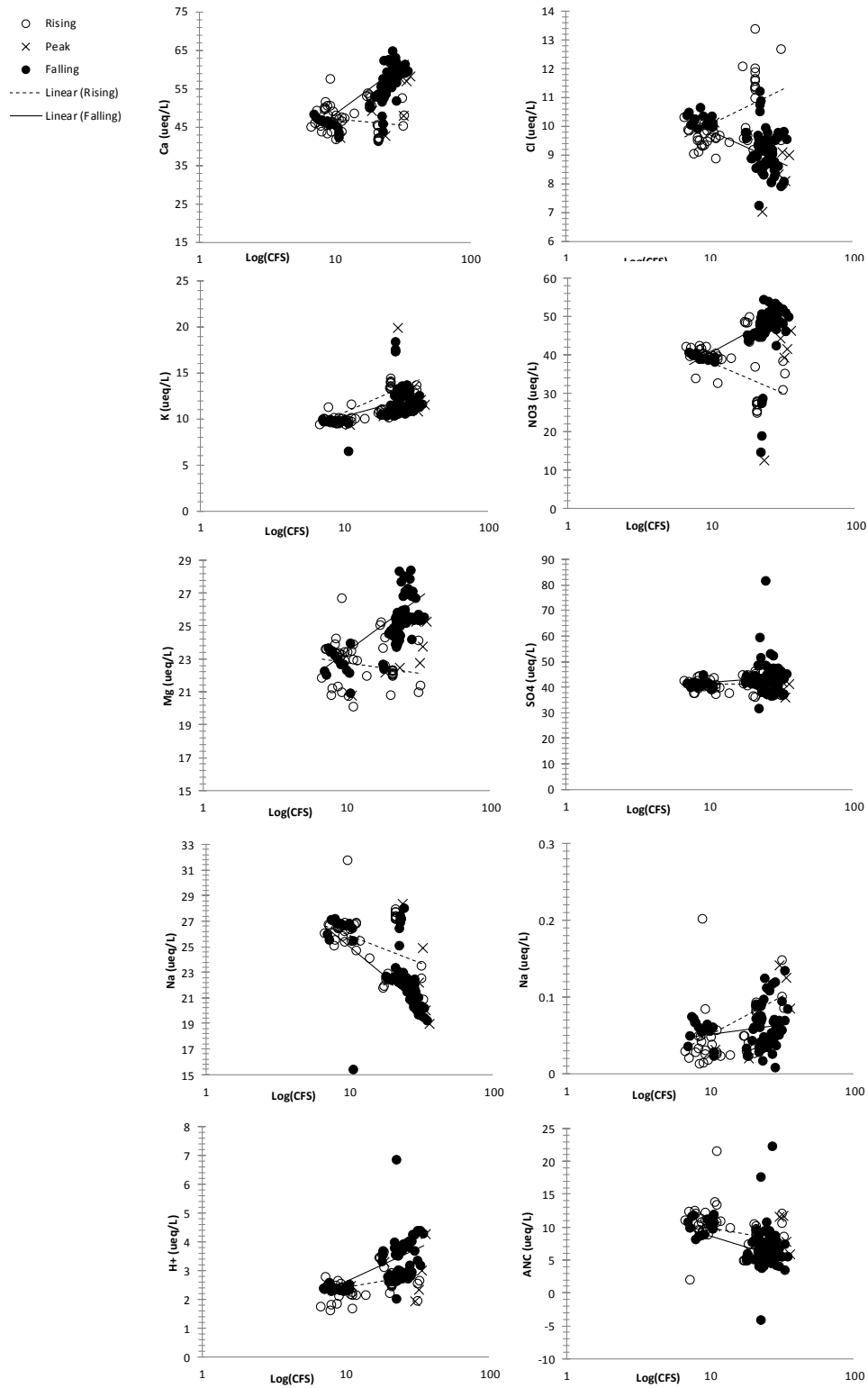


Figure 15: Ion concentration vs $\log(\text{flow CFS})$ correlation at Rock Creek

Proton concentration (derived from pH) and chloride show a much stronger correlation to flow in the rising limb indicating the fast pH change that occurs during storm events at NDW (Figure 14). Proton concentrations at Rock Creek showed lesser increase with flow than at NDW (Table 6). ANC showed more of a correlation with flow at Rock Creek than NDW. NDW ANC values tended to fluctuate with a slightly negative trend throughout events. Both sites showed steady declines in ANC throughout the rising limb and falling limb.

3.4 Sulfate and Nitrate Mass Loading

Exported mass transport (kg/ha) was calculated for sulfates and nitrates between the rising limb and falling limb of each storm that was sampled throughout an entire event or sampled through the entire rising limb or falling limb. Sulfate mass transport was higher than nitrate at NDW and the falling limb showed a slightly higher amount of mass then the rising limb for most events (Figure 16).

