ABSTRACT

Title of Dissertation: EFFECTS OF SALINIZATION ON BASE CATION, NUTRIENT, CARBON, AND TRACE METAL BIOGEOCHEMISTRY IN HUMAN-IMPACTED RIVERS IN THE EASTERN US

Shahan Haq
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Dissertation directed by: Professor Sujay S. Kaushal
Department of Geology
Earth System Science Interdisciplinary Center

Urbanized watersheds in colder climates experience episodic salinization due to anthropogenic salt inputs and runoff from impervious surfaces. We conducted laboratory experiments and analyzed high-frequency sensor data to investigate the water quality impacts of freshwater episodic salinization across 12 watersheds draining two major metropolitan regions along the U.S. East Coast. Sediments from watersheds spanning land use gradients were incubated across a range of replicated salinity treatments (0–10 g/L sodium chloride). Our results suggested that episodic salinization can mobilize base cations, nutrients, and trace metals to streams through accelerated ion exchange and biogeochemical processes induced by shifting pH ranges and ionic strength. The response of dissolved carbon concentrations to experimental salinization varied between sites, and dissolved silica did not show any

significant response. The growing impacts of freshwater salinization syndrome on nutrient mobilization, shifting acid–base status, and augmenting eutrophication warrant serious consideration in water quality management.

EFFECTS OF SALINIZATION ON BASE CATION, NUTRIENT, CARBON, AND TRACE METAL BIOGEOCHEMISTRY IN HUMAN-IMPACTED RIVERS IN THE EASTERN US

by

Shahan Haq

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Advisory Committee:
Professor Sujay S. Kaushal, Chair
Professor Karen L. Prestegaard
Dr. Shuiwang Duan

Dedication

To my mother – who has been a staunch advocate for recycling for as long as I can remember, because her love for the Earth is as unconditional as her love for me.

And to the past, present, and future members of the Kaushal lab group – for our shared quest to understand and measure nature provided everlasting motivation and excitement. In the words of A. Milne, “How lucky I am to have something that makes saying goodbye so hard.”

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List of Abbreviations

DIC – Dissolved Inorganic Carbon

DOC – Dissolved Organic Carbon

NPOC – Non Purgeable Organic Carbon

SRP – Soluble Reactive Phosphorous

TDN – Total Dissolved Nitrogen

DON – Dissolved Organic Nitrogen

PAH – Polycyclic Aromatic Hydrocarbons

CMA – Calcium Magnesium Acetate

Chapter 1: Background Information

Background on River Sediment Geochemistry

One of the major controls of steam water chemistry is the interface between the river sediment and overlying water. The transportation, transformation, and ultimate fate of any chemical inputs to the stream system is governed in-part by the sediment geochemistry. The reactivity (e.g. sorption processes) of the river sediment is a function of the reach's bedrock lithology, ecological processing, and hydrology.

The mineral composition of sediments match the bedrock from which they have physically eroded. Once removed from their parent body, these sediments undergo chemical weathering processes (such as carbonation, oxidation, dissolution, and hydrolysis) which generally result in the release of ions from the sediment/rock. Thus, the mineral surface of sediments has exposed ions which may have unsatisfied bonding, and once in water, the areas on the sediment surface binds with the water compounds (e.g., hydroxide, hydronium) and shed hydrogen ions. Therefore, the dominant mineral composition of sediment controls the pH of the stream water, and this control can be assessed via the zero point of net proton charge (i.e., the pH value at which the net electrical charge on a mineral-particle surface is 0 when it is submerged in an ionic solution) (Stumm and Morgan 1996, Honeyman and Santschi, 1988).

The zero point of net proton charge for quartz and feldspars (and other minerals such as montmorillonite) dominated sediments will tend to be low, indicating weak anion sorption to sediment particles, and resulting in sediment particles that are negatively charged. The zero point of net proton charge for oxide (and other minerals such as chrysotile) dominated minerals will tend to be high, indicating strong anion sorption, and resulting in neutral to positively charged sediment particles (Stumm and Morgan 1996, Honeyman and Santschi, 1988).

Generally for most minerals, as the pH of the solution increases above its zero point of net proton charge, the surface charge of the particle becomes more net negative, and thus more likely to undergo electrostatic reactions resulting in sorped cations. However, independent from stream water pH and deprotonation, sediment particles be permanently negatively charged due to hydroxyl edge charges and the replacement of original atoms with lower-charged atoms during the upstream erosion and transportation process (Stumm and Morgan, 1996, Honeyman and Santschi, 1988). The resulting charge and distribution of exchange sites within a sediment particle is complex and warrants further study.

Microbial processing can further alter the geochemical affinities of river sediments. Reduced organic compounds are readily sorped onto sediment surfaces. Organic compounds on sediments create a pathway for the bonding of hydrocarbons (e.g., covalent bonding) or water insoluble (e.g., hydrophobic) inorganic compounds (e.g., via van der Waals bonding) as they tend to bond directly to humic organic matter (Gardner et al, 1991). The flocculation, settling, and build-up of organic colloids and detritus on sediments can stabilize the sediment layers, and can serve as a constant substrate for benthic organisms and microbes (House, 2003). These microbes, along with algae biofilms, can remove/consume ions directly from the sediments (i.e., assimilatory metabolites) or they can contribute ions to the sediments (i.e., dissimilatory metabolites) (Seitzinger et al 1991, Gardner et al 1991). Because many of these activities and microbes consume oxygen, the oxic layer at the sediment-water interface can only be 1-3mm in depth, and this can lead to rapid changes in redox conditions, pH, and sediment sorption/desorption processes (House, 2003).

In addition to being vital in the transport of sediment and the formation of river channels, the hydrology/hydrodynamics is also vital in controlling the geochemical behavior of sediments. Metal chemistry and speciation, along with all soption/desorption processes, largely take place on the surfaces of sediments. The exposure surfaces to stream water (and air) increases the favorability and rates of these processes (Honeyman and Santschi, 1988). Furthermore, the hydrologic flowpaths of the stream water and of storm water en route to a stream (i.e., precipitation, overland soil, groundwater) and the residence times in hydrologic reservoirs (e.g. groundwater, wetlands) imparts a range of ionic strength and pH which can limit or enhance the geochemical affinities of sediments (Vengosh 2003, Kaushal et al, 2018).

