

The Influence of Road Salts on the Mobilization of Bioreactive Elements in Regenerative Stormwater Conveyance Systems

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Abstract

Application of road salts such as sodium chloride (NaCl), magnesium chloride (MgCl_2), and calcium chloride (CaCl_2) has detrimental effects on the environment as part of the freshwater salinization syndrome, which includes the direct and indirect effects of salt ions on water quality and ecosystem restoration and management. Increased salinization due to salt pollution has the ability to mobilize bioreactive elements from soil and stream sediments that may pollute drinking water supplies and impair functioning of stream restoration and urban stormwater control measures (SCM) to retain salts, nutrients, and metals. Over the summer 2019, a regenerative stormwater conveyance (RSC) system—one type of infiltration-based SCM—was installed along a reach of Campus Creek, MD. While RSCs may be successful at mitigating stormflow, little is known about the impact of road salts on influencing contaminant mobilization and water quality in RSC step pools. This study will address this research gap by comparing the mobilization of bioreactive elements from streambed sediments in RSCs and two reference streams using laboratory experiments. To our knowledge, little work has compared the varying effects of different salt ions on mobilization potentials, and most work has focused almost exclusively on NaCl. My initial work has focused on the characterization of mobilization potential from the reference stream for the full suite of salts (NaCl, MgCl_2 , and CaCl_2) with comparison to the effects of NaCl—the most common deicing salt—in the RSCs. One-day incubations of sediments and streamwater across five salt levels (0, 1, 2, 4, and 8 g Cl L^{-1}) and three different salts (NaCl, MgCl_2 , and CaCl_2) were conducted to investigate the relative differences in solute fluxes from sediments between the RSC and reference stream. In order to compare mobilization potentials across the different salt levels, different salt types, and study sites, statistical analyses will include linear regression, two factor analysis of variance (ANOVA), analysis of covariance (ANCOVA), and Fischer's and Welch's one-way ANOVA. Results show sodium chloride has the strongest influence on potassium mobilization when used as the experimental deicer, which is likely due to charge balances. Furthermore, it was found that there was not a statistically significant change in base cation concentrations across the three sites for the NaCl treatment. This may indicate that SCMs are neither significantly degrading nor enhancing the water quality relative to other urban stream sediments. By integrating the laboratory experiments with ambient streamwater chemistry data, it is suggested that the bulk mobilization of bioreactive elements from sediment surfaces during snow-and-ice events may be stoichiometrically similar to the concentration of those elements in the stream. Results from this study can be used to guide future management of road salts by providing information on how different salt ions mobilize other bioreactive elements from sediments to streams. Results may also suggest which salt ions have the most potential impacts on water quality and how they can influence restoration efforts. These results can begin to inform decision making of

highway salt application, surface-water-ecosystem management, and the efficacy of stormwater BMPs at maintaining water quality. In the future, more work is necessary to characterize and compare the effects of these different salt ions on elemental mobilization across a broad range of urban streams and stormwater management controls.

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Chapter 1

Introduction

Average annual road salt sales in the United States have increased from 0.28 million metric tons in the 1940s to 16 million metric tons in 2008 (Corsi et al., 2010; Jackson and Jobbágy, 2005). While deicer salts are vital to keeping roads safe, many find their way into the hydrosphere. A case study by Perera et al. (2013) estimated that 60% of Toronto's applied road salt drains to surface water and leaves the catchment, but the remaining 40% infiltrates into the subsurface aquifer. In addition, previous research has shown the chloride concentrations in urban streams of Maryland can reach elevated levels that are approximately 25% the level of sea water during winter months and chloride concentrations remain elevated in urban streams all year round due to accumulation in soils and groundwater (Kaushal et al., 2005). Over the last decade, many studies have increased our understanding of the complex relationship between road salts and the environment, and some are cited throughout this paper. However, the interactions between different salt ions and impacts on water quality are not fully unraveled yet.

1.1 Freshwater salinization

The application of deicing salts, such as sodium chloride (NaCl), magnesium chloride (MgCl_2), and calcium chloride (CaCl_2) for snow and ice removal is contributing to the global increase of salinization in surface waters; NaCl, MgCl_2 , and CaCl_2 are among the most common deicers used on roads in the U.S. (Kaushal et al., 2018). These road salts can accumulate in the subsurface due to their ionic nature, increasing the total concentration of major cations in groundwater (Cooper et al., 2014; Findlay and Kelly, 2011). It is unknown what the long-term effects are of salt loading in the subsurface, particularly effects on the mobilization of other ions from soil and sediment exchange sites.

Salt pollution can manifest itself in the form of episodic salinization—a short-lived pulse in salinity that occurs directly following a winter road salting event (Haq et al., 2018). Episodic salinization has been suggested to have the potential to permanently alter aquatic ecosystem and disrupt biogeochemical processes (Haq et al., 2018; McClain et al., 2003). These high-impact pulses subscribe to the concept of *freshwater salinization syndrome*, which conceptualizes how road salts and human-accelerated weathering of substrates drive widespread salinization and

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alkalinization primarily because 1) road salts contain strong bases that act to neutralize pH and 2) increased Na from salt pollution mobilizes base cations from soil exchange sites (Kaushal et al., 2018).

Freshwater salinization has many deleterious impacts for the environment: biodiversity degradation, disruptions in food web dynamics, and the mobilization of contaminants that may affect drinking water supplies (e.g. Hintz and Relyea (2017); Schuler and Relyea (2018)). Williams et al. (2016) (2016) found that higher concentrations of chloride (Cl) and sodium (Na) cause physiological stresses to aquatic organisms and degrade aquatic ecosystems. The accumulation of chloride along roadside soils is known to accelerate the browning of plant leaves and needles, which eventually lead to plant death (Devitt et al., 2014). In addition to inducing plant toxicity, road salts can degrade soil structure, alter soil pH, and increase ammonification through H^+ ion displacement (Green et al., 2008). In regards to human health implications, some groundwater aquifers contain sodium concentrations that threaten human consumers with high blood pressure (Talukder et al., 2017). While desalination technology exists, the process is expensive and not efficient for salt-contaminated drinking water supplies.

1.2 Mechanisms for mobilization

Many studies suggest a link between increased road salt input and the mobilization of trace metals such as Cd, Cu, Pb, Hg, and Zn in watersheds in the northeast US, Europe, and Canada (Amrhein et al., 1994; Amrhein and Strong, 1990; Backström et al., 2004; Bauske and Goetz, 1993; Kelly et al., 2008; Nelson et al., 2009; Norrström and Jacks, 1998). Heavy metals accumulate in roadside soils primarily due to automobile traffic (Schuler and Relyea, 2018), but can be readily released into solution in contact with road salt. Violante et al. (2010) found that heavy metals that are not readily bioavailable can be mobilized and transformed into more bioavailable species by salts. Road salts can drive the mobilization of bioreactive elements into the water column through biogeochemical processes such as accelerated ion exchange (Fig. 1.1) and complexation reactions with chloride and organic materials (Amrhein et al., 1994; Lumsdon et al., 1995; Nelson et al., 2009). In a study by Sun et al. (2015), increased NaCl-concentrations in soils was linked with the increase of lead and mercury into the interstitial water, but revealed that the mechanisms behind mobilization are more nuanced; their data suggests that the release of certain metals into the dissolved phase not only depends on salt concentrations, but also redox conditions, dissolved organic matter content, competition for exchange sites, and source bedrock material.

Road salts are also linked to the mobilization of elements besides trace metals. High concentrations of Na ions can displace Ca and Mg in roadside soils, leading to soil structure disruption (Backström et al., 2004; Cooper et al., 2014; Norrström and Bergstedt, 2001). This disruption of soil structure is another mechanism in which metals and their associated compounds can be mobilized. Moreover, increased Na^+ retention in groundwater reservoirs may lead to the exchange of Ca^{2+} and Mg^{2+} ions in soils (Löfgren, 2001; Norrström and Bergstedt, 2001; Shanley, 1994).

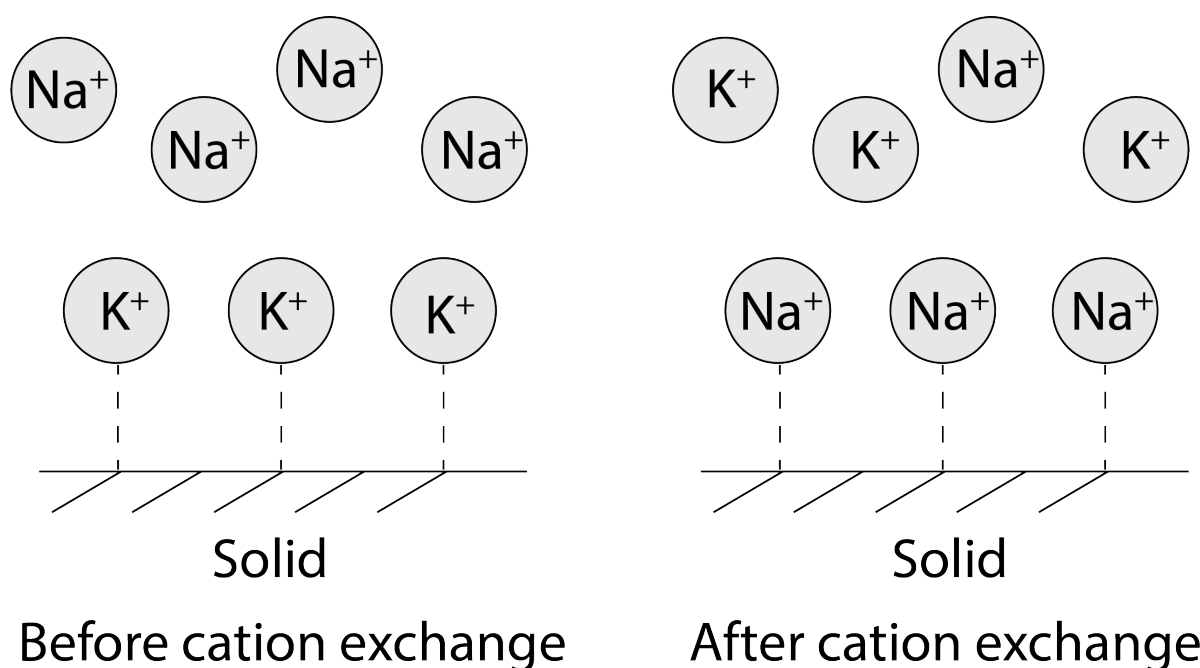


Fig. 1.1 Idealized illustration of acceleration ion exchange via NaCl input. Dashed lines represent exchange sites on solid surfaces. In this case, the surface is negatively-charged (which is common for clays and organic matter in the natural pH range of streams) and attracts positively-charged ions such as K^+ . High Na^+ input will likely displace K^+ ions from exchange sites and mobilize them downstream.

1.3 Regenerative stormwater conveyance systems

Regenerative stormwater conveyance systems (RSCs) are a relatively new type of infiltration-based stormwater control measure (SCM) used throughout the mid-Atlantic, and installed recently over the summer 2019 along Campus Creek, MD. Infiltration-based SCMs are thought to be better at mitigating the hydrological effects of stormwater runoff than detention-based SCMs (Bhaskar et al., 2016; Jarden et al., 2016; Jefferson et al., 2017). Moreover, infiltration-based SCMs (i.e. permeable pavement and green roofs) have shown potential to increase groundwater recharge and improve water quality (e.g. Bernhardt and Palmer, 2011; Bhaskar et al., 2016; Fanelli et al., 2017; Jarden et al., 2016; Shuster and Rhea, 2013; Walsh et al., 2009).

Incised headwater channels and stormwater drainage ditches are common sites for RSC construction, with artificial sand, wood-chips and riparian soils as the primary bed composition (Brown et al., 2010). RSCs are also characterized by boulder weirs that support a series of step pools separated by riffles (Fig. 1.2). Large woody debris such as tree trunks and roots are often placed within the channel to serve as a habitat and additional source of organic carbon (Williams et al., 2016). This source of organic carbon can lower water pH and dissolved oxygen (O) (Duan et al., 2014; Keller et al., 2008), and may lead to enhanced nitrogen removal via microbial denitrification (Saleh-Lakha et al., 2009; Thomas et al., 1994).