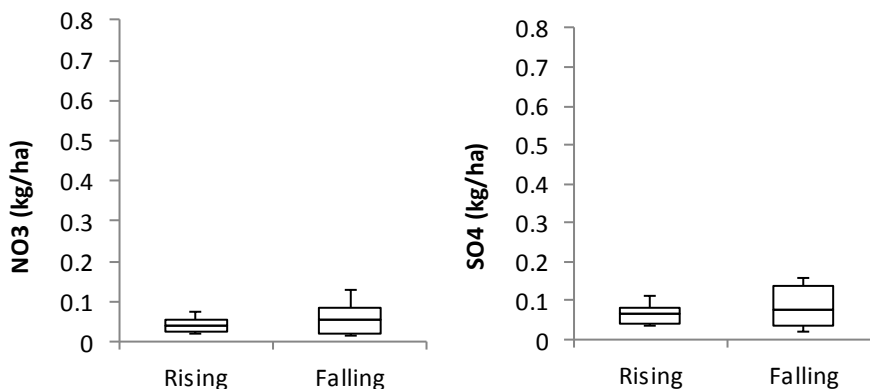


Figure 16: Noland mass transport per unit area of watershed

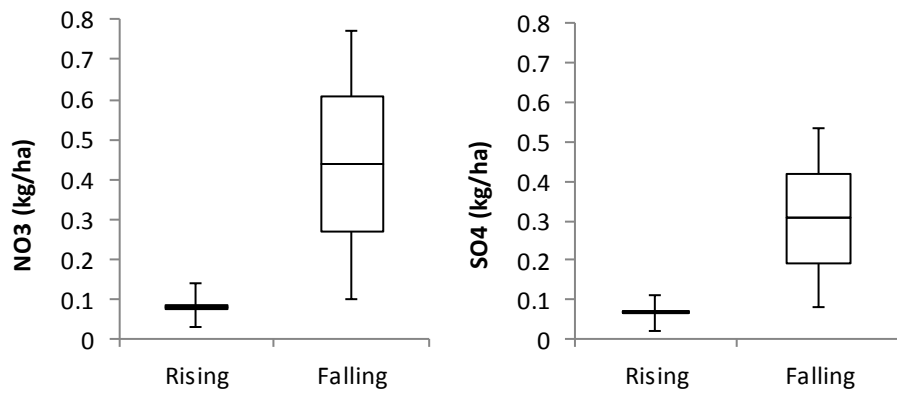


Figure 17: Rock Creek mass transport per unit area of watershed

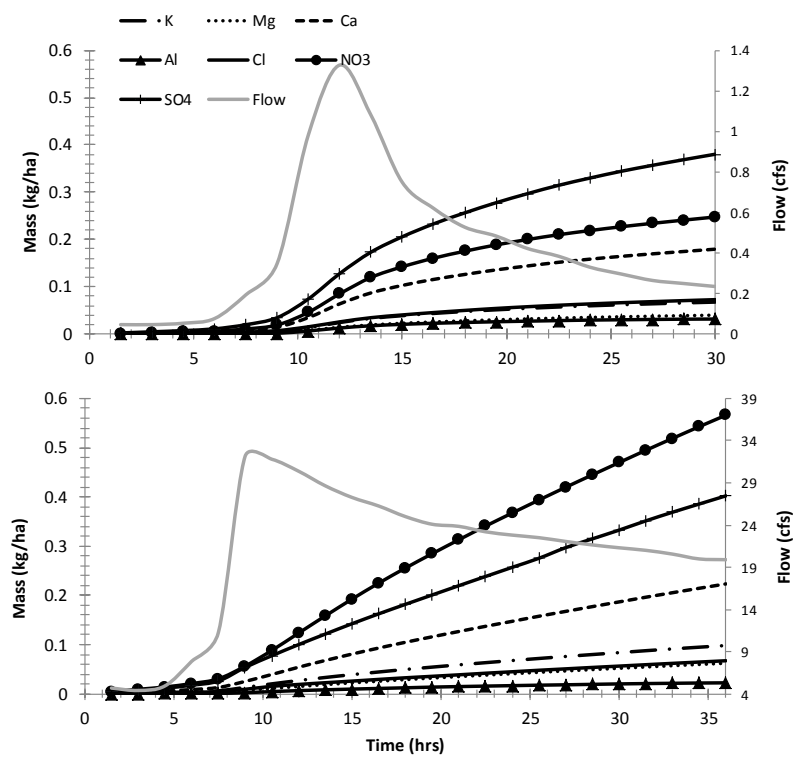


Figure 18: Cumulative mass loading for two events sampled on 5/15/2014 at NDW (top) and Rock Creek (bottom)

Rock Creek showed a higher mass (kg/ha) of sulfate than nitrate throughout events, opposite to NDW. The mass transport on the falling limb of the storm was shown to be much higher than the rising limb during storm events (Figure 17). Two events sampled during the same storm front on 5/15/2014 showed different patterns for mass loading at each site (Figure 18). NDW showed more of a gradual increase in mass loading as sulfate and nitrate concentrations are not changing significantly during events. Rock Creek shows the impact of long drawdown times with more mass continuing post-peak flow. Cumulative mass export of nitrate was much higher at Rock Creek than at NDW.

3.5 Throughfall

Sulfate and nitrate concentrations in NDW and Rock Creek throughfall samples were much higher than the exported concentrations in stream stormflow with the exception of nitrate at Rock Creek (Figure 20). Nitrate mass flux remained higher than sulfate at Rock Creek in stream flow, while sulfate mass remained higher in throughfall. Throughfall samples collected at NDW yielded an average pH of 4.62 and very high concentrations of sulfate and nitrate. A maximum of $113.3 \mu\text{eq/L SO}_4^{2-}$ and $156.99 \mu\text{eq/L NO}_3^-$ were found. Deposition mass flux of sulfate and nitrate in throughfall samples were much higher than in stream stormflow (Figure 19).

Stream export of sulfates at NDW was found to be 23% on average of throughfall input. Nitrate concentrations were found to be much higher than other anions in throughfall samples at Rock Creek, similar to the stormflow samples. When compared to each other, nitrate was higher in throughfall samples than in stormflow for some events while throughfall mass was slightly

higher for both nitrate and sulfate in others (Figure 20). Throughfall measurements showed an average pH of 5.78, a minimum of 5.42, and a maximum of 6.31 at Rock Creek, much higher than NDW. Means and standard deviations of chemical concentrations, pH, and ANC for throughfall samples can be found in Appendix A. NST 5, for example, indicates storm event number 5 at NDW and RST 5 indicates storm number 5 at Rock Creek. Information on each storm can be found in Appendix A.