The suspension of sediments during storms or turbulent river reaches can disturb the sediment-organic matter matrix (mentioned above), altering sediment redox conditions and enabling dissolution of compounds and the exposure of sediment surfaces forcing an interaction with dissolved or suspended compounds

(House, 2003). For example, sediments are a sink for both SRP (via sorption and assimilation processes) and TP (via particle flocculation and settling). However, if the sediments are re-suspended (due to hydrodynamics) or if the dissolved P concentration in the overlying water is quickly reduced (due to dilution), the sediments switch to a potential source of P (House, 2003). Of course, the extent to which the hydrology affects sediment geochemistry depends heavily on the chemical composition of the sediments (i.e., sediment with more exchangeable ions will behave differently), and on the type of soils and reservoirs present in the watershed.

In conclusion, resolving specific interactions that control the chemistry at the sediment-water interface is difficult as there are various physiochemical, biochemical, seasonal, mineralization, and diagenetic processes that are all happening at the same time resulting in constant completing redox, exchange, and complexation reactions (sensu, House, 2003). It is simpler to quantify the sediment's geochemical processes by observing their contribution to in-stream chemical transformations (sensu, House, 2003).

Background on Freshwater Salinization

Many streams and rivers in the US and elsewhere are experiencing increased salinization due to salt pollution from anthropogenic inputs and accelerated weathering in human-impacted watersheds (e.g., Kaushal et al. 2005; Canedo-Arguelles et al. 2013; Corsi et al. 2015; Kaushal et al. 2017) (Fig. 1). This salinization can manifest itself as chronically high concentrations of a mixture of salts throughout all seasons or episodically high concentrations contributing to a “freshwater salinization syndrome” on a continental scale (Kaushal et al. 2018). The freshwater salinization syndrome impacts biodiversity, contaminant mobility, built infrastructure, and drinking water quality (e.g., Corsi et. al. 2015; Ramakrishna and Viraraghavan 2005; Stets. et al. 2018; Novotny et al. 1998). Natural sources of salinity include the chemical weathering of rock throughout watersheds, dissolved ions in precipitation, and sea spray aerosols in coastal areas (Meybeck 2003; Kaushal et al. 2013). Anthropogenic activities can dramatically increase the salinity of water both directly (e.g., inputs of road salts, mining waste, industrial detergents, fertilizer salts, sewage discharge) (Kaushal et al. 2018), and indirectly (e.g. inducing acid rain, building concrete and limestone infrastructure, increasing flood frequency, and changing land-use) (Barnes and Raymond 2009; Kaushal et al. 2017; Steele and Aitkenhead-Peterson 2011) (Fig. 2). Dissolved salts influence acid neutralizing capacity, pH, and nutrient mobilization in watersheds (Kaushal et al. 2018; Green et al. 2008; Compton and Church 2011). This can occur via ion exchange or complexation reactions, organic matter dispersal, or by alterations in microbial processes (Duan and Kaushal 2015; Corsi et al. 2010; Oren 2001; Kim and Koretsky 2013).

Due to their ionic nature, most salts are retained in soils and groundwater (Cooper et al. 2014; Findlay and Kelly 2011). As such, salts accumulate in the watershed, and long-term salinization has been reported in rivers on most continents and biomes (Williams 2001; Herbert et al. 2015). Urban areas are particularly vulnerable to salinization due to the combination of salt inputs (e.g., road salts, gypsum), impervious surfaces, drainage infrastructure, and flowpath modifications

(Snodgrass et al. 2017; Kaushal et al. 2017; Marsalek 2003). In the Northeastern USA, for example, salinity has doubled from 1990 to 2011 and has exceeded the rate of urbanization (Corsi et al. 2015). Previous studies suggest that rural streams and rivers in the Eastern USA with as little as 5 percent impervious surface coverage within their watersheds can also be at significant risk for long-term salinization (Kelly et al. 2008; Conway 2007), while in the Midwestern USA, recent studies suggest that lakes with as little as one percent impervious surface coverage are at risk (Dugan et al. 2017). Here, we propose studying sites that range in impervious surface coverage from 0 to 61%.

Episodic and long-term salinization of fresh water can have ecosystem scale impacts such as the loss of native vegetation, disruptions in the food web, and the mobilization of inorganic contaminants (e.g., heavy metals) (Lofgren 2001; Norrstrom 2005; Backstrom et al. 2004; Amrhein et al. 1992). However, less is known regarding impacts of salinization on carbon and nutrient cycles in fresh water (Duan and Kaushal 2015). While billions of dollars have been spent to reduce nitrogen and phosphorus loading by stream and riparian restoration (Bernhardt et al. 2005), salt pollution has been largely unmanaged and unregulated. Part of the reason why effects of salinization on carbon and nutrient dynamics in streams and rivers is not well understood may be the different temporal and spatial scales at which salinization can occur. For example, salinity (e.g., chloride) concentrations in urban rivers may temporarily reach up to 33% the salinity of sea water in the hours to days following a snow storm, but they gradually accumulate in watershed reservoirs (e.g., groundwater, soil, lakes) (Kaushal et al. 2005; Kelly et al. 2008; Cooper et al. 2014).

Acute and episodic salinization occurs over the course of hours to days following a snow event (e.g., road salt pulse) and chronic long-term salinization can occur over the course of seasons to decades (Kaushal et al. 2018). Some water quality effects of salinization, such as nutrient and cation mobilization, would likely occur over the course of several hours and would likely immediately follow increases in salinization (e.g., post-storm). However, these effects may not be captured by traditional water quality monitoring, which is conducted by sampling a fixed point in a stream or river on a weekly to monthly interval (as better explained in Rode et al. 2016; Pellerin et al. 2012).

Chapter 2: Questions and Hypothesis

Broadly, the goal of this study is to investigate the potential water quality effects of episodic salinization in urban watersheds induced by acutely elevated salinity across the sediment-water interface. More specifically, this study explores the potential mobilization of base cations, carbon, nutrients, and trace metals from sediments to stream water using a combination of experimental incubations and observations in the field from high-frequency sensor data. Episodic salinization can potentially enhance the mobilization of carbon, nutrients, and cations due to coupled biotic and abiotic processes, such as ion exchange, rapid nitrification, pH, increased ionic strength, organic matter dispersal, and chloride complexation. Furthermore, this study explores short-timescale chemical mechanisms with a combination of ex-situ lab experiments and in-situ high-frequency sensor data. An improved understanding of the interaction between salinization pulses and nutrient pollution is necessary to better manage streams and rivers and to identify unanticipated geochemical relationships that may impact stream restoration strategies, water quality, and ultimately human health.