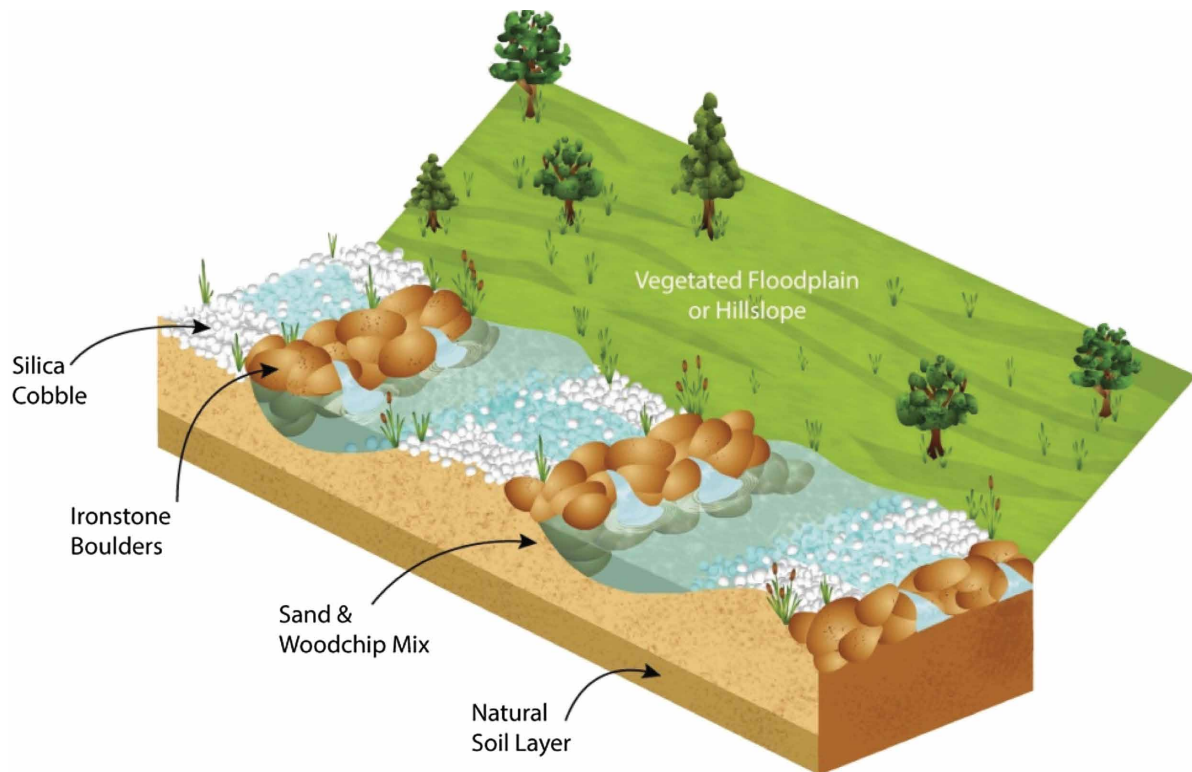


Fig. 1.2 Depiction of typical RSC system. Step pools are separated by weirs constructed by silica cobble and ironstone boulders. Source: Williams et al. (2016)

Despite the increasing implementation of RSCs throughout the Northeast, there is a lack of information on any unintended consequences of the reconstruction. In a recent study, Williams et al. (2016) aimed to address whether the large quantity of iron flocculate in some step pools along RSCs is natural and if the flocculate is detrimental to water quality or stream habitat. They found that while flocculate formation varied spatially and temporally, dense accumulations of flocculate on benthic substrate prohibit use by many aquatic organisms, which may limit other beneficial biogeochemical processes and thereby decrease RSC performance. Another study by Duan et al. (2019) found that soluble reactive phosphorus (SRP) and iron were mobilized under high temperatures within RSCs, which may be a negative water quality tradeoff. While RSCs may achieve some of their intended functions, such as mitigating runoff and recharging groundwater, some of their properties may enhance degradation of the stream ecosystem in a different respect (i.e. reducing nutrient loads by excessive Fe flocculation in step pools).

1.4 Broader impacts

Sodium chloride is the most common road salt applied globally (> 90%), but alternative salts are commonly used in some locations (Fay and Shi, 2012). Many studies have explored the effect of deicing salts on contaminant mobility (e.g. Amrhein and Strong, 1990), but preferentially focus on sodium chloride as the experimental deicer. Another fallacy in the literature

pointed out by Fanelli et al. (2017) is that many studies on stormwater management practices often lack reference sites, making it difficult to compare across sites of similar characteristics. The goal of this study is to investigate if road salts impede the ability of restoration systems to restore water quality. To this end, I will be comparing elemental mobilization in RSCs to another nearby urban restored reference stream by controlled incubation experiments. The reference stream, Paint Branch, was restored by stream floodplain reconnection and is nearby on the UMD campus. Sediments and streamwater were collected from both sites in October 2019. In particular, I will highlight the relative differences in solute concentrations from sediments based on treatments from a range of deicers, including NaCl, MgCl₂, and CaCl₂ (among the most common deicing salts used on roads in the U.S.). The results will inform decision making of highway salt application, surface-water-ecosystem management, and the efficacy of BMPs at maintaining water quality.

1.5 Hypothesis

Because urban restored streams allow for longer residence times of water in their pools and subsequently have a greater capacity for contaminant loading, I hypothesized that RSC sediments will experience greater mobilization potential of bioreactive elements (base cations and metals) in response to experimental salinization relative to urban restored reference stream sediments. It is important to note that the varying effects of different salt ions on contaminant mobilization potentials has not been analyzed for either type of stream restoration to our knowledge, and this project can yield useful information guiding efforts to improve urban stream restoration or understanding unintended consequences. To compare solute fluxes across sites, I primarily used two factor analyses of variance (ANOVA) and covariance (ANCOVA). If solute fluxes are a function of treatment level of a particular salt and site,

$$C_x = f(t, S) \quad (1.1)$$

where C_x is the concentration of the solute x , t is the treatment level (g Cl L⁻¹), and S is the site location, then a two factor ANOVA can uncover whether RSCs are stronger vectors of contaminants than unrestored sites. Site locations include the RSCs, Campus Creek (CC), and Paint Branch (PB). As such, the testable null hypothesis is:

$$H_0 : \mu_{t_x-S_{RSC}} = \mu_{t_x-S_{CC}} = \mu_{t_x-S_{PB}} \quad (1.2)$$

$$H_0 : \mu_{t_0-S_y} = \mu_{t_1-S_y} = \mu_{t_2-S_y} \dots = \mu_{t_8-S_y} \quad (1.3)$$

$$H_0 : \mu_{t_{x_1}-S_{y_1}} = \mu_{t_{x_2}-S_{y_2}} \quad (1.4)$$

where μ is the mean concentration of the solute. The subscripts of t and S refer to treatment levels and study sites, respectively. Eq. 1.2 assumes that when treatment levels are fixed, there is no significant difference in concentration based on study site. Eq. 1.3 assumes that when study sites are fixed, there is no significant difference in concentration based on different

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treatment levels. Eq. 1.4 refers to the null hypothesis that t and S are independent variables and $cov(t, S) = 0$. An ANCOVA will be similar to the ANOVA, with the independent variables being treatment level and type of salt used. The assumption is that there will be covariance between the two independent variables in which $cov(t, d) \neq 0$, where d is the type of salt (NaCl, CaCl₂, MgCl₂).

Chapter 2

Experimental Design

2.1 Study sites

Samples for incubation were taken from three sites in the Baltimore-Washington Metropolitan Area along the Chesapeake Bay watershed. All of the sites are nested along the Anacostia River watershed that flows into the Potomac River basin. Campus Creek is a small-order stream flowing through the University of Maryland campus into Paint Branch, which is a 54,000 ha stream flowing south towards the Northeast Branch. Over summer 2019, a large reach (500-1000 m) of Campus Creek was converted into an RSC system, spanning from where Campus Creek is parallel to the Eppley Recreation Center to where it meets Route 193 (downstream of the University of Maryland Golf Course). A comparison site was established near the confluence of Campus Creek and Paint Branch (a restored stream with stream-floodplain reconnection). The reference site along Paint Branch is located 400-600 m upstream of the confluence. Incubation samples were taken from three pools along the RSC system. Three transects perpendicular to streamflow were established at the other sites, located 30-100 m apart from each other. The RSC sites are between 800-1000 m upstream of the confluence (Campus Creek side) as shown in Fig. 2.1 and Fig. A.1. Pools/transects at each site are enumerated (1-3) by distance downstream, with 1 indicating location furthest downstream. For example, CC3 is upstream of CC2 and CC1.

2.2 Sample collection and processing

Roughly 1 kg of sediment was collected from the streambed per site using a shovel and a Ziploc bag during fall 2019 for laboratory experiments and chemical analyses. In order to attain a representative sediment sample for each site, surface sediments were collected from three places along a transect at each site (left bank, center, right bank) and were composited. Two liters of streamwater were also collected along each transect into acid-washed amber bottles. After collection, the sediments and streamwater were immediately transported to a walk-in fridge (4°C) and stored until experimentation. In the field, basic water quality parameters (pH, temperature, and conductivity) were measured.

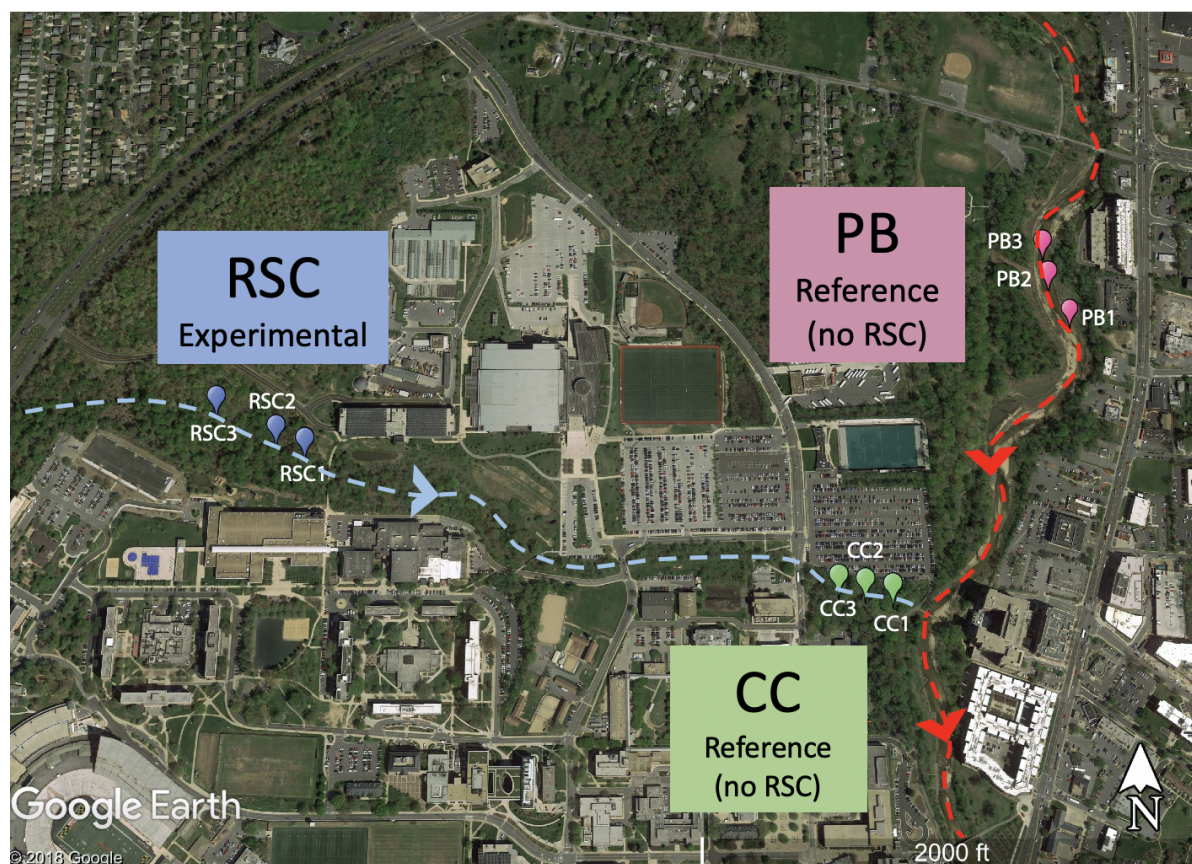


Fig. 2.1 Google Earth map of the study area, with waypoints indicating different sites. The RSC sites are denoted as the blue waypoints, the Campus Creek sites are located near the confluence with Paint Branch denoted by green waypoints, and the Paint Branch sites are denoted by red waypoints.