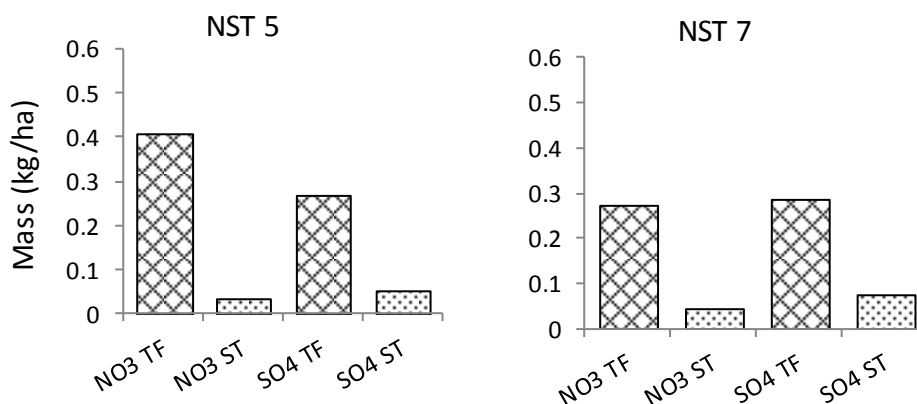


Figure 19: Throughfall ion differences for 2 events at NDW

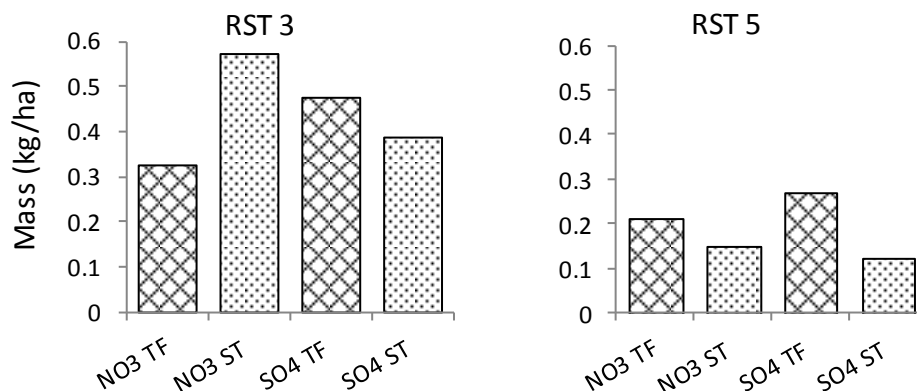


Figure 20: Throughfall ion differences for 2 events at Rock Creek

4. Discussion

Mean constituent deviations, event dominating ions, and hydrologic observations within an event-scale analysis provided significant insight with respect to ion flux, retention, and transport. The low elevation, larger basin site showed evidence of longer hydrologic time of concentration, high concentrations of nitrate, and longer contact with geochemical processes and basin characteristics while the results from the high elevation, small basin watershed showed rapid hydrologic movement, high concentrations of sulfate, and potentially minimal contact with deeper soils.

NDW showed higher concentrations of sulfate in all samples which is consistent with knowledge that stormflow dominated by flowpaths in the upper layers of soil with transient and perched saturation zones showed higher concentrations of sulfates (Mulholland 1993). A steep basin with shallow soils, NDW most likely routes stormwater rapidly through the macropores and mesopores in the upper layers of soil as described in Mulholland (1993). The decreasing trend found in sulfate during events at NDW while still having a higher concentration than other ions measured is consistent with a study on event-based response in the Catskill Mountains indicating a steady-state scenario or zero net retention of sulfates (Rochelle et al. 1987, Wigington et al. 1996). In this study by Wigington et al. (1996) the overall concentrations of sulfate were high, but acidic and non-acidic episodes showed decreases in sulfates in mountainous, steep watersheds in comparison to lower elevation basins that showed increases during storm events. Increased sulfate deposition can create a higher steady-state, baseline concentration of sulfate (Rochelle et al. 1987). A high baseline concentration of sulfate and nitrate were found to be major contributors to reductions in ANC in Wigington et al. (1996) even though retention of any excess sulfate was occurring, maintaining a constant concentration

throughout storm events. The lack of any retention of sulfates from deposition could be representative of acid sensitive soils (Cronan and Schofield 1990, Palmer et al. 2004). However sulfate retention (or a lack of desorption) from deposition seems evident at NDW as the concentration of sulfate remains the same throughout most events and showed a slight decline during peak flows.

One exception at NDW was a storm preceded by a wetting front that showed an increase in sulfate concentration as opposed to typical events with no prior wet periods showing little change in concentration (Figure 21). This scenario was similar to a study in the Hubbard Brook Experimental Forest showing more severe acidic episodes followed by wet antecedent conditions (Wellington and Driscoll 2004). While one storm event cannot prove statistically that wet antecedent conditions create higher sulfate concentrations, it is still possible that sulfate desorption is occurring with wet antecedent days. Further studies utilizing soil moisture could expand upon this finding.

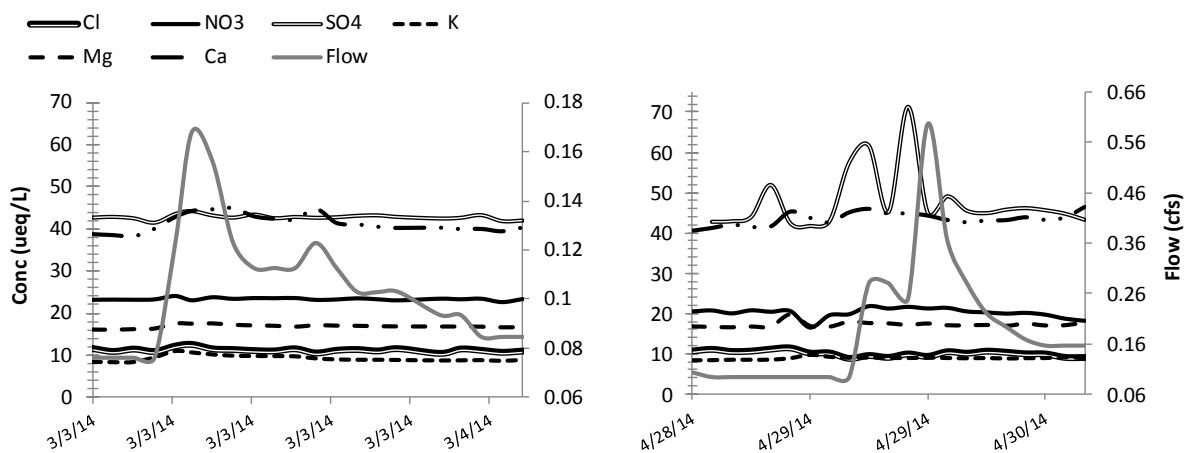


Figure 21: Ion concentration flux in storm number 5 (NST 5) at NDW (left) and storm number 7 (NST 7) with prior wet period (right).