We ask three overarching questions and conjecture a testable hypothesis. First, what is the magnitude of salinity-induced mobilization for various elements from urban sediments to streams? Second, what are the mechanisms behind the mobilization and what are the controlling geochemical, hydrological, or land use characteristics? Third, does an apparent geochemical coupling appear between salinity and N from high-frequency sensor measurements, and if so, to what degree can salinity be used as a proxy for N?

We hypothesize that increasing the salinity will leach elements and compounds from the sediment into the water column and increase the dissolved concentrations due to synchronous biotic and abiotic mechanisms. At lightly elevated salinity, the linkage may be due to an abiotic mechanisms such as cation exchange on the sediment surface or organic-metal ligand dispersal. At significantly elevated salinity (or prolonged salinity), the cation exchange sites could saturate, and the coupling may be due to a biotic mechanisms such as a rapid reduction in nutrient processing, a breakdown of the lotic ecosystems, and/or microbial lysis.

We have grouped the response elements into 4 groups, based on their hypothesized response to salinization. The elements/compounds in each group and further detailed are in table 1.

Group (1) are elements/compounds with affinities to complex with organic matter. Salinization increases the chloride concentration, which could increase the formation of chloro-complexes on colloids. Salinization increases the ionic strength of water which could disperse colloids from the sediment surface into suspension. Through dissolution reactions, elements on colloids could enter the dissolved water, and so we hypothesize the concentration of these elements to increase after salinization.

Group (2) are elements/compounds with outer-sphere electrostatic affinities to sorp onto sediment particles. Through increases in chloride concentrations, salinization increases the ionic strength of water, which could affect sorption properties. More importantly, through increases in sodium concentrations (for road salt salinity), salinization could increase the competition for cation exchange sites on sediment surfaces. Within an isovalent series, the response of these elements are dominated by their ionic radii as larger cations have a greater sorption affinity due to lower ionic potentials than smaller cations. Across oxidation states, we the response of these elements may be due to their location/exposure on the sediment surface. We hypothesize the concentration of these elements to increase after salinization, with the exception of potassium (due to a larger ionic radius than sodium).

Group (3) are redox sensitive elements/compounds. Due to ion-exchange with hydrogen, salinization could induce abrupt shifts in pH, which could affect the reduction potential at the sediment-water interface. Increases in ionic strength could cause organic matter dispersal off the sediment surface and shifts in microbial processing (or cellular lysis) – both of which could expose the deeper sediment to oxygen and also affect the reduction potential. We hypothesize the concentration of these elements to decrease upon salinization and their response to be coupled with DOC concentrations (which is also highly redox sensitive).

Group (4) are transition metals with geochemical affinities that are controlled by their electron configuration. Unlike group (2), the sorption behavior of these cations are due ligand field effects and not ionic radius. Because of their valence election uncertainty, these elements are also most likely to form inner-sphere surface reactions with the sediment surfaces, which tend to be stronger attractions than outer-sphere reactions. As such, we hypothesize the concentrations of these elements to remain constant upon salinization.

In a statistically testable format, our hypothesis is that there is a significant difference between the dissolved elemental concentrations before and after a salinity treatment (increase in salinity). This hypothesis can be accepted or rejected by conducting a variance test on the data (one-way ANOVA), and by fitting linear regressions (if parametric) or theil-sen regressions (if non-parametric) to the data for each variable.

Elemental Compound	Geochemical Affinities	Major Process affected by salinization	Unknown in geochemical behavior	Group and Directional Hypothesis	Response Variable	Other studies
NH_4	Production in sediments during organic matter decomposition, Strong adsorption onto sediment particles in freshwater (especially clay)	Increase in Na, competition for exchange sites, inhibition of nitrification microbes	Temperature dependency of adsorption, desorption contribution to N mineralization	2,3, Increase	TDN	Weston et al, 2010, Seitzinger et al, 1991
NO_3	Relatively mobile form on N, Product of nitrification in shallow sediments	Increase in NH_4 leading to increases in nitrification, inhibition of microbes	Hydrologic flowpath sources in human-dominated watersheds	2, Increase		
DON	Protein and amino acids, largely refractory, Intermediate reduced products during N cycle by microbes or humification reactions, Redox sensitive, coupled with DOC	Increases in ionic strength inducing organic matter colloid dispersion, inhibition of ammonification microbes	Measurement and classification of DON is difficult.	3, Decrease		Burdige and Zheng, 1998
Ortho PO_4	Complexation reactions with metals (Fe, Al, Mn) and base cations to insoluble forms, Flocculation/settling of insoluble forms, Redox reactions Behavior coupled with S	Increased ionic strength inducing competing processes of flocculation and colloid dispersal, Changes in pH increasing reduction potential and dissolution, Presence of anions (Cl, NO_3) increase PO_4 sorption due to keeping Fe oxidized	Microbial cycling pathways and buffer system, exchange-able phosphorous content on sediment and soils, anaerobic-aerobic transition in stream sediments	1,3, Constant	SRP	Baldwin et al, 2006, Duan and Kaushal 2015, House, 2003
Poly/Organic PO_4	Amino and fatty acids bound within organic matter colloids,	Changing ionic composition inhibiting microbial cycling			N/A	

SiO_4	Sediment surface reactions with alkali complexes to form sodium complexes, Ionic composition increases reactivity and hydrolysis reactions, Stable behavior in soils	Increased ionic strength can increase the dissolution kinetics of Silica from quartz or oxide sediments, Increase Na concentrations	Microscopic role of Na at the oxide mineral-solution interface, stoichiometric relationship with aluminum	1, Increase	Si	Dove and Elston, 1992
CO_2	Solubility of CO_2 decreases with salinity, microbial metabolism and chemical weathering byproducts	Inhibition of microbial respiration and mineralization, pH induced dissolution of carbonate minerals	Temperature kinetics in sediments and rivers	1, Increase	DIC	Weiss, 1974
HCO_3	Solubility increases with salinity, chemical weathering byproducts			1, Increase		Meybeck, 2003
Humic/Fulvic Acids	Protein-like, Redox sensitive, Generally coupled with polyphosphates and DON, potentially hydrophobic, binds to colloidal, tendency to flocculate, complexation reaction with base and metal cations	Na dispersal could increase solubility of protein-like material, inhibition of microbial process	Lability of specific compounds and influence of hydrologic flowpaths	1,3, Constant	DOC	Green et al, 2009, Duan and Kaushal 2015
Ca	Outer-sphere surface Reactions (hydrated), High Ionic Potential, Sorption affinity controlled by oxidation state, then ionic radius, Potential redox reactions	Increased Na concentrations increases competition for sediment exchange site	Effect of changing ionic composition on sediment and reduction potential	1,2,3, Increase	Ca	Stumm and Morgan 1996, Honeyman and Santschi, 1988, Vengosh, 2003
Mg				1,2, Increase	Mg	
K				1, 2, Constant*	K	