2.3 Laboratory salinization experiments

Methods for incubations are primarily derived from Duan and Kaushal (2015) and Haq et al. (2018). To homogenize the samples for particle size, the sediments were sieved with a 4 mm sieve and the fine fraction (< 4 mm) were used for the incubation experiments. Aliquots consisting of 60 g of homogenized sediment from each site were added to acid-washed glass containers to simulate a vertical water column with a sediment-water interface. Sodium chloride was added to these aliquots at various treatment levels: 0, 1, 2, 4, and 8 g Cl L^{-1} . Selection of this range in levels is based on reported ranges in the literature; Kaushal et al. (2005) and Kaushal et al. (2017) reported chloride concentrations up to 8 g L^{-1} during winter months at nearby Baltimore sites. These treatments were repeated for magnesium chloride (MgCl_2) and calcium chloride (CaCl_2).

To compare experimental concentrations across the suite of different salts, treatment levels were normalized to concentration of Cl in solution (Fig. 2.1). The salt treatments were dissolved into 100 mL unfiltered streamwater in a separate volumetric flask before being pipetted onto



Fig. 2.2 One of the stormwater step-pools located along Campus Creek. This is one sampling area for the RSC site. The opaque, orange color is likely due to iron flocculation. Photo courtesy of Kelsey Wood, 2019.

sediment in the glass containers to replicate salt inputs to surface waters and not disturb sediments. The containers containing the sediment and salt solutions were then capped loosely to allow air exchange (simulating open-system) and then placed on a shaking table in the dark for 24 hours at room temperature (20 °C). A control sample of the unfiltered streamwater was also incubated with the treatment containers for each site to isolate background solute concentrations in the streamwater. After incubation, the solutions were pipetted from the sediment jars to avoid any disturbance from the sediment and then filtered through combusted Whatman® GF/F 47 mm glass microfiber filters. Thirty mL aliquots of the filtered water samples were subsequently acidified in a small acid-washed HDPE Nalgene bottle to contain 0.5% high-purity nitric acid (HNO_3) for elemental analysis and were stored at room temperature.

2.4 Chemical analyses

Base cation (Na^+ , K^+ , Ca^{2+} , Mg^{2+}) concentrations in the acidified water samples were measured via inductively coupled plasma optical emission spectrometry in an acidified an-

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Table 2.1 Treatment levels for each salt normalized by chloride concentration

Salt Treatment	0 g Cl L ⁻¹	1 g Cl L ⁻¹	2 g Cl L ⁻¹	4 g Cl L ⁻¹	8 g Cl L ⁻¹
NaCl (g)	0.0	0.16	0.33	0.66	1.32
CaCl ₂ (g)	0.0	0.16	0.31	0.63	1.25
MgCl ₂ (g)	0.0	0.13	0.27	0.54	1.07

alytical matrix on a Shimadzu Elemental Spectrometer (ICPE-9800; Shimadzu, Columbia, MD, USA). Stock solution used for major cation calibration standards contain a concentration of 1000 $\mu\text{g L}^{-1}$ with 3% HNO_3 . These major ion standard concentrations range from 1 ppm to 2500 ppm based on 1000 $\mu\text{g mL}^{-1}$ starting concentrations. These stock solutions certify concentrations of each element with $\pm 1\%$ error. Five mL aliquots from acidified water samples with high salt concentrations ($> 2 \text{ g Cl L}^{-1}$) were diluted with acidified MilliQ water to fit within standard curves. Linear concentration-intensity relationships were calculated using known concentrations of the calibration standards and blank samples. Unknown concentrations were determined by peak intensity at corresponding wavelengths based on the calibration relationship and all samples were corrected for background noise. Every sample was measured three times in each view condition axial and radial, and an average quantity and relative standard deviation (RSD) was calculated.

2.5 Statistical analyses

Post-incubation concentrations were averaged between the duplicates for each treatment level, and the average values were used for all statistical analyses. Concentrations measured from the untreated control flasks for each site were subtracted from the respective concentrations from the treatments to isolate the background fluxes of solutes. The resulting concentrations were statistically analyzed using linear regression for each site; the salt treatments are the independent variables and the bioreactive element concentrations are the dependent variables. Regression slopes with $p < 0.5$ were assumed statistically significant and indicate that experimental salinization significantly mobilizes the solute of interest. Two-way analyses of variance (ANOVA) were used to compare solute fluxes from sediments across sites; the two independent variables are site location and salt treatments and the dependent variable is elemental concentrations. In addition, an analysis of covariance (ANCOVA) was utilized to better understand the differential effect of road salt type (NaCl, CaCl₂, MgCl₂) on solute mobilization. All statistical analyses were conducted using MATLAB, R, and Python.

2.6 Streamwater comparison

Another goal of the study was to extrapolate how much of the observed stream concentrations are represented by sediment fluxes as a result of altering water quality regimes. This approach was attempted along a downstream reach of CC, nearby where the CC sediment

2.6 Streamwater comparison

samples were taken. Because CC is ungauged, a linear regression model was used to estimate instantaneous discharge based off of discrete, manual measurements at this site and instantaneous readings from the nearby USGS 01649500 Northeast Branch Anacostia (NEA) River at Riverdale, MD. Estimation by ordinary least squares (OLS) was used to predict continuous discharge along CC from May 2019 - March 2020. Historical daily rainfall data was taken from the NOAA National Centers for Environmental Information Climate Data Online (CDO) database for the Beltsville, MD station. In order to assess the area's mobilization potential due to road salting, historical specific conductance measurements (2016-2020) were also obtained from the USGS gauge 01649190 Paint Branch near College Park, MD. Discrete grab samples of stream water on certain dates were taken during the study period for further chemical composition analyses in our laboratory.

Chapter 3

Results and Discussion

Streamwater and sediment samples were collected at the RSC sites on October 17, 2019, and the CC and PB samples were collected a week later. Basic water quality parameters (e.g. pH) were recorded in the field and the laboratory (Table A.1). Due to a lack of enough streamwater samples for all treatment levels, additional streamwater samples were collected at all sites on November 11, 2019. Salt incubations for PB samples with all treatments were ran from November 3rd, 2019 until November 24th, 2019. Incubations for CC and RSC were limited to NaCl treatments and conducted over January-February 2020. After incubation, samples were immediately filtered and an aliquot was taken and acidified for ICP-OES processing. Incubation samples were analyzed for their dissolved base cation concentrations (K^+ , Na^+ , Ca^{2+} , and Mg^{2+}) in response to experimental salinization.

3.1 Results

Two-Factor ANOVA

A preliminary analysis of variance was completed on the potassium response in PB with the independent factors as the site location and type of salt. An interaction plot using summary statistics (Fig. A.2) shows that sites responded similarly across PB, but indicates that the type of salt ions used for laboratory salinization experiments, particularly NaCl, can significantly influence mobilization of K^+ . The increased mobilization of K^+ by NaCl is likely due to how these base cations (K^+ and Na^+) hold the same number of valence electrons. This is further exemplified by the two-way ANOVA table (Table 3.1) using a Type II model. With a significance level of 0.05, the Site variance is not associated with potassium response (p -value is 0.2079), but the Salt variance is significant (p -value is $2.964e-9$). This places an emphasis on comparing responses across the different salt treatments. Because the interaction between Site and Salt is not significant (p -value is 0.7652), it is possible to interpret the response of potassium without the interaction effect from site.

Observations consistent with the K^+ responses were evident with the other base cations (Na^+ , Ca^{2+} , Mg^{2+}) in PB and the other study sites (CC and RSC). The homogeneous responses across transects is indicative of pseudoreplication; for example, cation responses of a sample at

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PB1 is representative of samples across all PB transects. This allows a basis for comparing results across PB, CC, and RSC.

Table 3.1 Two-way ANOVA table (Type II) for potassium response in PB

Variance	SS	Df	F value	Pr(> 5)
Site	21.83	2	1.6020	0.2079
Salt	345.55	2	25.3528	2.964e-09
Site:Salt	12.45	4	0.4568	0.7672
Residuals	545.19	80		

NaCl Treatments Across Sites

Base cation responses varied slightly between sites in response to NaCl treatment. There were statistically significant linear increases in K^+ , Ca^{2+} , and Mg^{2+} at all sites, albeit at varying degrees (Fig. 3.1). Conversely, there was statistically significant linear decreases in Na^+ concentration with increased treatment level. Across all three sites, the change in Na^+ concentration was most statistically correlated with treatment level at CC. The change in K^+ , Ca^{2+} , and Mg^{2+} were statistically correlated with treatment level at RSC, CC, and RSC, respectively. At the highest treatment level (8 g Cl L^{-1}), the average change in Na concentration was most negative at CC (1857 mg L^{-1}) and least negative at RSC (1168 mg L^{-1}).

Fischer's and Welch's one-way ANOVA tests (Fig. 3.2) were used to isolate the effect of study site in regards to base cation mobilization and retention. Based on an alpha level of 0.05, mean base cation mobilization responses were significantly different among sites when analyzing for K^+ and Ca^{2+} . Average K^+ mobilization response was strongest in the RSC incubations (13 mg L^{-1}) and weakest at PB (7.1 mg L^{-1}). Average Ca^{2+} mobilization response was greatest at CC (24 mg L^{-1}) and lowest at PB (12 mg L^{-1}). There were not statistically significant variations in Na^+ and Mg^{2+} mobilization responses among the study sites.

Salt Treatments Across PB

All salt treatments were conducted for PB. Analyzing for the K^+ mobilization response (Fig. A.3), there was significant mobilization in all transects with NaCl and $MgCl_2$ as experimental deicers. K^+ mobilization response was null in all samples treated with $CaCl_2$. Mobilization of dissolved Na concentrations responded positively to $MgCl_2$ treatment at all PB sites (Fig. A.4). $CaCl_2$ mobilized Na in PB2 and PB3. Interestingly, there is a negative, but significant Na^+ response to increased salt treatment when NaCl is the deicer, indicating some retention of sodium to the sediment. Dissolved Ca^{2+} concentrations were significantly linked to treatment level when $CaCl_2$ was the deicer, but also negative showing retention of added Ca in the sediment (Fig. A.5). Mg^{2+} responses were similar to Na^+ and Ca^{2+} . There was significant mobilization in all PB sites with all experimental deicers, but there was a negative relationship for added Mg^{2+} across increasing treatment levels suggesting increased Mg^{2+} retention with increased $MgCl_2$ inputs (Fig. A.6).