With a short hydrologic time of concentration, small drainage basin, and little groundwater flow during events, long interactions with basin geology or soils seems unlikely at NDW. The data collected at Rock Creek, however does show evidence of interactions with deeper soils. Nitrogen deposition and saturation typically occurs in the higher elevation streams in the GRSM while the lower reaches have decreased nitrogen due to uptake by stream periphyton (Schwartz et al. 2014a). While the mean concentrations indicate much higher nitrogen concentrations throughout events at the low elevation site, evidence of flow from deeper soils with less nitrogen due to uptake was evident. Studies involving tracer elements like chloride propose that incoming water from precipitation during events will displace and therefore release water already stored in drainage basins (Luxmoore et al. 1990). As an example, a storm event at Rock Creek (RST 8) on 5/15/2014 (Figure 31 in the Appendix B) showed a decrease in nitrate concentration during post-peak flow but a steady increase in concentration past that of pre-event levels. Soil water that is present prior to the event that resides in deeper soil layers should have less nitrate concentrations due to uptake and/or microbial activity. However the stormwater or “new” water just after the rising limb shows elevated concentrations of nitrate, higher than pre-event levels. This was also evident in the ANOM analysis as nitrate concentrations decreased in the rising limb and then increased above pre-event levels in the falling limb indicating some nitrogen uptake with less concentration in the displaced soil water than in the groundwater and interflow within the falling limb.

Higher concentrations of nitrate than sulfate at Rock Creek was consistent with a study by Neff et al. (2013) in the GRSM showing that basins with larger percentages of high elevation and sub-alpine forests had high nitrogen levels, but counter to the understanding that larger low-elevation watersheds typically have less nitrate than high-elevation watersheds (Schwartz et al.

2014a, Wellington and Driscoll 2004). The elevated levels of nitrate concentrations at Rock Creek, when compared to NDW in the student's t test and in cumulative mass export, indicated that uptake was not occurring as much in this particular watershed, possibly due to the watershed existing in stage 2 of nitrogen saturation. In stage 2 of nitrogen saturation, cycling of nitrogen is diminished and base flow concentrations are elevated (Wellington et al. 1996). Neff et al. (2013) proposed that high rates of nitrification was due to excess deposition (nitrate saturation), particularly in the high-elevation forest basins, and that could be the reason for higher proton and nitrate concentrations in these GRSM basin types. The high nitrate concentrations could be contributing to prolonged acidity within the watershed. Lower elevation watersheds should provide base-cation interaction and greater potential for absorption of acid anions (Palmer et al. 2004), however reductions in base cation mean concentrations were found to be statistically significant during the rising limb for calcium and magnesium indicating that cation-depletion was occurring at times. This is evident in the mean base cation surplus calculations for individual storms as negative mean values were found. A dilution effect could be occurring with a lack of decline in sulfate concentration during the same hydrograph category (rising limb) that showed declining base cation and nitrate concentrations.

ANC concentration and pH showed declines during all of the events sampled and the significance of the change in pH from pre-event to the rising limb indicating the rapid rate at which the stream chemistry was adjusted at NDW. The correlation between constituent concentrations and flow at NDW showed that sulfate levels remained the highest in concentration but unchanged throughout an event while chloride, pH, and nitrate showed stronger correlations with flow. Chloride is ubiquitous in drainage basins (Shaw et al. 2008) and this may explain its increase in concentration with an increase in flow in this study. As the pH

continues to decrease with events at NDW, the concentrations of anions and base cations tended to rise and fall with each other or the sulfate and nitrate concentrations remained unchanged. While the stormwater at NDW does not have long contact with deeper soils, it does move rapidly through the upper soil horizon. Higher elevation soils can be derived from base-poor organic matter and can harvest organic acids (Palmer et al. 2004). While the chloride concentrations may be due to its abundance, the drops in pH and higher proton concentrations could be associated with these organic acids. The ion differences between the acidic anions and base cations alone do not represent the decline in pH at NDW. In some cases the BCS was greater with a decline in pH. In a study by Deyton et al. (2008), high accuracy in lab analytics with respect to ion concentrations led the author to attribute the differences in titrated ANC and base cation surplus to organic acids. This could be the reason for the increase in acidity at NDW as well. The variation between titrated ANC concentrations and BCS indicates that additional research is needed to examine other constituents in stream water at NDW that could be contributing to pH and ANC declines.

In most cases nitrate was the dominating concentration in throughfall at NDW while throughfall sulfate was higher at Rock Creek. The opposite was found in stream concentrations as nitrate was higher at Rock Creek and sulfate was higher at NDW. The concentrations found in throughfall at NDW were high, although mass per unit area of watershed showed relatively similar amounts of mass at both sites. The stream mass flux at Rock Creek represented higher amounts of sulfate and nitrate in some cases when compared to throughfall while the Noland NE stream mass flux did not come close to throughfall measurements at NDW. The considerable difference in sulfate throughfall and storm mass output suggests that desorption was still taking place at NDW. Throughfall consists of not only wet deposition, but also fog, gaseous, and

particulate derivations (Weathers et al. 2006). For this reason levels were very high, although Rock Creek showed higher stream mass flux in some cases. The one throughfall apparatus placed at Rock Creek should not be considered a complete and representative throughfall collection of the entire 362 ha watershed however.

5. Conclusion

The evidence collected from multiple storm events and simultaneous throughfall supports the ongoing study of acid deposition in the GRSM and its lingering effects by focusing on event-based retention and transport of chemical constituents. The results of this research suggest that sulfate desorption, on average, was not occurring during storm events at either high or low elevation streams and throughfall data implied that sulfate soil absorption was still occurring. However, high levels of nitrate in the low elevation stream could be indicative of nitrogen saturation. A lack of exchangeable cations could also be seen in storm events at the low elevation site, another lingering effect of excessive acid deposition (Driscoll et al. 2001).