Zn	Redox Reactions, Surface Protolysis Reactions, Electrolyte Surface Reactions, Cation Inner-sphere Surface Reactions, Low Ionic Potential, Sorption affinity controlled by oxidation state, then ionic radius	Increased Na concentrations increases competition for sediment exchange site	Effect of changing ionic composition on sediment and reduction potential	2,3, Increase	Zn	Stumm and Morgan 1996, Honeyman and Santschi, 1988, Vengosh, 2003
Sr				2,3, Increase	Sr	
Cu	Redox Reactions, Complexation Reactions, Chelation-ligand formation, Surface Protolysis Reactions, Electrolyte Surface Reactions, Cation Inner-sphere Surface Reactions, Low Ionic Potential, Transition metal: sorption affinity depends on electron configuration	Shift in pH affects reduction potential, changes in ionic strength causing colloid dispersal from sediment layer to suspension, increased chloride concentration enabling formation of chloro-organic matter complexes, inhibition of microbial metabolisms	Electrostatic thresholds for sorption affinity, anaerobic-aerobic transition in stream sediments, effect of changing ionic competition on reduction potential	3,4, Constant	Cu	
Mn				3,4, Constant	Mn	

*Table 1: A broad summary of the geochemical affinities of species of nitrogen, phosphorus, carbon, base cations, and trace metals. Based on their affinities, the elements/compounds were demarcated into 1 or more of the 4 categories mentioned in the above text, and a directional hypothesis was postulated. *Although we hypothesize the concentrations of elements in group 1 and 2 to increase and we place K within these groups by behavior, K has a larger ionic radius than Na and we suspect stronger sorption affinities and thus hypothesize a constant response to salinization.*

Chapter 3: Method and Study Design

We conducted laboratory experiments from 12 sites across 2 metropolitan areas, measured the response of nutrients, cations, and metals, and then compared the response with patterns of episodic salinization and nutrient loading from 3 high-frequency field sensor sites. Sediment, streamwater, and sodium chloride were incubated in a controlled lab environment to mimic post snowstorm conditions and to characterize biogeochemical relationships. The methods for incubations were previously described in Duan and Kaushal (2015). The high-frequency sensor data is from the U.S. Geological Survey, was in the same vicinity as our laboratory experiments sites, and was analyzed to investigate whether there were similar relationships between specific conductance (a proxy for dissolved salts), chloride, and nitrate, and to identify underlying mechanisms, and controlling factors during snowstorms in streams.

Episodic salinization is a short-lived pulse in streamwater salinity and occurs during finite periods of time (i.e., several hours to several days) directly following a winter road salting event (i.e., winter snowstorm). As with other chemical pulses, the stream salinity can increase by several orders of magnitude during episodic salinization, which is an immense deviation from both the long-term norm and represents a disturbance to ecosystem processes (e.g., Kaushal et al. 2014). In addition, salt concentrations during episodic salinization can exceed thresholds for sensitive organisms (Kaushal et al. 2005). As such, episodic salinization can be a hot moment in biogeochemical cycling, and have the potential to permanently alter the aquatic community and associated chemical processing (e.g., McClain et al. 2003).

In our experiments, we simulated episodic salinization as it is a realistic exposure scenario that is faced by streams and rivers. When it comes to the response of organisms to salinization, recent research suggests that the extent of deviation from the norm (i.e., dosage and recovery time) is more important that the duration of exposure, and may largely determine the adversity of its impact (Woo and Salice 2017). The same principal may be extended to the geochemical and biogeochemical behavior of a stream ecosystem upon salinization. Episodic salinization can rapidly alter the pH and ionic strength of streamwater, which can change the sediment dispersal and coagulation dynamics, chemical complexation reactions, and the microbial processing of nutrients (Kaushal et al. 2017, Kaushal et al. 2018). Unlike at lower salinity levels, during episodically high salinity, cation exchange sites may become saturated, biotic mechanisms might be inhibited, and there may be corresponding changes to nutrient and carbon cycles, which can impact ecosystems (Duan and Kaushal 2015).

Laboratory Sediment Incubations

We conducted laboratory sediment incubations from 12 sites across 2 metropolitan areas with similar methods as Duan and Kaushal (2015) as described below. Two replicates from each site were incubated under 6 salinity treatments (0-10 NaCl g/L) and the response of dissolved Mg, Ca, K, N, P, Si, Cu, Zn, Mn, and Sr were assessed. A control (no sediment) from each site was also incubated in conjunction with treated experiments to isolate the sediment-to-water column flux.

Laboratory Sediment Incubations Site Description

Sediment and streamwater were incubated form 12 sites in the Baltimore-Washington Metropolitan Area in the Chesapeake Bay Watershed. Eight of the stream sites are within the U.S. National Science Foundation (NSF) supported Baltimore Ecosystem Study Long Term Ecological Research Project (BES-LTER), and are long-term, routinely monitored, and well characterized sites (e.g., Groffman et al. 2004; Shields et al. 2008; Duan et al. 2012). These 8 stream sites are located in Baltimore, Maryland, where they exhibit a land use gradient (Fig. 3). These sites vary in drainage area (8 ha to 8350 ha), percent of watershed area covered in impervious surfaces (0% to 61%), population density (0 people/ha to 20 people/ha), and dominant land use (undisturbed forest in a state park, suburban, agricultural, urban residential, and heavily urban commercial) (Table 2). All 8 of these sites are in close proximity and share the same hydrologic, geologic (piedmont), and biome. Seven of these 8 sites are collocated with US Geological Survey gaging stations (Table 2). Two of these 8 sites (POBR, BARN) are nested in the relatively undisturbed Beaver Dam Watershed (5500 ha; drains into gunpowder watershed then Chesapeake Bay) in Northern Baltimore County, while the other 6 sites are in nested in the heavily modified suburban and urban Gwynns Falls Watershed (17500 ha; drains into Patapsco watershed then Chesapeake Bay) in Southern Baltimore County and Baltimore City (Fig. 1).