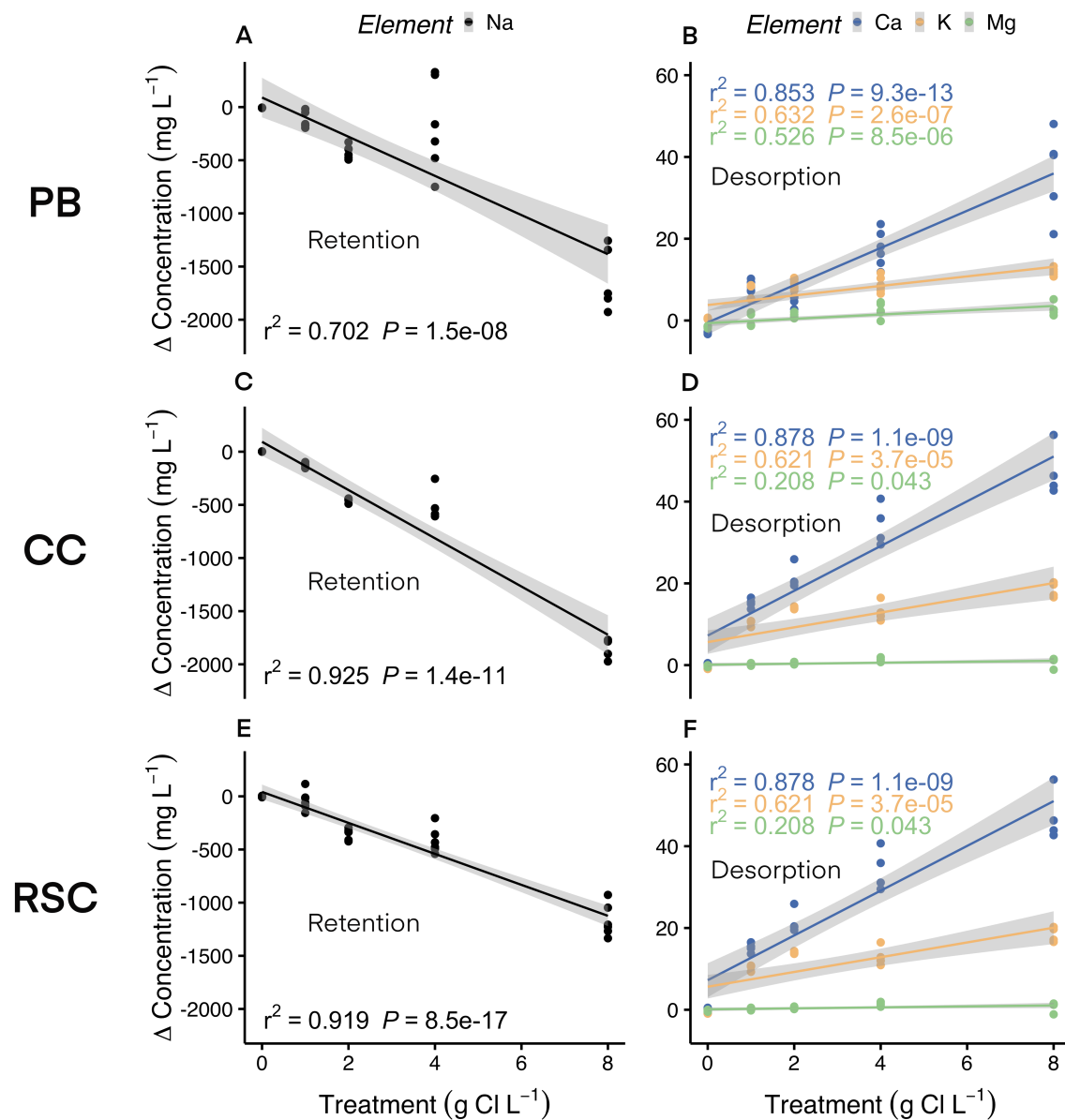


Fig. 3.1 Base cation concentration responses to experimental NaCl input (relative to an untreated control incubation) along **PB** (A-B), **CC** (C-D), **RSC** (E-F). There was significant mobilization of K^+ , Ca^{2+} , and Mg^{2+} based on slopes with $p < 0.5$. Na was significantly retained with increased NaCl treatment. Solid lines represent interpolated regression slope and gray regions define confidence bounds (95%).

Stream Conditions

Several discrete measurements of CC discharge were collected between 2017 and 2019 ($n = 49$) and used in the OLS linear model with corresponding Northeast Branch of the Anacostia (NEA) instantaneous discharge estimated by the USGS (Figs. A.7-A.8). Once this regression

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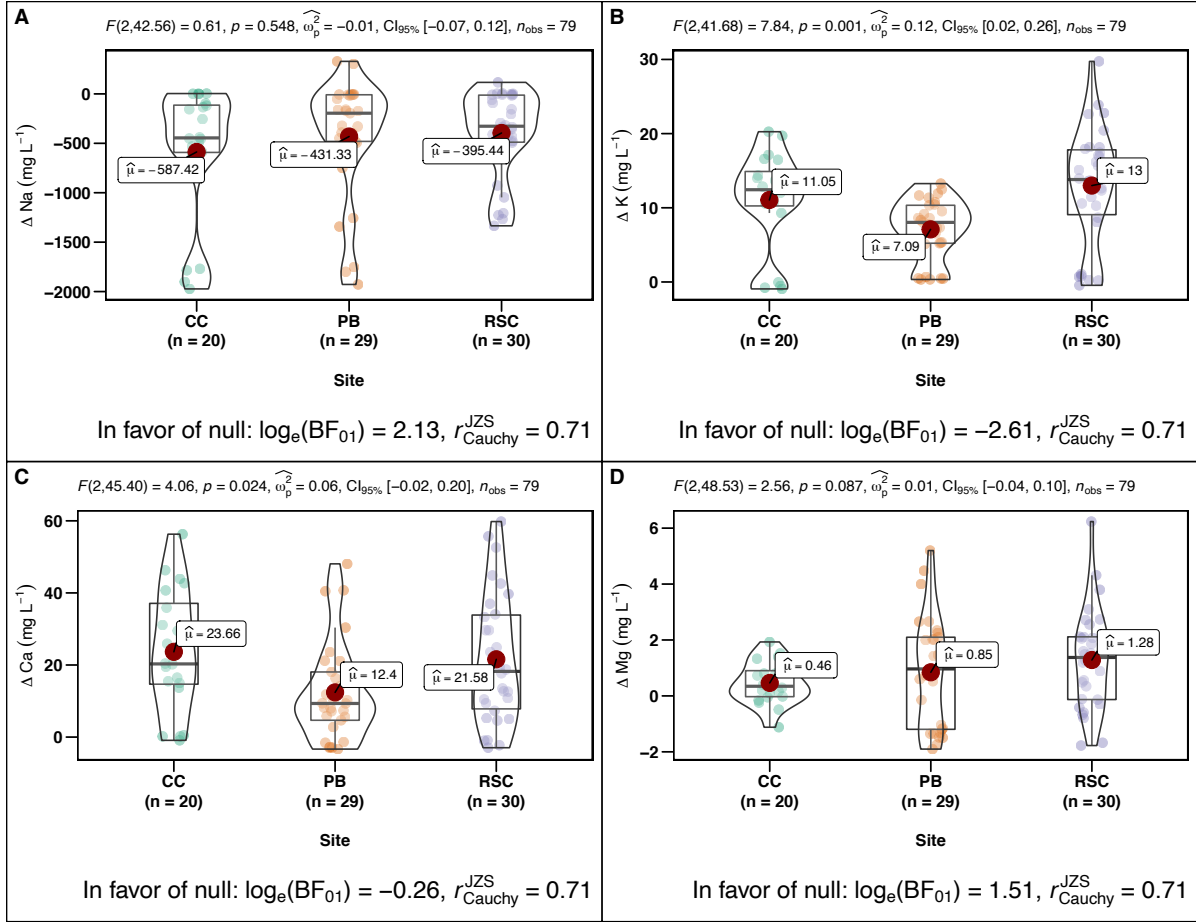


Fig. 3.2 Violin plots showing results of Fisher's and Welch's one-way ANOVA tests among the different cations for all sites in response to NaCl treatment where A) is Na⁺ response, B) K⁺ response, C) Ca²⁺ response and D) Mg²⁺ response.

model was established ($R^2 = 0.43$), the continuous discharge along CC was estimated at a 5-minute interval between May 2019 - March 2020, corresponding to streamwater conditions before and after the RSC construction (Fig. 3.3). It should be acknowledged that not all of the variance for the CC discharge could be predicted by the nearby NEA gauge operated by the USGS, but it can allow an exploration of how the laboratory results may relate to field conditions as a discussion point. Discrete grab samples of stream water on certain dates were also taken during this time period for further chemical composition analyses in our laboratory.

For comparison to sediment incubation fluxes, the role of base cation exchange was emphasized in analyzing the streamwater concentrations. Base cation concentrations did not vary much during the construction period in CC (Fig. 3.3). On average, Na⁺ concentration was 30.7 ± 9 mg L⁻¹, K⁺ concentration was 4.29 ± 0.4 mg L⁻¹, Ca²⁺ concentration was 40.3 ± 8 mg L⁻¹, and Mg²⁺ concentration was 6.76 ± 2 mg L⁻¹. In all cases, elemental concentrations reached their peak after the construction period: 67.9, 8.01, 73.8, and 14.2 mg L⁻¹ for Na⁺, K⁺, Ca²⁺, and Mg²⁺, respectively. Similar patterns are observed for some trace metals (Fig. A.9).

For example, dissolved Cu and Sr concentrations were as high as $23.1 \mu\text{g L}^{-1}$ and $154 \mu\text{g L}^{-1}$, respectively. In contrast, the PB streamwater chemistry does not show similar, obvious responses to the RSC construction (Figs. A.10-A.11). During this construction period, dissolved concentrations for Na^+ , K^+ , Ca^{2+} , and Mg^{2+} were 32.6 ± 5.5 , 3.25 ± 0.32 , 31.0 ± 6.7 , and $6.89 \pm 1.6 \text{ mg L}^{-1}$, respectively. It is unclear if base cation or trace element concentrations significantly increased after the construction period.

3.2 Discussion

Fig. 3.4 highlights the specific conductance trends along Paint Branch from January 2016-2020. It is evident that during the winter period (December to March), there is a peak in specific conductance as a result of deicer input to remove snow and ice. If these winter spikes were due to NaCl input, there is concern that large amounts of Na^+ may be accumulating in the subsurface. High Na^+ concentrations can be linked to soil dispersion, and may expedite the movement of accumulated heavy metals from soil to groundwater via colloid-assisted transport (Amrhein et al., 1994; Grolimund et al., 1996; Norrström and Bergstedt, 2001; Norrström and Jacks, 1998). Accordingly, the many factors that influence cation exchange capacity and preferential ion exchange must be addressed.

Cation exchange capacity (CEC) refers to the capacity of soil particles to hold on to positively-charged ions. Yukselen and Kaya (2006) found that the soil engineering properties that accounted for the most variability in CEC was specific surface area, which can be linked to the amount of clay and organic matter in the sediment sample. An important extension of this project would be to conduct a detailed grain size analysis and determination of organic matter content (i.e. by measuring moisture content) to understand the influence of these fine particulates on the results.

In the incubation experiments, the change in base cation concentrations had different rates of increase/decrease (Fig. 3.1). For example, it is evident that Ca^{2+} is more mobilized from sediment than Mg^{2+} across all sites for the NaCl treatments, which may be due to natural abundance in the environment. Interestingly, the decrease in the change of Na concentrations is almost two magnitudes higher than the increases of the other base cation fluxes. This provides crucial evidence for ion exchange where Na^+ ions are being retained and Ca^{2+} , K^+ , and Mg^{2+} ions are desorbing from particle surfaces. Equal exchanges between Na^+ and other base cations are not occurring, which suggests that the particle surfaces were not fully saturated. Moreover, there may be a greater capacity for retention of Na^+ ions without the necessity to exchange with other ions at binding sites.