As biogeochemical processes in the GRSM continue to interact with previous and current anthropogenic pollutant sources, a continuous monitoring effort was needed to investigate potential negative impacts on aquatic biota health. Continuous monitoring of streams in the Park is vital in understanding its recovery from years of deposition from anthropogenic sources as well as current pollutant sources. While the constituent mean deviations showed little change in sulfate concentration through events, dominating ions at NDW also did not support the observed decline in pH and ANC at the high elevation site. The sharp change in pH did indicate the rapid rate at which stream chemistry was adjusted at NDW and the fast movement of interflow. With the sharp decline in pH it could possibly suggest that organic acids are playing a larger role in acidification (Palmer et al. 2004). Further studies on the presence of organic acids are needed to confirm this theory and to continue to monitor the progress of the Park as its recovery continues.

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Appendices

Appendix A: Tables

Table 7: Storms collected at Noland Divide Watershed (NDW) and Rock Creek (09/2013 – 05/2014)

Location	Event #	Start Date	Precipitation (in)	Duration (hrs)	# BF Samples	# SF Samples	Total Samples Collected
NDW	NST 1	9/13/2013	1.45	30	0	14	14
	NST 2	11/26/2013	1.62	17.25	3	20	23
	NST 3	2/21/2014	0.83	8.5	20	2	23
	NST 4	3/3/2014	0.45	19.5	6	15	21
	NST 5	4/7/2014	2.21	16	13	8	21
	NST 6	4/14/2014	0.46	18.5	6	17	23
	NST 7	4/28/2014	0.61	9	13	8	21
	NST 8	5/14/2014	1.5	35.25	3	17	20
Rock Creek	RST 1	11/18/2014	0.53	65	0	23	23
	RST 2	2/4/2014	0.23	12.25	14	9	23
	RST 3	2/21/2014	0.81	32.25	1	23	24
	RST 4	3/2/2014	0.79	33.75	4	19	23
	RST 5	3/16/2014	2	152	10	14	24
	RST 6	3/28/2014	0.8	45.5	16	8	24
	RST 7	4/7/2014	1.28	79.25	3	21	24
	RST 8	5/14/2014	0.38	33.25	3	21	24
Σ					115	239	355

Table 8: Results for throughfall samples collected at Rock Creek (09/2013 – 05/2014)

	pH	ANC	Cl ⁻	NO ₃ ⁻	SO ₄ ²⁻	Na ⁺	K ⁺	Mg ²⁺	Ca ⁺	Al
		μeq/l	μeq/l	μeq/l	μeq/l	μeq/l	μeq/l	μeq/l	μeq/l	ppm
Average	5.78	31.38	7.74	12.42	20.53	16.91	7.35	10.12	39.05	0.01
SD	0.25	22.70	3.14	6.89	5.23	17.94	4.02	6.66	23.29	0.03

Table 9: Results for throughfall samples collected at Noland Divide Watershed (09/2013 – 05/2014)

	pH	ANC	Cl ⁻	NO ₃ ⁻	SO ₄ ²⁻	Na ⁺	K ⁺	Mg ²⁺	Ca ⁺	Al
		μeq/l	μeq/l	μeq/l	μeq/l	μeq/l	μeq/l	μeq/l	μeq/l	ppm
Average	4.62	-0.10	19.92	44.54	51.11	24.74	25.43	17.89	41.28	0.02
SD	0.19	0.23	13.86	48.59	36.23	0.50	0.62	0.22	0.81	0.06

Appendix B: Figures

Each figure is titled with the location (NST = Noland Divide storm event and RST = Rock Creek storm event) and the number of the event collected.