The remaining 4 of the 12 incubation stream sites are from the heavily urbanized Anacostia watershed (46000 ha) in Southern Maryland, near Washington DC. The Anacostia is a major tributary of the tidal Potomac River and the

Chesapeake Bay as described in Smith and Kaushal (2015), and Devereux et al. (2010). These 4 sites vary in both drainage area (200 ha to 18800 ha) and impervious surface cover (27% to 41%), are near each other (some are nested), and offer a slightly different hydrology, geology (coastal plain and piedmont fall line), land use (Fig. 1), and drainage infrastructure (less leaky, less old, more Green/BMP stormwater features) than the Baltimore LTER sites. Three of these 4 Anacostia watershed sites are collocated with US Geological Survey gaging stations (Table 2).

Site	Land Use Context	Drainage Area (ha)	Impervious Surface (%)	USGS Gaging Station	Metropolitan Area	Purpose
POBR	Forest	38	0	01583570	Baltimore, MD	Incubation
BARN	Forest/Suburban	382	<1	01583580		
MCDN	Forest/Agriculture	8	0	01589238		
GFGL	Suburban	81	19	01589180		
GFGB	Suburban	1065	15	01589197		
GFVN	Suburban	8349	17	01589300		
DRKR	Urban	1414	31	01589330		
GRGF	Urban	557	61	NA		
CC	Urban	178	27	NA	Washington, DC	
PB	Urban	7925	32	01649190		
NERP	Urban	18777	29	01649500		Incubation/Sensor
SLIG	Urban	1676	41	01650800		Incubation
Difficult Run	Suburban	15000	13	01646000		Sensor
Rock Creek	Urban	16600	32	01648010		Sensor

Table 2: Characteristics of the all sites for the sediment incubation experiments and the high-frequency sensor data analysis

Laboratory Sediment Incubations Methods

Roughly 1 kg of sediment was collected from the streambed per site using a clean shovel and a new Ziploc bag during fall 2014. In order to achieve a representative sediment sample for each site, small amounts of sediment were gathered from three places (left bank, center, right bank) of two separate transects, roughly 20 meters apart. Two liters of streamwater were also collected (via acid-washed HPDE Nalgene bottles; no headspace). The sediment and streamwater were transported in a chilled cooler to a laboratory, and were kept cool and moist during the experiment set-up. In order to homogenize the sample for particle size, the sediment was sieved in the lab with a 2 mm sieve and the fine fraction (\2 mm) was used for the incubation. Sixty grams of homogenized sediment were added to each acid-washed glass Erlenmeyer flask along with 100 mL of unfiltered streamwater to simulate a vertical water column with a sediment–water interface. Sodium chloride was added to increase the salinity of the simulated stream columns at various treatments; 0, 0.5, 1, 2.5, 5, and 10 g/L. This is a plausible range of salinity (0 to 6 g/L chloride, 0 to 4 g/L of sodium), as long-term studies have reported elevated measurements of both chloride (e.g. 8 g/L) and sodium (e.g. 3 g/L) during winter months at the Baltimore sites (Kaushal et al. 2005; Kaushal et al. 2017); regression models have suggested even higher concentrations of salinity (e.g. 14,000 µS/cm) following road salt applications at the Anacostia sites (Miller et al. 2013).

In order to represent salt inputs to rivers (snowmelt with road salt), sodium chloride was dissolved into 100 mL unfiltered streamwater in a separate volumetric flask before being pipetted onto sediment in the Erlenmeyer flask. We acknowledge that salinization can actually be a mixture of ions (sensu Kaushal et al. 2017; Kaushal et al. 2018; Kaushal et al. 2013), but used sodium chloride because it is commonly used as a deicer. In order to isolate the sediment–water interaction, a control flask of just unfiltered streamwater was also incubated along with the treatment flasks. All experiments for each site were incubated together in duplicates within 12 h of field collection. The flasks were capped loosely with aluminum foil to limit evaporation but allow for air exchange to simulate open system conditions. The flasks were incubated on a shaking table (slow mode) in the dark for 24 h at room temperature (20 C). After the incubation, the water was immediately and carefully removed from the flask using a pipette as to avoid any disturbance to the sediment, and then filtered through a pre-combusted Whatman 0.7 micron glass fiber filter. The filtered post-incubation water was stored in a fridge at 4 C for water chemistry analysis (described below). An aliquot of the post-incubation filtered water was immediately acidified in a small acid-washed HDPE Nalgene bottle to contain 0.5% high-purity nitric acid for base cation analysis and was stored at room temperature for up to 12 months. Flask weights and initial sediment weights were recorded prior to the incubation. After the incubations, sediments were dried in their flasks in a drying oven at 95 C for 12 h, then combusted in a furnace at 550 C for 12 h. Sediment weights were recorded at every step and were used to calculate ash free dry mass to approximate organic matter content.

Laboratory Sediment Incubations Chemical and Statistical Analyses

DIC, DOC (as NPOC), and TDN concentrations in water were measured within 24 hours after the incubation using a combustion-catalytic-oxidation-NDIR method on a Shimadzu Total Organic Carbon Analyzer (TOC-V CPH/CPN; Shimadzu, Columbia, Maryland, USA). SRP concentrations in the water were measured within 10 days after the incubation using an automated colorimetric-blue method on a Lachat QuickChem 8500 Series 2 FIA System (Hach, Loveland, Colorado, USA). Mg, Ca, K, Si, Cu, Zn, Mn, and Sr concentrations in the acidified water samples were measured within 12 months after the incubation via inductively coupled plasma optical emission spectrometry in an acidified analytical matrix on a Shimadzu Elemental Spectrometer (ICPE-9800; Shimadzu, Columbia, Maryland, USA). The instrument was calibrated to the range of trace metals that are commonly observed in urban streams. In order to do so, a custom method was developed on the instrument over the course of 10 weeks. The goal of the method was; to follow all analytical guidelines for surface water analysis issued by the Environmental Protection Agency (US EPA), to minimize costs while maximizing sample throughput, to switch between axial and radial nebulization modes based on element, to limit intra-elemental spectral interference, to compute and adjust injection timing using dyes and tracers until ultrapure water spectra is matched, and most importantly, to measure base cations and trace metals with adequate precision within the range that is commonly observed in river water. The method was compared with a similar method developed by a nearby group who also measures dissolved cations; the Maryland Water Resource Research Center (UMD-MWRRC).