Base cation fluxes were determined to be significantly different among sites in the case of K^+ and Ca^{2+} (Fig. 3.2B, C). Only for K^+ fluxes were the RSC samples greater, on average, in base cation concentrations among sites. Returning to the hypothesis, it may appear that RSCs do, in fact, mobilize more contaminants than the reference sites when only considering K^+ ions with a NaCl treatment. While it appears that RSCs are not statistically more prone to contaminant loading (with the other base cations), a greater suite of chemical analyses awaits. As highlighted by Kim and Koretsky (2013), ion exchange reactions are non-specific; addition

Results and Discussion

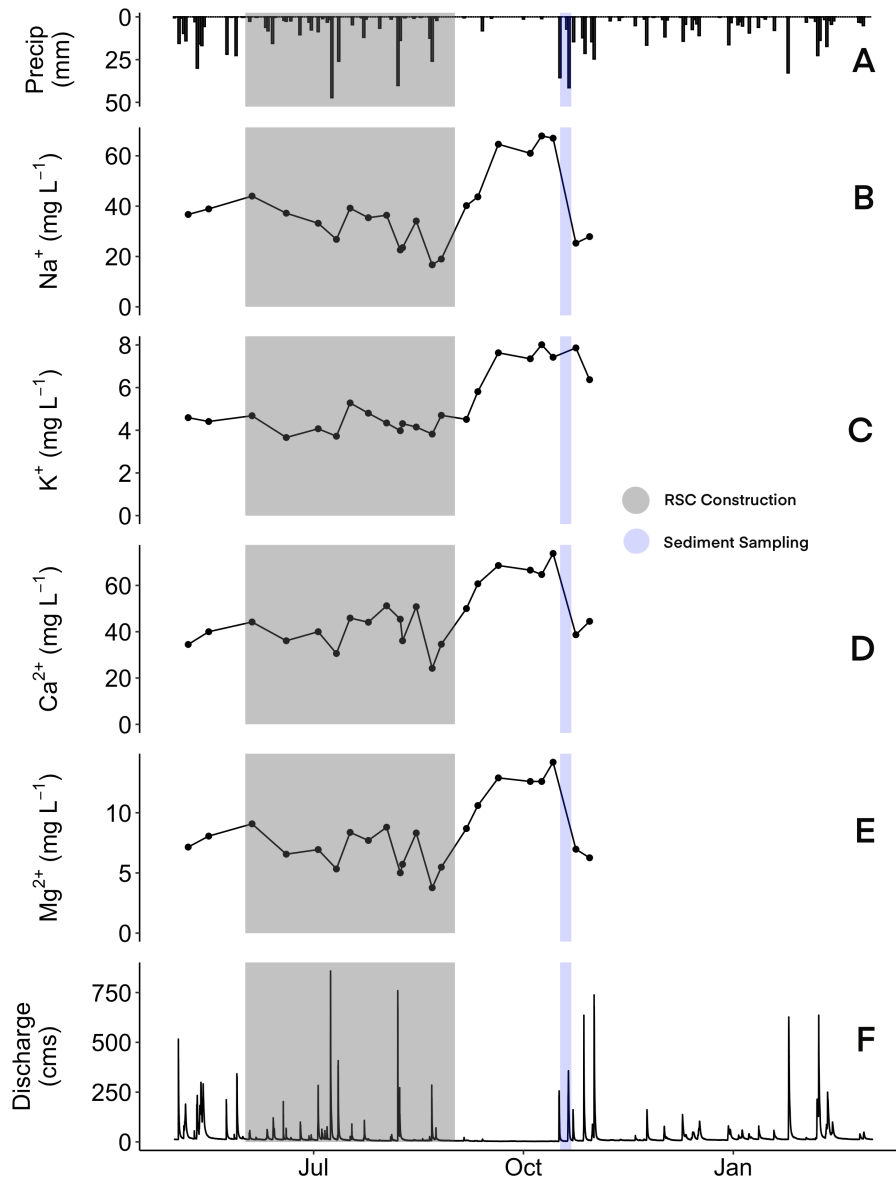


Fig. 3.3 Ladder plot displaying hydrological and chemical concentration trends for Campus Creek: A) hyetograph, B) dissolved Na⁺, C) dissolved K⁺, D) dissolved Ca²⁺, E) dissolved Mg²⁺, and F) hydrograph. The grey-shaded region represents the approximate time period in which Campus Creek underwent the RSC construction (June-September 2019). Sediment samples for the incubation experiments were collected during the span of the blue-shaded region (October 17-22, 2019).

of deicing salts will release a range of major ions, trace elements, and nutrients, all at varying degrees.

Discrete streamwater samples reveal that while base cation concentrations did not vary much over the construction period, there is a significant increase in all base cation concentrations

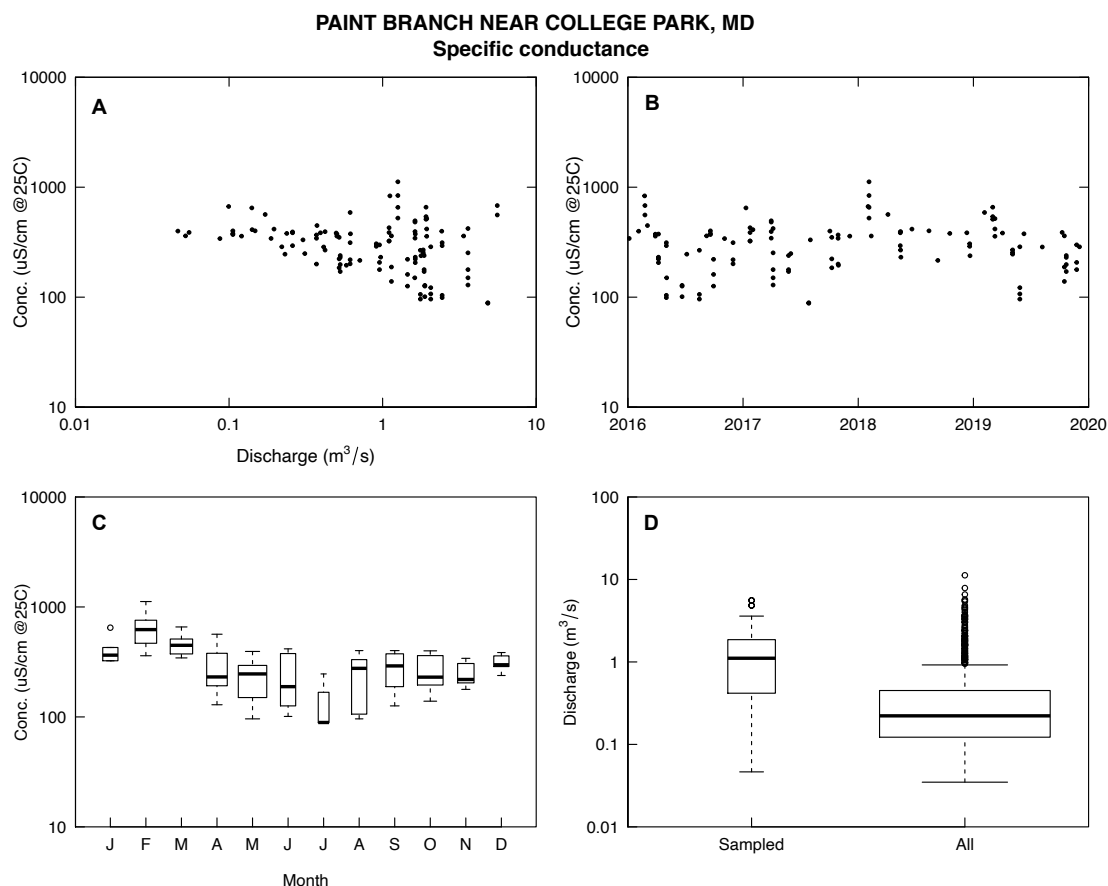


Fig. 3.4 Four panel plot displaying A) log specific conductance versus log discharge, B) log specific conductance versus time (2016-2020), C) boxplot of log specific conductance by month, and D) boxplots of sampled discharge and all daily discharges.

afterwards (Fig. 3.3) along CC. However, it should be pointed out that there is a lack of rainfall following the construction period and baseflow conditions are evident for this period. While rainfall may produce a dilution effect on streamwater chemistry, it is possible that natural increases in dissolved Na may have had a cascading effect on the mobilization of the other major base cations in CC. Conversely, a significant increase in base cations and trace elements in the PB grab samples after the construction period is not evident (Figs. A.10-A.11). It may be possible that these bioreactive elements are considerably taken out of the dissolved phase along the CC flowpath or their concentrations are too diluted along PB due to other stream inputs.

Nevertheless, the CC streamwater chemistry indicates that there was at least a higher dissolved load of bioreactive elements in the RSCs following their construction, but the rate of retention on sediment surfaces is unknown. By integrating the laboratory experiments with the ambient stream chemistry data, it appears that solid-phase base cations concentrations may match or exceed the highest concentrations of base cations in the aqueous phase at all sites. For example, when RSC sediments were incubated with NaCl at 8 g Cl L^{-1} , the change in

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concentration of Ca^{2+} was almost 50 mg L^{-1} , on average. Ca^{2+} concentrations peaked at 73.8 mg L^{-1} in the CC grab samples after the construction period. This suggests that during major snow-and-ice events with high road salt input, there may be almost twice the concentration of base cations in streams, depending on the road salt. As demonstrated above, the major base cation making up the road salt is likely to be retained on solid surfaces with or without exchange with other ions. Further analyses with chemical equilibrium models would complement this work. In addition, more analyses should be done comparing the mobilization potentials among the large range of road salts.

With continued monitoring and experimentation, it would be possible to evaluate the long-term projection of water quality in the watershed. EGRET (Hirsch et al., 2010) is an R-package developed by the USGS to analyze long-term trends in water quality and discharge. The advantage of using this model is to conduct Weighted Regressions on Time, Discharge, and Season (WRTDS) to link point and non-point sources to historical changes in concentrations and fluxes of bioreactive elements. The major limitations of this approach is that datasets must span at least 20 years and must have a complete record of daily discharge values at the study site. Nevertheless, a WRTDS analysis would reveal if the development of the RSCs has a significant effect on water quality and watershed functioning over time.

Another approach to the study is to develop a reactive flow and transport model to numerically simulate the integration of the complex hydrological process and biogeochemical reactions involved with road salting at this site. A detailed analysis of the hydrogeology and complete record of observed aqueous and solid phase chemistry along the RSCs would be needed to develop such a model. In this particular study, the process of transport and cation exchange was realized, but it is unknown what other reactions may be taking place. For example, reductive dissolution of iron oxides with the increased input of DOM by introduction of the RSCs may have increased dissolved concentrations of species such as arsenic and lowered contaminant loading on sediment surfaces, but there is no conclusive evidence. The use of 1D column experiments to simulate 1D flow and chemical exchange is a starting point. Development of a reactive flow and transport model for these sites can inform the long-term loading of salt ions in the subsurface and the corresponding concentrations of bioreactive elements on sediment surfaces and in surface waters.

Chapter 4

Conclusions

The continued use of road salt deicers, such as NaCl, CaCl₂, and MgCl₂, will have a profound impact on the environment and drinking water supplies in the future. This study attempted to simulate the effects of road salt on streambed sediments with a particular focus on regenerative stormwater conveyances (RSCs). While it was hypothesized that a greater amount of contaminants would be mobilized from RSC sediments relative to more naturalized streams (CC and PB) in response to deicer treatments, there did not appear to be major, significant differences in base cation concentrations—aside for K⁺ and Ca²⁺ ions. Only for K⁺ were the RSC sediments statistically greater vectors for the selected contaminants. The major implication is that stormwater control measures (SCMs) like RSCs may not be worse at maintaining water quality in comparison to natural stream types, but are not enhancing it either. Although the data was in favor of the null hypothesis, the study did find that there were consistent and statistically significant increases in the base cation concentrations, depending on the type of road salt used in the laboratory experiments. Moreover, it was documented that the type of road salt used determined the speciation of what is notably retained and subsequently desorbed from sediment surfaces. Another major finding was what there may be almost twice the concentration of base cations in streams during snow-and-ice events based on a comparison analysis of the laboratory experiments and ambient streamwater chemistry. These results can begin to inform decision making of future road salt use, ecosystem management, and the efficacy of stormwater BMPs at maintaining water quality.