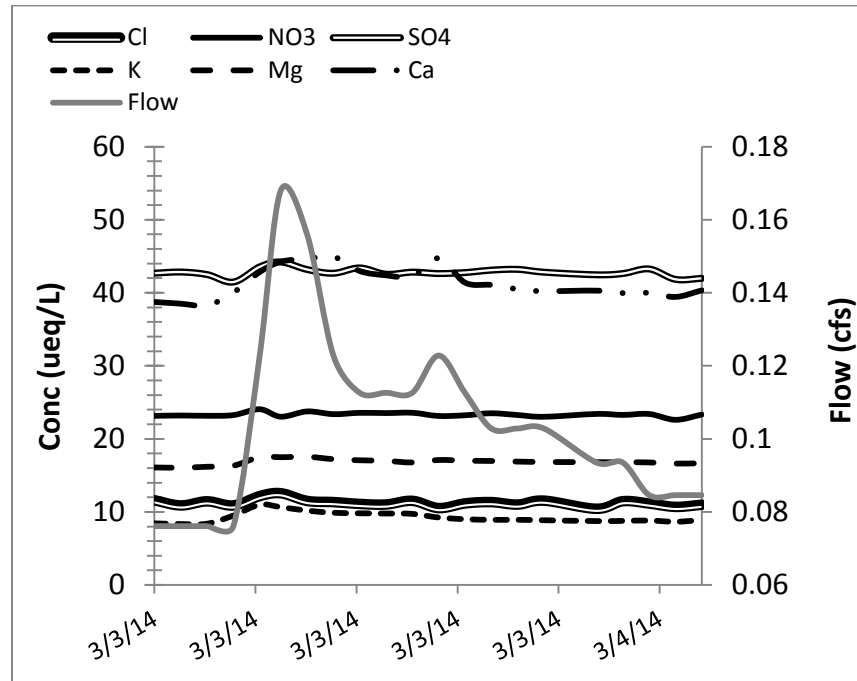


Figure 22: NST 4

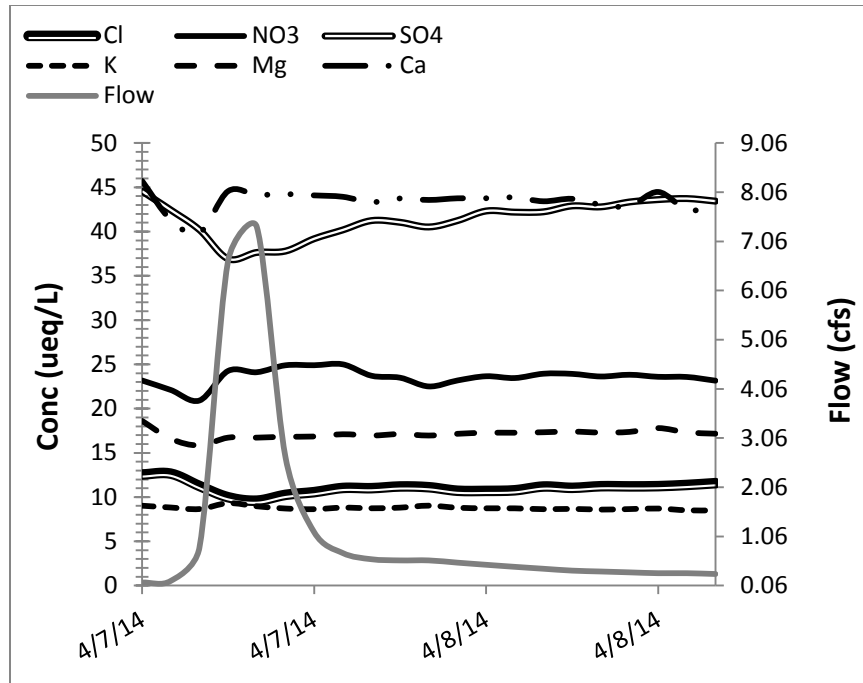


Figure 23: NST 5

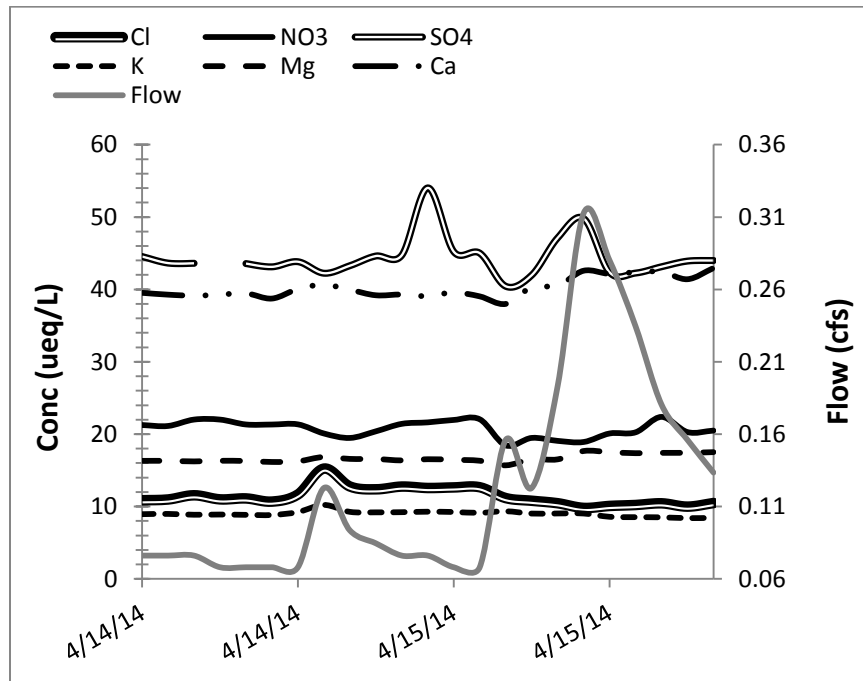


Figure 24: NST 6

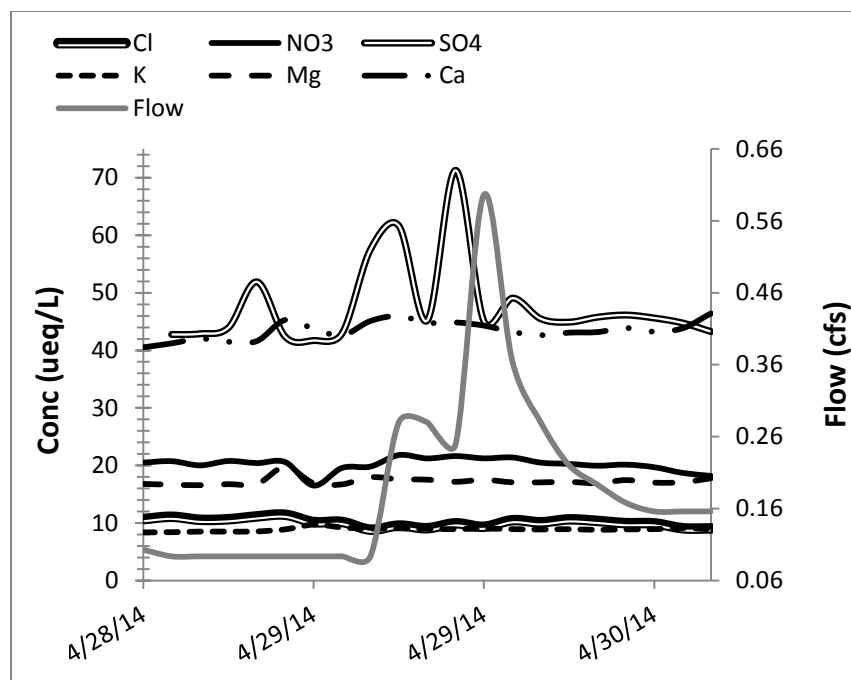


Figure 25: NST 7

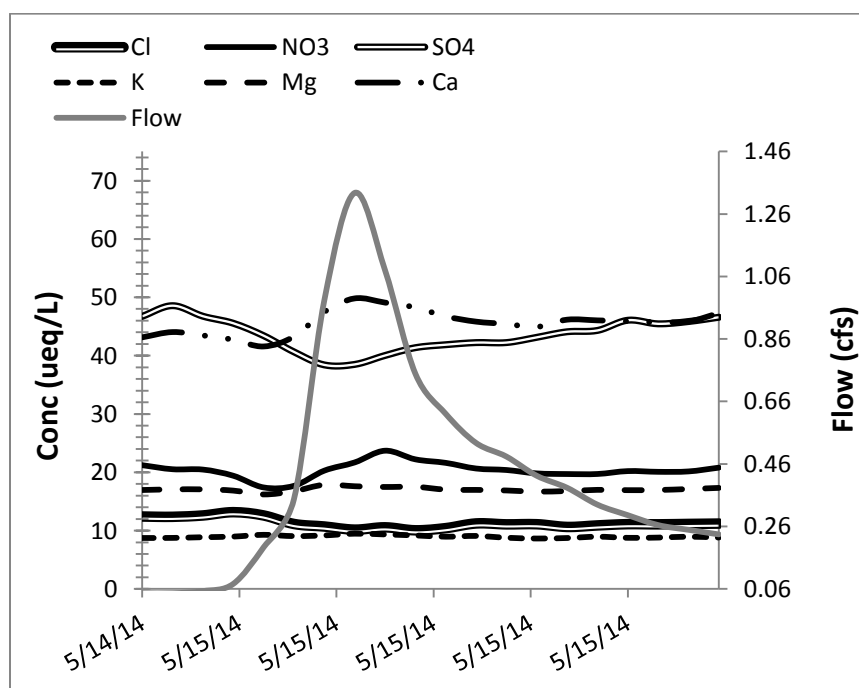


Figure 26: NST 8

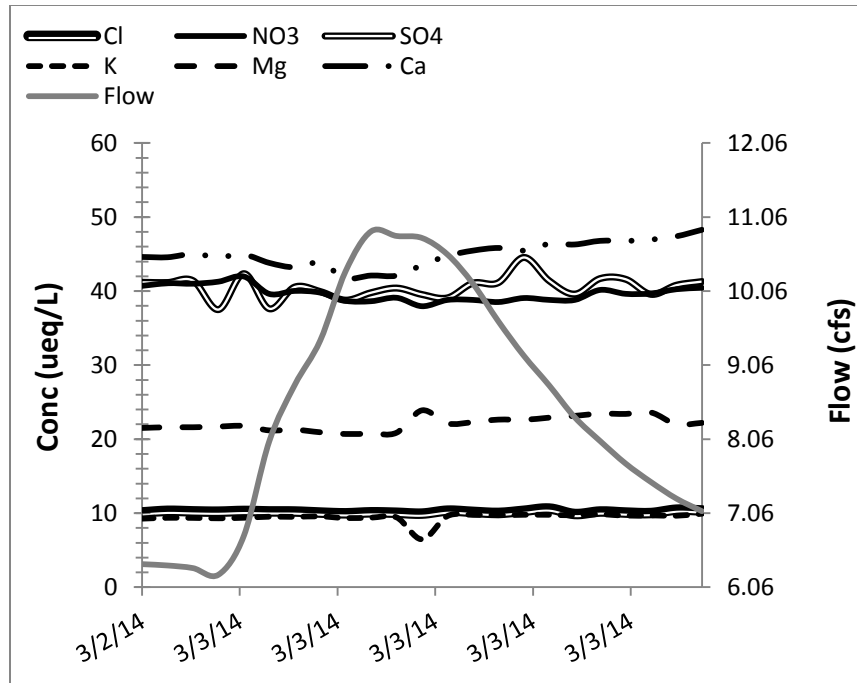


Figure 27: RST 4

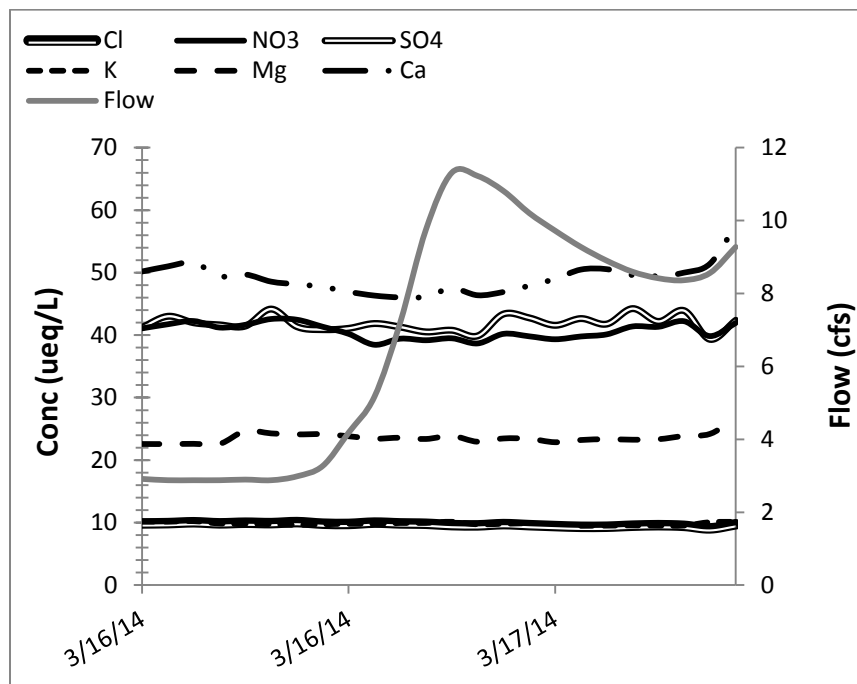


Figure 28: RST 5

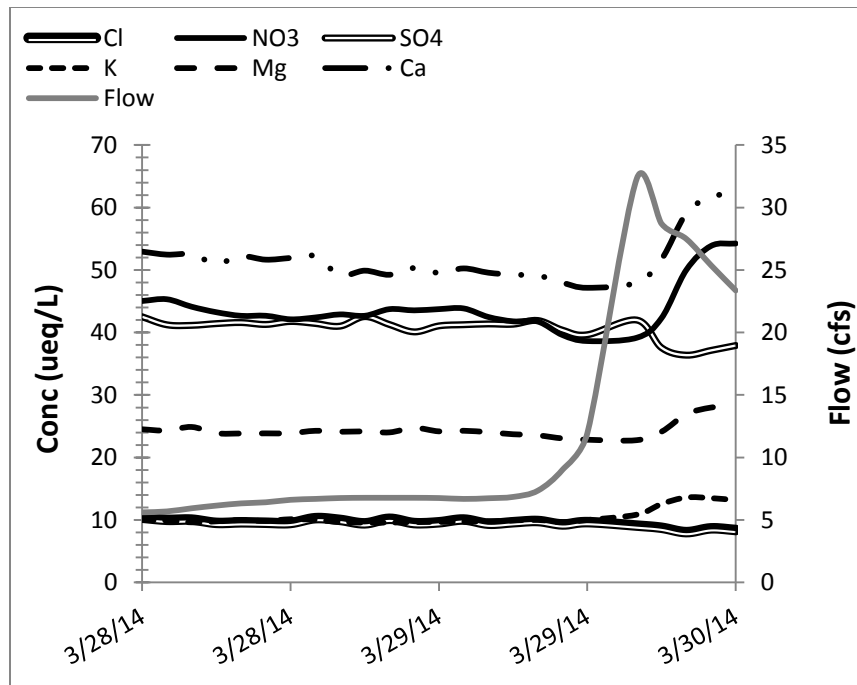