Nutrients	Base Cations	Carbon	Trace Metals
TDN (Combustion-catalytic-oxidation NDIR)	Mg (ICP-OES, Radial)	DIC (Combustion-catalytic-oxidation NDIR)	Mn (ICP-OES, Axial)
SRP (Automated Colorimetric)	K (ICP-OES, Radial)	DOC (NPOC, catalytic-sparging-combustion NDIR)	Zn (ICP-OES, Axial)
Si (ICP-OES, Radial)	Ca (ICP-OES, Radial)		Sr (ICP-OES, Axial)
			Cu (ICP-OES, Axial)

Table 3: A summary of the response variables and their analytical method of measurement.

For each site, the incubation experiment were conducted in duplicates (using the same sediment and streamwater sample grab), the resulting dissolved concentrations were averaged, and the averaged values were used for all statistical analyses. In order to isolate the effects of episodic salinization on the mobilization of base cations, carbon, nutrients, and trace metals from the sediment to streamwater, the results from an untreated control flask for each site were subtracted from the results of each treatment (Duan and Kaushal 2015). The resulting dissolved water chemistry was statistically evaluated using ordinary linear regressions with sodium chloride treatment as the independent variable and base cation, carbon, nutrient, or trace metal concentration as the response variable. Slopes with a p-value <0.05 were assumed statistically significant, and this p-value criteria was used to ascertain whether episodic salinization in laboratory experiments significantly affected the dissolved concentrations of different elements. The r2 coefficient of determination was estimated for experiments and was used to characterize the variability in dose-responses. For the experimental incubations, all data and statistical analysis was conducted using Microsoft Excel (Microsoft Corporation, Redmond, Washington, USA).

High-frequency In-situ Chemical Sensors

The results of our experimental could be used to interpret the sensor data and postulate a biogeochemical mechanism. The incubation experiment and sensor sites were located within the Baltimore Washington Metropolitan area and extended over a range of size and land use.

High-frequency In-situ Sensor Site Descriptions

Data from 3 sensors located in the Washington DC Area were used in this study; Difficult Run, Rock Creek, and Northeast Branch Anacostia. All three sensors are in close proximity to the Anacostia Watershed incubation sites (Fig. 3), and are maintained and operated by the US Geological Survey. The Northeast Branch Anacostia site was selected because the sensor is precisely co-located with one of the experimental incubation sites (NERP), and it has a 14 year continuous record of high-frequency specific conductance (15 minute intervals) and discrete (grab-sample) chloride data. The NERP sensor (gaging station 01649500) is a heavily urban site (Fig. 3) with short reaches of boulder embankment (previously channelized), and has a watershed size of 18800 ha. The NERP sensor does not have high-frequency nitrate measuring capabilities.

The Difficult Run and Rock Creek sites were selected due the availability of high-frequency nitrate measurements, and because of similarities in their discharge and watershed size to experiment incubation sites (described above). Although both sites have a predominately suburban and urban land cover, they also have a wide and undeveloped riparian zone consisting of hiking trails, recreational areas, and a thin band of intact forest with temperate deciduous trees (as described in Miller et al. 2013). The Difficult Run sensor (gaging station 01646000) is located near Great Falls, Virginia, approximately 15 miles northwest of Washington DC, and the Rock Creek sensor (gaging station 01648010) is located in the northern corner of Washington DC (Fig. 3). Difficult Run has a watershed size of 15000 ha, and Rock creek has a watershed size of 16600 ha. Difficult Run has 5 years of continuous high-frequency 15 minute interval measurements of specific conductance and nitrate, and Rock Creek has a 2 year length of record, also in 15 minute intervals. Both Difficult Run and Rock Creek are tributaries of the Potomac River and the Chesapeake Bay. Previous studies have characterized the sediment and biogeochemical dynamics in Difficult Run (e.g., Hupp et al. 2013; Batson et al. 2015), and the nutrient loading and emerging contaminants in the Rock Creek watershed (e.g., Miller et al. 2013; Battaglin et al. 2009).

Although these watersheds are urban watersheds that are hydrologically connected to impervious surfaces (Kaushal and Belt 2012), they lack an appreciable nitrate source aside from sewage leaks (Pennino et al. 2016; Newcomer-Johnson et al. 2014; Kaushal et al. 2011), and so it is more likely that the nitrate signals are generated from flow-path biogeochemical processes (e.g., nitrification) than from being washed-in into the channel during snowstorms. Furthermore, because both nitrate and chloride concentrations in these watersheds can be higher in groundwater than streamwater (Mayer et al. 2010; Kaushal et al. 2005), it is also possible that signals may be confounding due the elements being derived from the same groundwater hotspot in the riparian zone near the sensors.

High-frequency In-situ Sensor Methods

High-frequency sensor data from US Geological Survey stations 01649500 (NERP), 01646000 (Difficult Run) and 01648010 (Rock Creek) (sites described above) were analyzed to empirically characterize the in-situ relationship between salinity and nitrogen. We compared the potential relationships between salinity and nitrate from the incubation experiments with sensor data from nearby sites. Specific conductance is measured using a submersible electrode sensor, calibrated to each site, and adjusted to represent the cross-sectional mean at the time of observation (Radtke et al. 2005). At Difficult Run and Rock Creek, nitrate is measured using a Submersible Ultraviolet Nitrate Analyzer (SUNA, Sea-Bird Scientific, Bellevue, Washington, USA) with a 10 mm optical path length (Pellerin et al. 2013). The nitrate optical sensors are lab calibrated to grab samples from each site, and the optics are corrected for temperature and turbidity. Although the optical sensor cannot distinguish between nitrate and nitrite, the measurement were assumed to be nitrate (as nitrite is negligible in these streams) (Pellerin at al. 2013). The NERP sensor does not have nitrate measuring capabilities. Specific conductance (at all 3 sites) and nitrate (at 2 sites) are measured by the sensors in 15 minute intervals, which were averaged into a single daily value before analyses in this study.