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Table A.1 Initial field conditions for ambient water samples

Site	Date Collected	pH	Temp (°C)	Cond ($\mu\text{S cm}^{-1}$)
RSC1	10/17/2019	6.22	15.3	260
RSC2	10/17/2019	6.52	14.6	248
RSC3	10/17/2019	6.58	14.2	263
CC1 [*]	10/24/2019	6.86	10.9	368
CC2 [*]	10/24/2019	6.63	12.5	363
CC3 [*]	10/24/2019	7.13	10.1	358
PB1 [*]	10/24/2019	7.22	10.9	368
PB2 [*]	10/24/2019	7.21	9.8	363
PB3 [*]	10/24/2019	7.15	11.3	361
RSC1	11/17/2019	7.67	5.3	481
RSC2	11/17/2019	7.80	5.3	463
RSC3	11/17/2019	8.00	6.8	451
CC1	11/17/2019	7.59	6.4	608
CC2	11/17/2019	7.56	6.4	614
CC3	11/17/2019	7.54	6.3	616
PB1	11/17/2019	7.90	5.8	443
PB2	11/17/2019	7.90	5.7	444
PB3	11/17/2019	7.95	6.2	427

^{*} Sample was immediately refrigerated and measured later in the day

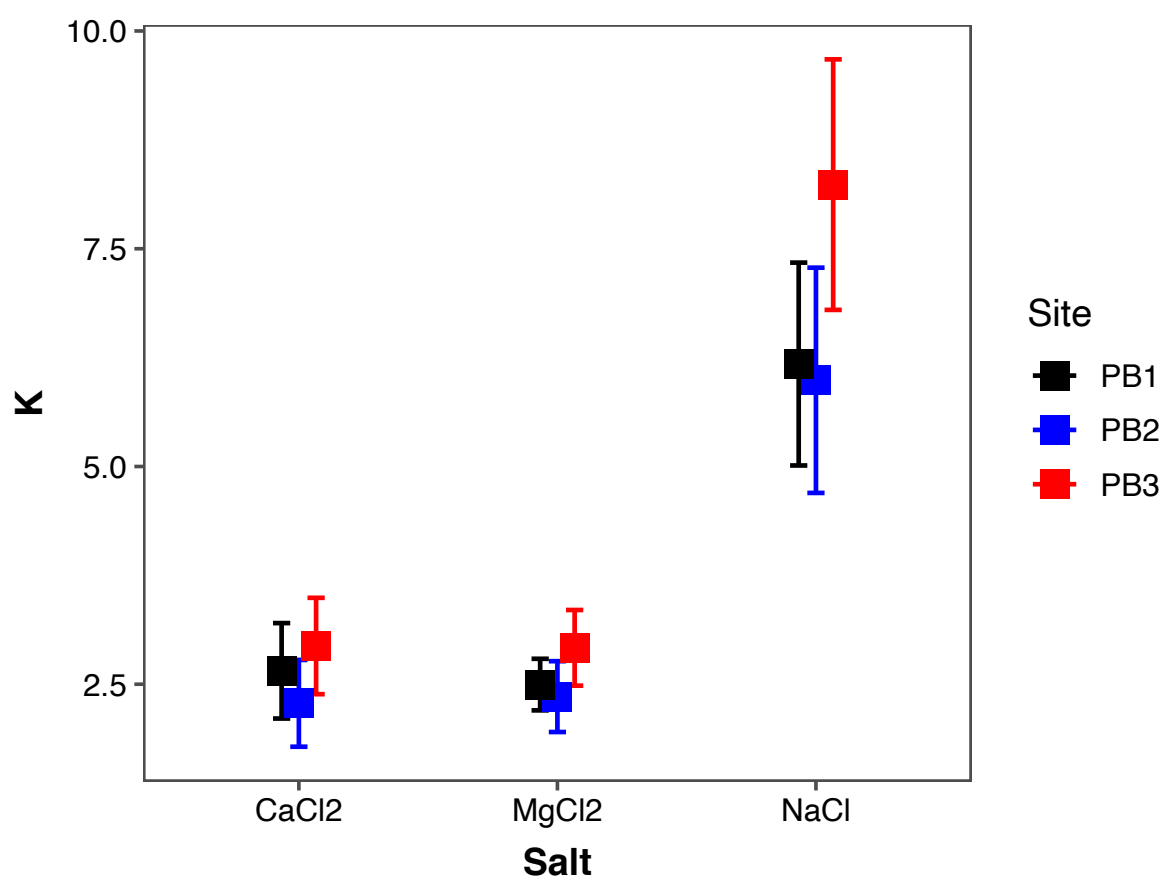


Fig. A.2 Interaction plot for a two-way ANOVA with potassium as the response factor and site and salt as variance factors. Square points represent means for groups, and error bars indicate standard errors of the mean.

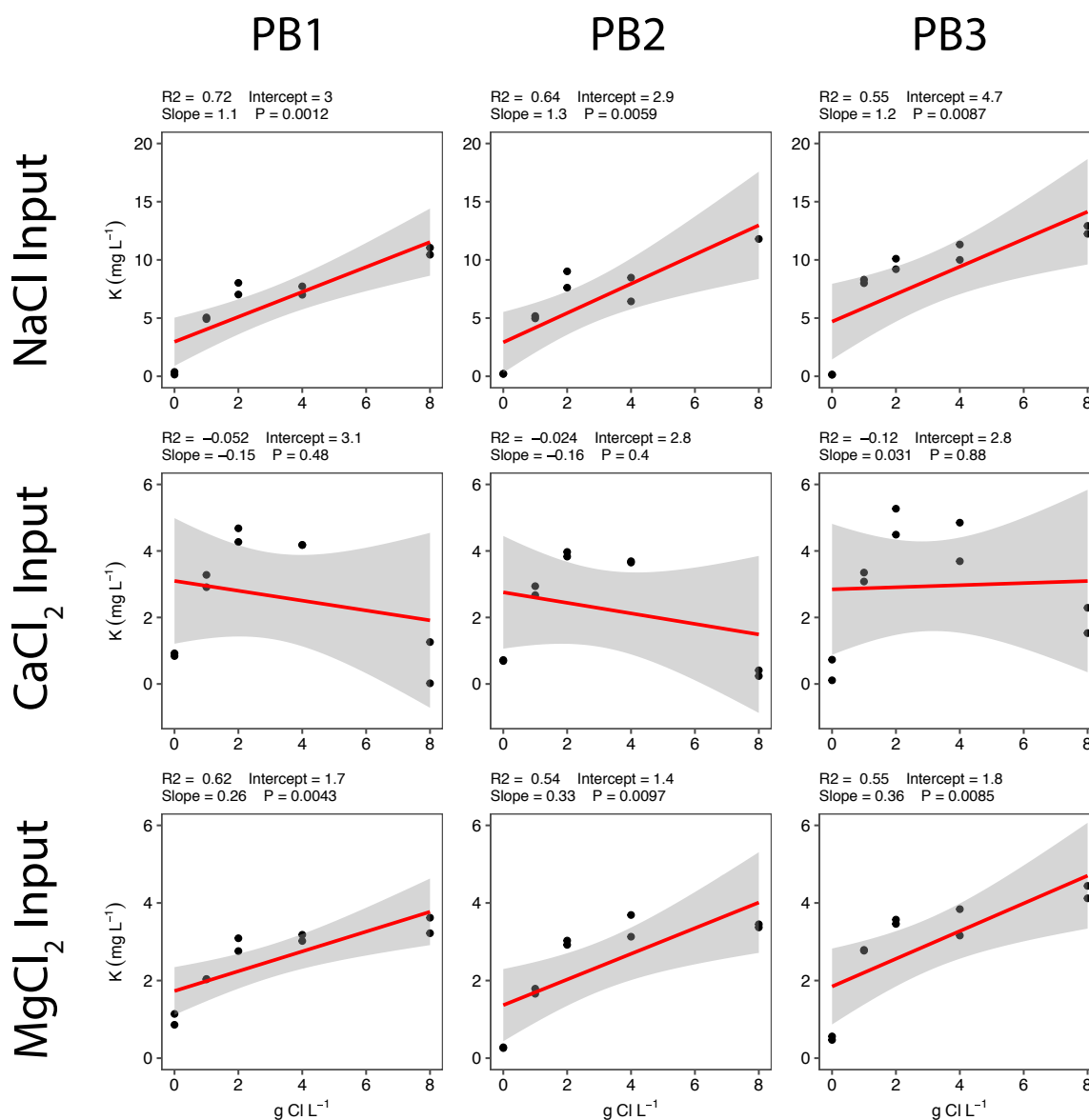


Fig. A.3 Preliminary results of potassium responses to experimental salinization (relative to an untreated control incubation) along the three PB sites. There was significant mobilization in all sites with sodium chloride and magnesium chloride as experimental deicers based on slopes with $p < 0.5$. Potassium response was not significant in any reference transect with calcium chloride input. Red lines represent interpolated regression slope and gray regions define confidence bounds (95%) made via R.

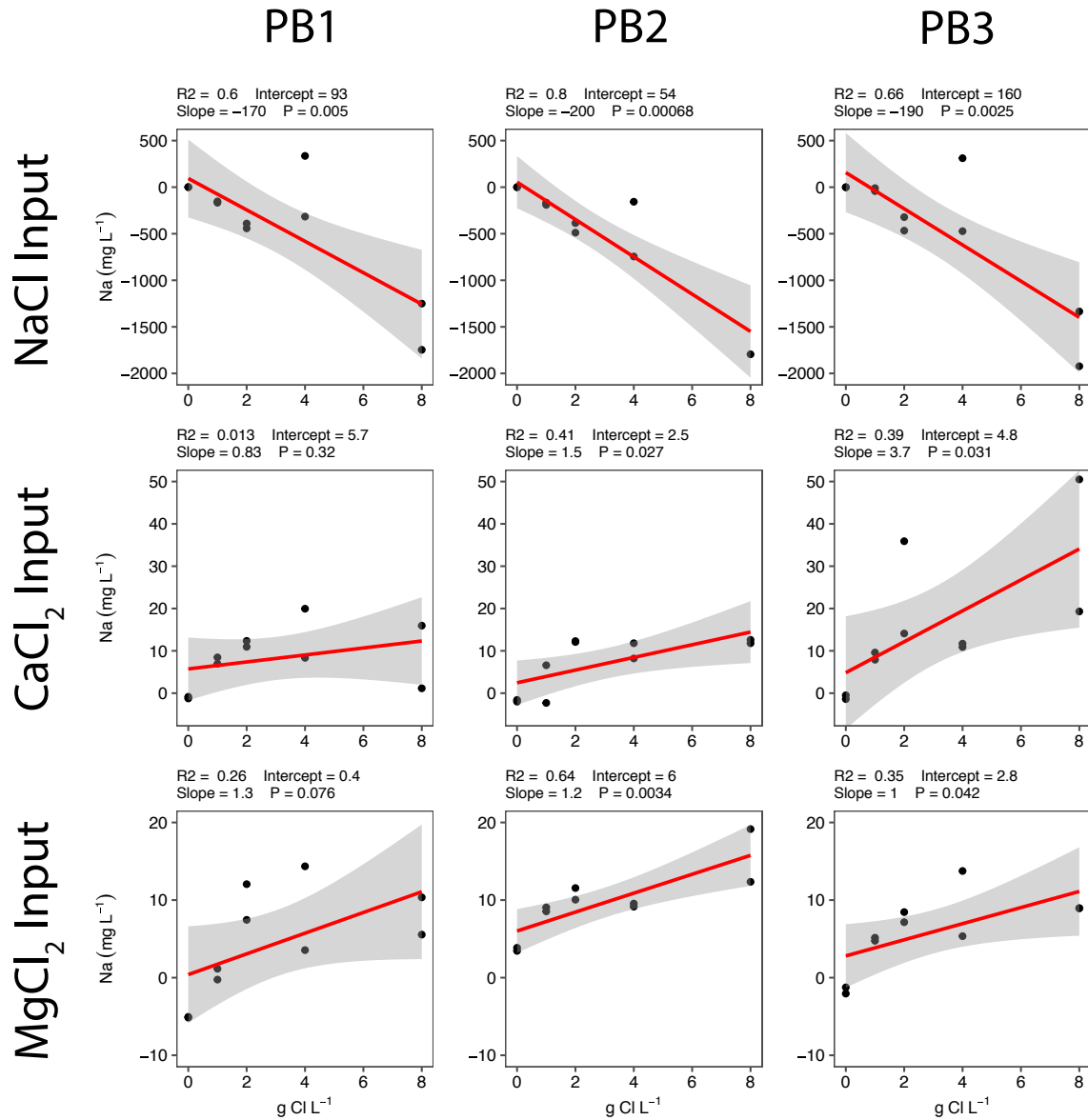


Fig. A.4 Preliminary results of sodium responses to experimental salinization (relative to an untreated control incubation) along the three PB sites. There was significant mobilization in all sites with magnesium chloride as the experimental deicer based on slopes with $p < 0.5$. Calcium chloride mobilized sodium in PB2 and PB3. The relationship between salt treatments and sodium concentrations is significant when sodium chloride is the deicer, but we observe the uptake of sodium instead. Red lines represent interpolated regression slope and gray regions define confidence bounds (95%) made via R.