Figure 29: RST 6

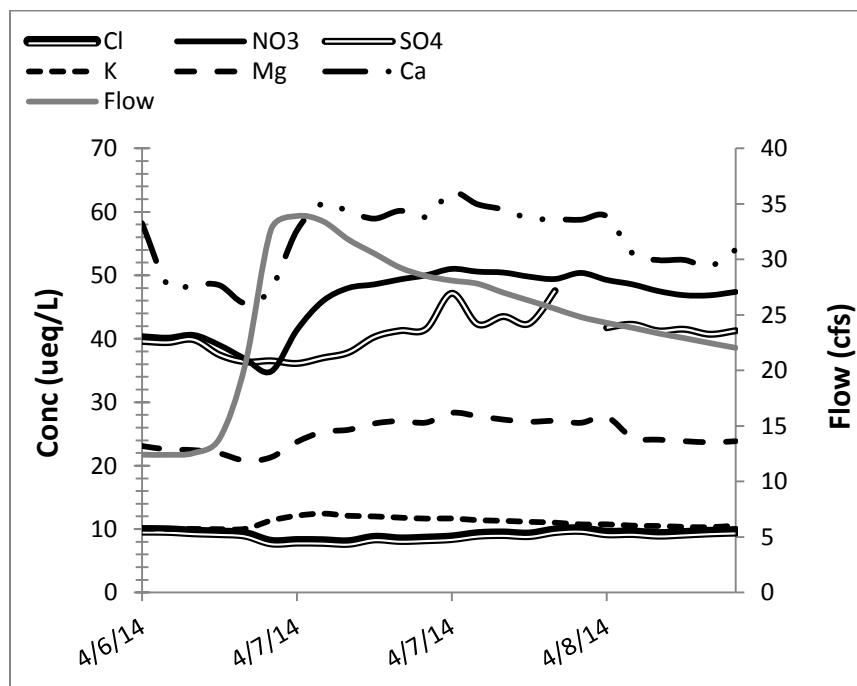


Figure 30: RST 7

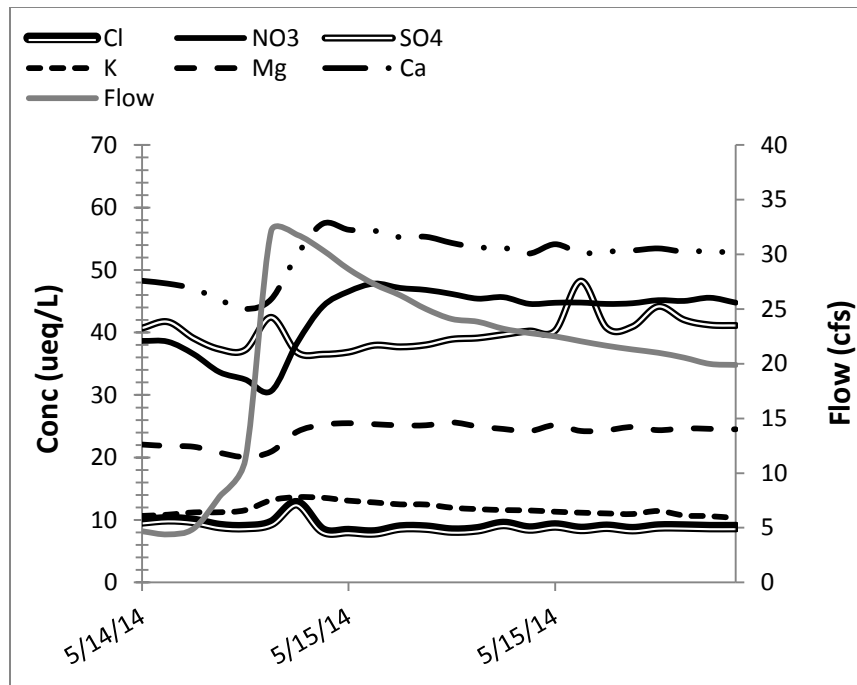


Figure 31: RST 8

Vita

Matthew Aplin is from Chattanooga, TN where he graduated from Baylor School. He attended the University of Tennessee, Knoxville in the spring of 2010 where he earned a Bachelor of Science in Civil Engineering with honors. Matthew was awarded a Graduate Research Assistantship from the Civil and Environmental Engineering Department at UT in the summer of 2013 in conjunction with the Department of the Interior and the Great Smoky Mountains National Park. Matthew has worked on numerous projects in civil engineering consulting, architecture, and work related to stream rehabilitation and sedimentary analysis. He is a member of the American Society of Engineers, Chi Epsilon (a Civil Engineering Honor Society), and the American Water Resources Association.