At all 3 sites, discrete dissolved chloride is measured by ion chromatography for samples approximately every 3 weeks by the US Geological Survey. For the NERP site, 174 chloride measurements are available spanning roughly 13 years (2004 to 2017). For the Difficult Run site, 143 chloride measurements are available spanning roughly 10 years (2007 to 2017). For the Rock Creek site, 259 chloride measurements are available spanning roughly 5 years (2012 to 2017). At each site, a regression model was used to determine the relationship between precisely-concurrent measurements of discrete chloride concentrations (from grab samples) and the continuous high-frequency specific conductance measurements (from sensors). From this relationship, a high-frequency chloride (e.g., salinity) record was estimated based on the continuous high-frequency specific conductance record.

High-frequency In-situ Sensor Statistical Analysis

Gaps in the high-frequency nitrate and specific conductance sensor measurements were not estimated by interpolation as they were normally distributed about their means, with the exception of some specific conductance outliers (e.g., the episodically high specific conductance). The magnitude of the relationship between estimated continuous chloride and sensor-measured continuous nitrate was assessed by ordinary linear regression with estimated chloride as the independent variable and sensor-measured nitrate as the response variable. In order to assess the impact of extreme outliers, a least squares linear regression with iterative bi-square weighting was performed, and the resulting slope as compared to the ordinary linear regression slope for agreement. A p-value <0.01 was used to demarcate statistical significance of the slope, and whether an in-situ empirical relationship exists between chloride and nitrate. The r2 coefficient of determination were used to assess the strength of the relationship. For the high-frequency sensors portion of this study, all data and statistical analyses was conducted using MATLAB (MathWorks Inc., Natick, Massachusetts, USA).

Chapter 4: Results

Laboratory Sediment Incubations Ambient Streamwater Chemistry

As expected, the ambient streamwater chemistry varied across sites (Table 2). Chloride varied from a minimum of 2.72 mg/L at a headwater forested site (POBR, Baltimore) to a maximum of 135 mg/L at a headwater suburban site (GFGL, Baltimore). TDN varied from a minimum of 0.33 mg/L N at a headwater forested site (POBR, Baltimore) to a maximum of 5.96 mg/L N at a small agricultural stream (MCDN, Baltimore). SRP varied from a minimum of 2.05 µg/L P at POBR to a maximum of 97.15 µg/L P at GFGL. DIC varied from a minimum of 2.61 mg/L at POBR to a maximum of 38.70 mg/L at GFGL, while DOC varied from a minimum of 1.45 mg/L at MCDN to a maximum of 4.52 mg/L at a small suburban creek (CC, Anacostia). Silica concentrations varied from a minimum of 0.87 mg/L Si at a second order urban stream (NERP, Anacostia) to a maximum of 6.75 mg/L Si at GFGL. Although elemental silicon was measured in this study, we are reporting the results as silica as it is the dominant form of silicon in streamwater (e.g., Treguer et al. 1995; Conley 2002). The sum of the base cations (calcium, magnesium, potassium, and sodium) varied from a minimum of 9.19 mg/L at POBR to a maximum of 192.45 mg/L at a suburban mid-size stream with sanitary infrastructure leak issues (DRKR, Baltimore). The sediment composition also varied between sites, with sediment organic matter ranging from a minimum of 0.17% at two mid-size streams (SLIG, Anacostia, suburban with old growth trees) and (GRGF, Baltimore, urban and heavily polluted) to a maximum of 0.99% at MCDN. Trace metal measurement capabilities were not available during the time of sample grab.

Laboratory Sediment Incubations Responses

There were consistent increases in base cation concentrations with increasing salinity across sites (Fig 2-4). There were statistically significant linear increases in calcium and potassium concentrations with increasing sodium chloride treatments at all 12 sites, with rates of increase ranging from 0.20 ± 0.02 to 3.96 ± 0.37 mg Ca^{2+} per g NaCl and 0.38 ± 0.12 to 7.60 ± 0.53 mg K^+ per g NaCl, respectively. There were statistically significant linear increases in magnesium concentrations at 11 of the 12 sites with rates of increase ranging from 0.38 ± 0.12 to 2.35 ± 0.51 mg Mg^{2+} per g NaCl. Salinization did not have a significant effect on magnesium at the remaining site (GFGB, Baltimore, suburban). Ambient stream chemistry was not a good predictor of the response of calcium or magnesium to salinization. However, there was a statistically significant linear correlation between ambient in-stream chloride concentrations during the sample grab, and the mobilization of potassium from the experiments (i.e., incubation rates of increase).

Increases in nutrient concentrations in response to salinization were not as consistent across sites as changes in cation concentrations. There were significant linear increases in TDN concentrations with increasing sodium chloride treatments at 9 of the 12 sites (Fig. 5), with rates of increase ranging from 0.03 ± 0.001 to 0.13 ± 0.02 mg N per g NaCl. One of the sites had a statistically significant decrease in TDN concentrations with increasing salinity (BARN, Baltimore, suburban), and salinity had no significant effect on TDN at the remaining 2 sites (PB and SLIG, Anacostia, Urban). There was a significant decreasing linear response in silica concentrations to increasing sodium chloride treatments at only 1 of the 12 sites (POBR, Baltimore, forested). At 7 of the 12 sites, there were statistically significant linear increases in SRP concentrations with increasing sodium chloride treatments (Fig. 6), with rates of increase ranging from 0.30 ± 0.08 to 5.63 ± 1.22 μg P per g NaCl (Table 4). Salinity had no statistically significant effect on SRP concentrations at the remaining 5 sites; however, all 5 of these sites responded with increases in SRP concentrations in the treatment experiments relative to the control experiment (Fig. 6). Although the response of SRP concentrations to episodic salinization was more variable than the response of TDN, the magnitude of the response was stronger (as indicated by the greater slopes in Table 4).

Broadly across all sites, the ambient stream chemistry was not a good predictor of the response of nitrogen or silica in the incubations (i.e., the presence or strength of a salinization effect). However, there was a statistically significant weak linear correlation between ambient in-stream SRP concentrations during sample grab and the strength of the response of SRP to experimental salinization (i.e., incubation rate of change). The site with the lowest ambient SRP concentration (POBR) had the weakest salinization effect (i.e., rate of SRP change), while the site with the highest ambient SRP concentration (GFGL) had the strongest salinization effect.