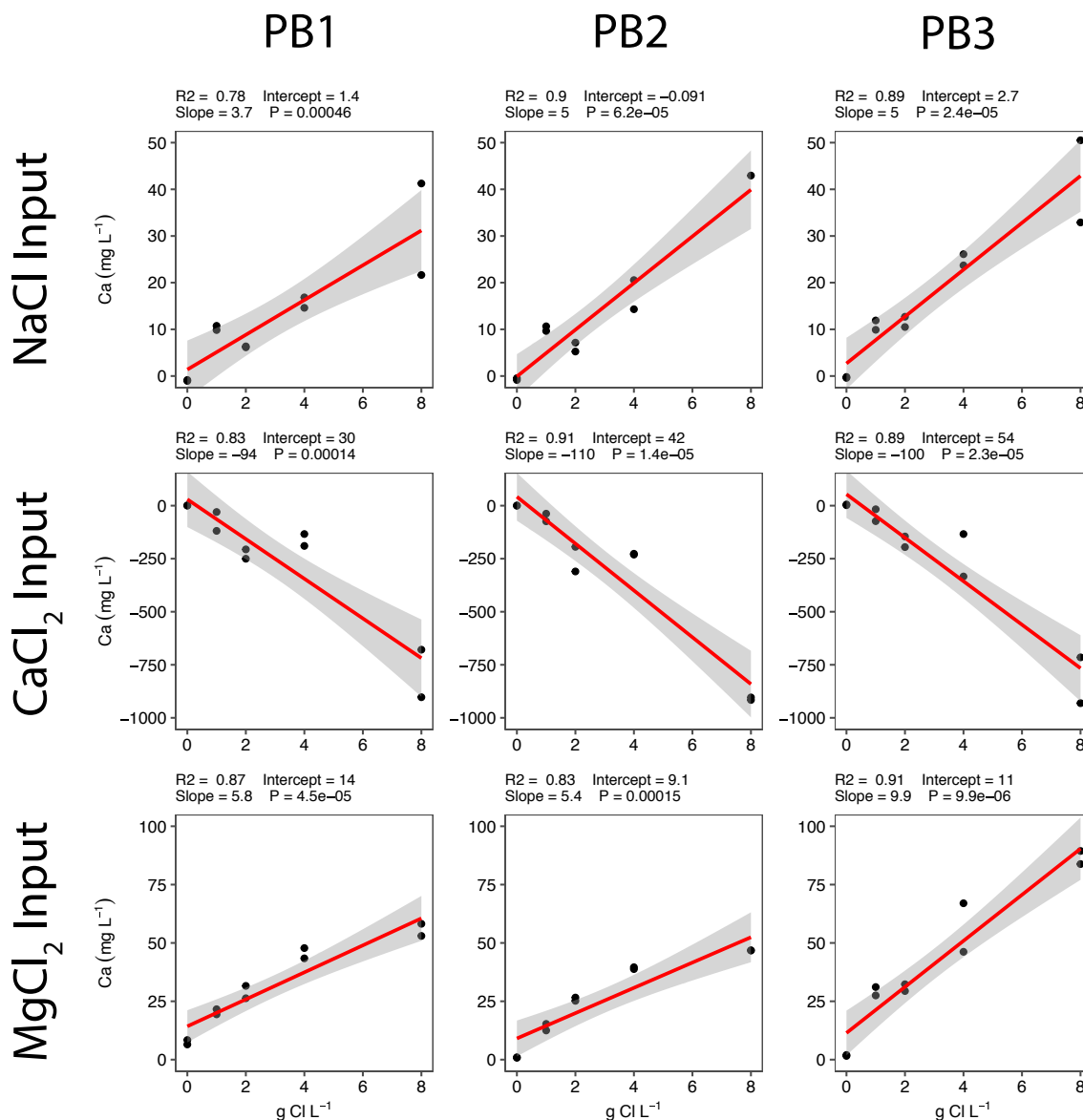


Fig. A.5 Preliminary results of calcium responses to experimental salinization (relative to an untreated control incubation) along the three PB sites. There was significant mobilization in all sites with all experimental deicers based on slopes with $p < 0.5$. As expected, the relationship between salt treatments and calcium concentrations is significant when calcium chloride is the deicer, but we observe the uptake of calcium instead. Red lines represent interpolated regression slope and gray regions define confidence bounds (95%) made via R.

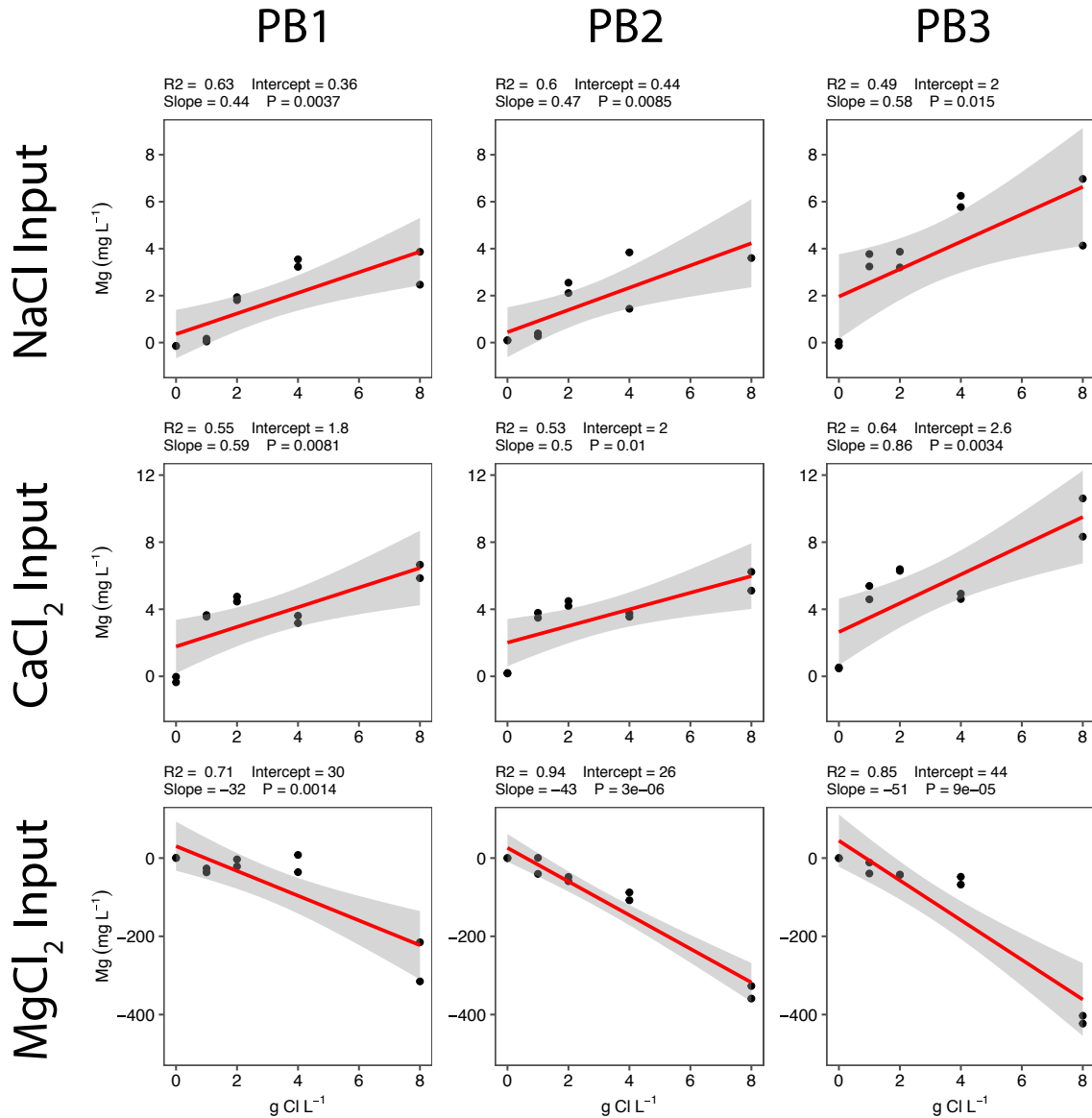


Fig. A.6 Preliminary results of magnesium responses to experimental salinization (relative to an untreated control incubation) along the three PB sites. There was significant mobilization in all sites with all experimental deicers based on slopes with $p < 0.5$. The relationship between salt treatments and magnesium concentrations is significant when magnesium chloride is the deicer, but we observe the uptake of magnesium instead. Red lines represent interpolated regression slope and gray regions define confidence bounds (95%) made via R.

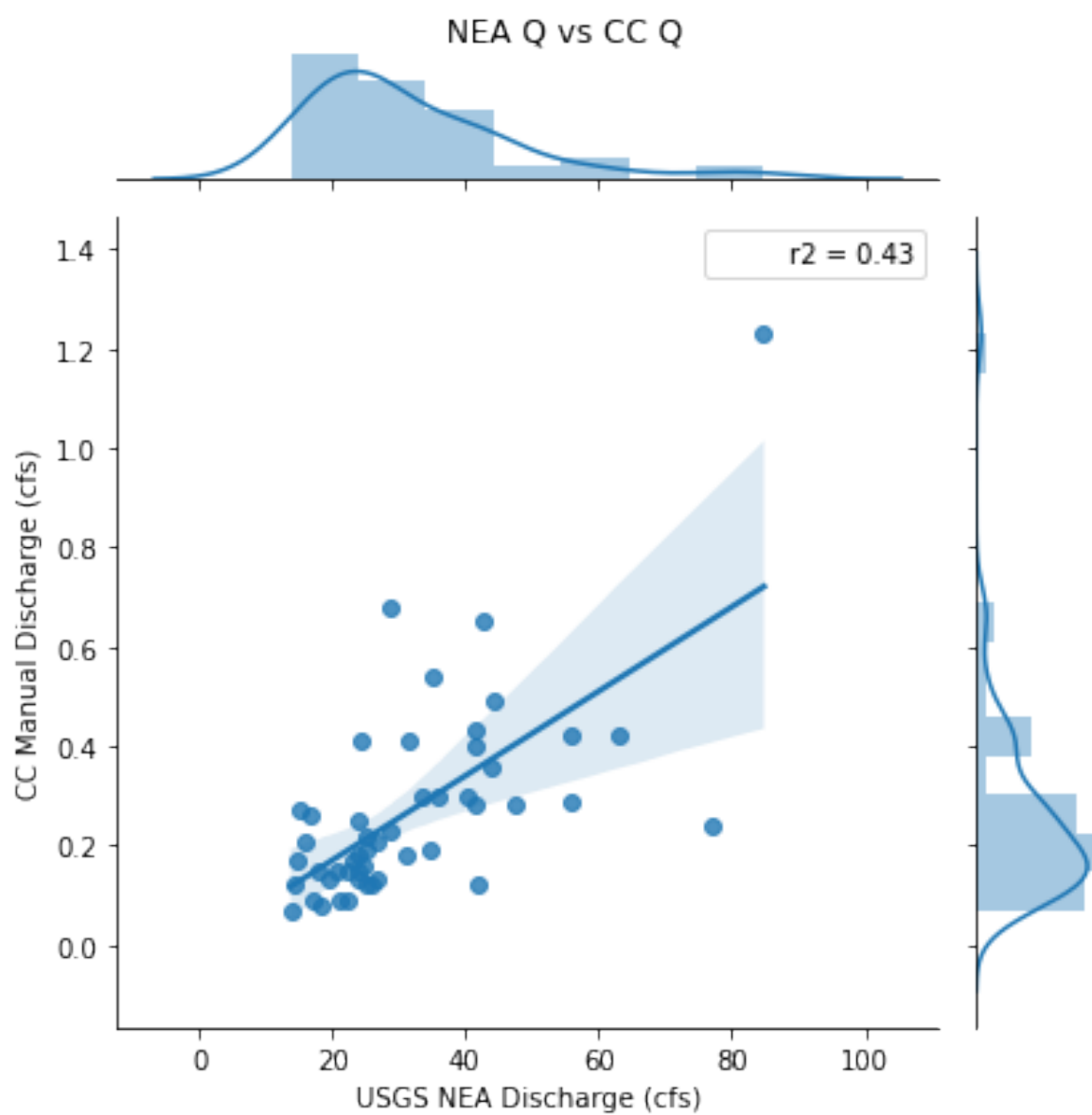


Fig. A.7 Bivariate plot of manual, instantaneous discharge measurements along CC vs. USGS-gauged discharge measurements at Northeast Anacostia.

OLS Regression Results

Dep. Variable:	CC_cfs	R-squared:	0.431
Model:	OLS	Adj. R-squared:	0.419
Method:	Least Squares	F-statistic:	35.67
Date:	Sun, 26 Apr 2020	Prob (F-statistic):	2.96e-07
Time:	12:43:26	Log-Likelihood:	23.333
No. Observations:	49	AIC:	-42.67
Df Residuals:	47	BIC:	-38.88
Df Model:	1		
Covariance Type:	nonrobust		

	coef	std err	t	P> t	[0.025	0.975]
const	0.0003	0.050	0.005	0.996	-0.101	0.101
Discharge	0.0085	0.001	5.972	0.000	0.006	0.011

Omnibus:	16.608	Durbin-Watson:	1.500
Prob(Omnibus):	0.000	Jarque-Bera (JB):	27.132
Skew:	1.006	Prob(JB):	1.28e-06
Kurtosis:	6.040	Cond. No.	80.6

Fig. A.8 OLS regression results of manual, instantaneous discharge measurements along CC vs. USGS-gauged discharge measurements at Northeast Anacostia.

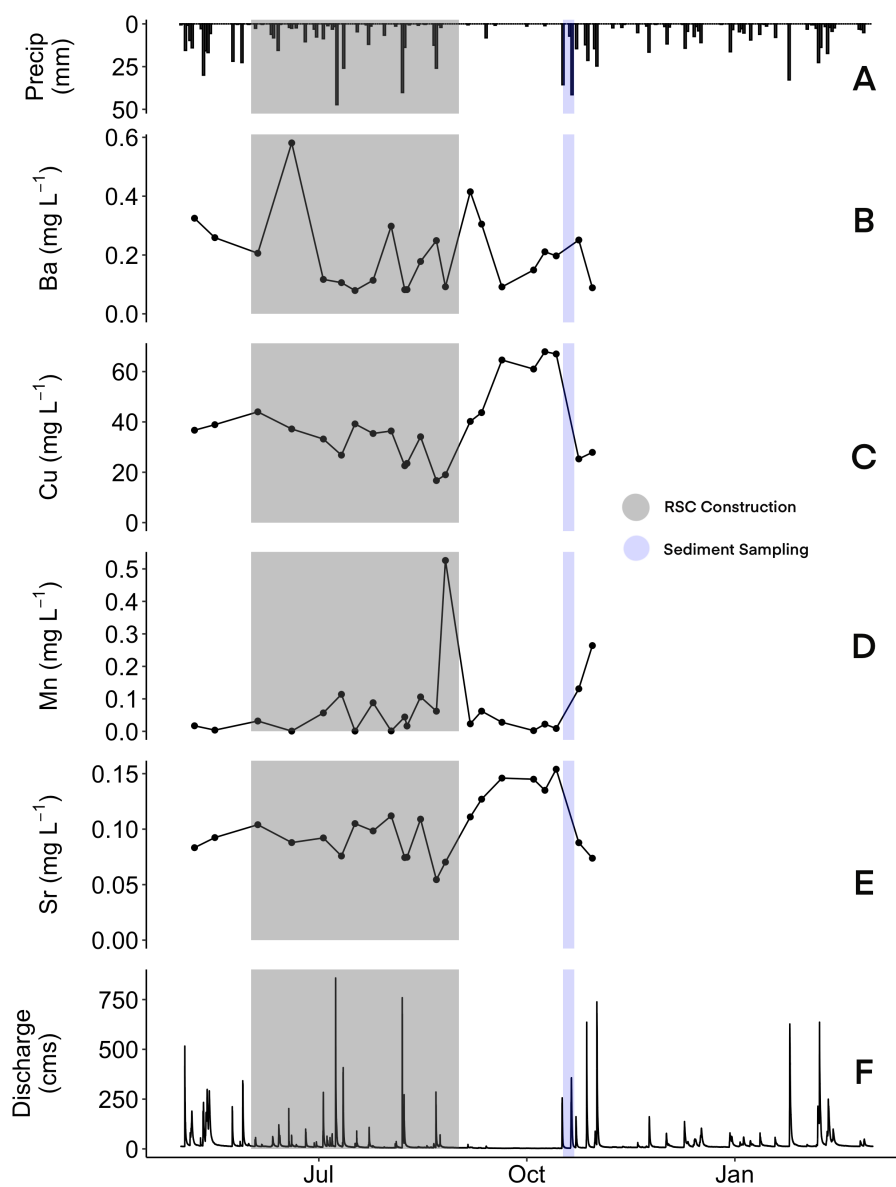


Fig. A.9 Ladder plot displaying hydrological and trace element concentration trends for Campus Creek: A) hyetograph, B) dissolved Ba, C) dissolved Cu, D) dissolved Mn, E) dissolved Sr, and F) hydrograph. The grey-shaded region represents the approximate time period in which Campus Creek underwent the RSC construction (June-September 2019). Sediment samples for the incubation experiments were collected during the span of the blue-shaded region (October 17-22, 2019).

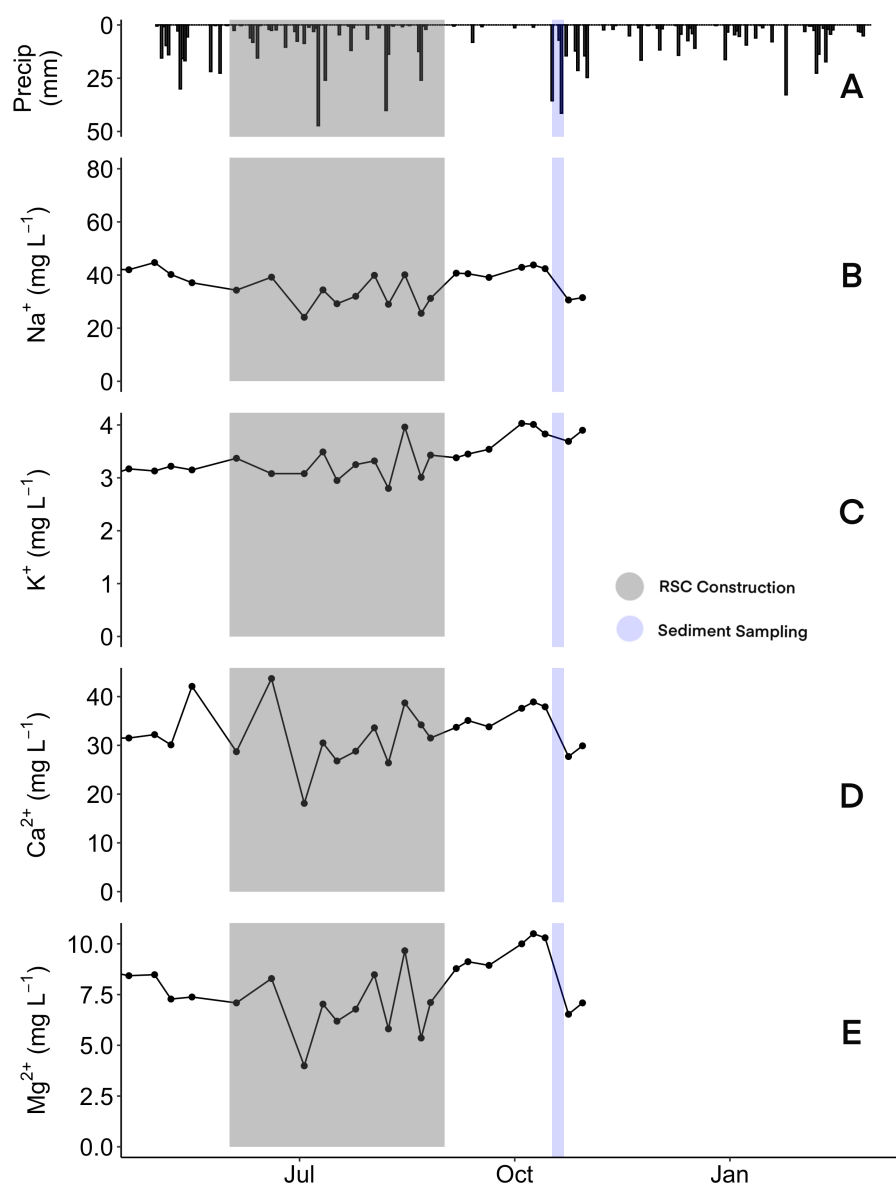


Fig. A.10 Ladder plot displaying hydrological and base cation concentration trends for Paint Branch: A) hyetograph, B) dissolved Na^+ , C) dissolved K^+ , D) dissolved Ca^{2+} , E) dissolved Mg^{2+} , and F) hydrograph. The grey-shaded region represents the approximate time period in which Campus Creek underwent the RSC construction (June-September 2019). Sediment samples for the incubation experiments were collected during the span of the blue-shaded region (October 17-22, 2019).

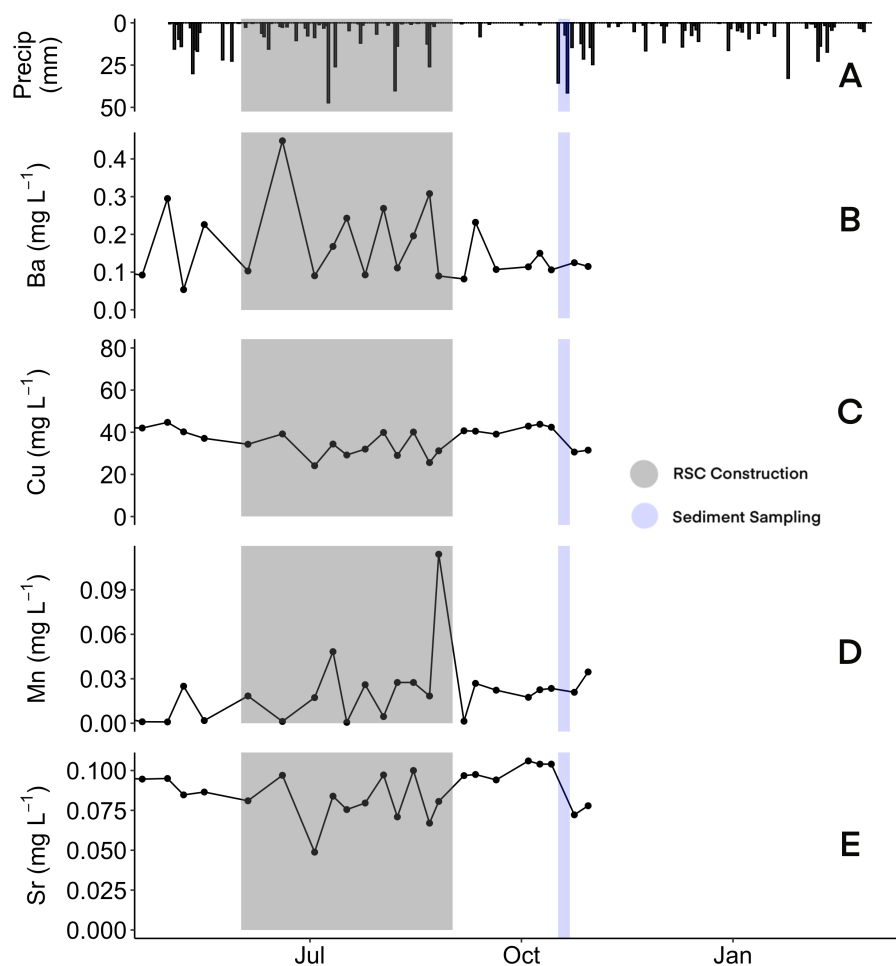


Fig. A.11 Ladder plot displaying hydrological and trace element concentration trends for Paint Branch: A) hyetograph, B) dissolved Ba, C) dissolved Cu, D) dissolved Mn, E) dissolved Sr, and F) hydrograph. The grey-shaded region represents the approximate time period in which Campus Creek underwent the RSC construction (June-September 2019). Sediment samples for the incubation experiments were collected during the span of the blue-shaded region (October 17-22, 2019).

Appendix B

Pledge

I pledge on my honor that I have not given or received any unauthorized assistance on this assignment/examination.

William Nguyen
04/28/2020