The response of carbon to episodic salinization varied largely across sites and across salinity treatment levels. There were statistically significant linear increases in

DIC concentrations with increasing sodium chloride treatments at 4 of the 12 sites, with rates of change ranging from 0.06 ± 0.02 to 0.32 ± 0.07 mg C per g NaCl (Table 4). At 2 of the sites (BARN and MCDN, Baltimore), there were significant linear decreases in DIC concentrations with increasing salinity with rates of change ranging from -0.30 ± 0.07 to -0.39 ± 0.08 mg C per g NaCl (Table 4). The remaining 6 sites did not show a significant increasing or decreasing trend for DIC; however, at most of these sites the DIC concentrations in the salinity treated experiments differed from their respective control experiments (Fig. 7). For the DOC response, there were statistically significant increasing DOC concentrations with increasing sodium chloride treatments at 3 of the 12 sites, with rates of increase ranging from 0.07 ± 0.02 to 0.19 ± 0.01 mg C per g NaCl. Although the remaining 9 sites did not show any significant trends for DOC, the concentrations varied between treated experiments relative to the control experiment, and between the individual salinity treatment levels at each site (Fig. 7). For example, at a small agricultural stream (MCDN, Baltimore), we observed an initial increase in DOC concentrations with the lower sodium chloride treatments, then a decrease in DOC concentrations with the higher salinization treatments (Fig. 7). Salinization did not have a detectable effect on sediment organic matter at any site (Supporting Fig. S4).

There were no observable patterns between the ambient in-stream chemistry at a site at the time of sample grab and the response of DOC to salinization in this study. However, there was a statistically significant positive linear correlation between the ambient in-stream DIC concentrations during sample grab, and the response of DIC to salinization (i.e., incubation rate of change). Among the 6 incubation sites which showed a significant DIC response, the rate of change was negative (i.e., salinization removed DIC from water column) when the starting ambient in-stream DIC concentration was low (<10 mg/L). At the sites with high ambient DIC concentrations during sample grab (>10mg/L), experimental salinization had a mobilization effect on DIC (Table 2 and 4).

High-frequency In-situ Chemical Sensors Salinity-Nitrate Relationships

Episodic salinization is shown in figure 8 as a pulse of elevated specific conductance in the winter months directly ensuing a snow storm (e.g., road salt application). At each site, the episodically high specific conductance is at least an order of magnitude above both the baseflow measurements and the long-term average, and the magnitude and duration of the pulse varied between sites. There was a large variation in the chloride and nitrate data at both sensor sites. As expected, there was a strong positive correlation between specific conductance and chloride concentration at these sites (Fig. 8). There were weak but still statistically significant increases in nitrate concentrations with increasing chloride concentrations at both high-frequency sensor sites (Fig. 9). At the Difficult Run sensor (near Great Falls, Virginia), the rate of increase was 1.46 ± 0.12 mg N per g Cl (ANOVA, r2 = 0.08, d.f. = 1583, p<0.01), and at the Rock Creek sensor (northern Washington DC), the rate of increase was 0.46 ± 0.06 mg N per g Cl (ANOVA, r2 = 0.10, d.f. = 484, p<0.01).

Site	<-- Ambient stream conditions at time of sample grab -->										
	TDN (mg/L)	SRP (μg/L)	DIC (mg/L)	DOC (mg/L)	Si (mg/L)	Sediment OM (%)	Ca^{2+} (mg/L)	Mg^{2+} (mg/L)	K^+ (mg/L)	Na^+ (mg/L)	Cl^- (mg/L)
POBR	0.33	2.05	2.61	2.23	1.49	0.46	0.44	1.80	1.90	5.05	2.72
BARN	1.49	3.50	4.37	1.71	3.68	0.24	8.25	4.40	2.40	15.45	40.6
MCDN	5.96	49.99	7.28	1.45	3.88	0.99	12.35	5.78	7.72	55.25	6.19
GFGL	1.09	97.15	38.70	2.89	6.75	0.70	75.20	39.50	5.15	23.90	135
GFGB	1.63	27.60	10.80	4.31	1.70	0.30	22.10	8.97	8.71	78.65	98.3
GFVN	1.69	31.35	18.21	2.53	2.00	0.35	38.85	20.65	10.02	59.25	51.6
DRKR	1.90	64.20	30.87	3.31	5.71	0.35	79.10	55.05	7.25	51.05	81.2
GRGF	2.18	12.20	29.27	4.49	4.48	0.17	65.60	21.05	7.95	54.90	89.7
CC	0.72	19.25	20.10	4.52	1.61	0.36	17.88	9.84	5.66	24.23	NA
PB	1.50	24.30	7.32	1.77	1.72	0.22	19.35	8.57	8.16	53.35	63.2
NERP	0.86	12.90	11.96	4.47	0.87	0.44	26.25	11.85	12.05	68.10	31.0
SLIG	1.83	61.10	18.27	2.16	2.17	0.17	56.85	23.55	13.85	81.75	89.3

Table 4: Ambient site chemistry at the time of the sample collection (i.e., starting in-stream conditions for the sediment incubation experiments). We will investigate whether the ambient chemistry is a good predictor of the effects of episodic salinization.

Site	<---------- Ca^{2+} ---------->			<---------- K^{+} ---------->			<---------- Mg^{2+} ---------->		
	Slope	p-value	r^2	Slope	p-value	r^2	Slope	p-value	r^2
POBR	**1.377 ± 0.356**	0.018	0.79	**1.054 ± 0.093**	3.E-04	0.97	**1.675 ± 0.424**	0.017	0.80
BARN	**2.840 ± 0.697**	0.015	0.81	**1.726 ± 0.291**	0.004	0.90	**2.228 ± 0.615**	0.022	0.77
MCDN	**0.199 ± 0.023**	0.001	0.95	**0.408 ± 0.037**	4.E-04	0.97	**0.589 ± 0.081**	0.002	0.93
GFGL	**2.446 ± 0.542**	0.011	0.84	**0.376 ± 0.118**	0.033	0.72	**1.311 ± 0.179**	0.002	0.93
GFGB	**1.494 ± 0.296**	0.007	0.86	**1.517 ± 0.239**	0.003	0.91	0.060 ± 0.131	0.673	0.05
GFVN	**0.338 ± 0.080**	0.014	0.82	**0.469 ± 0.038**	2.E-04	0.97	**0.382 ± 0.122**	0.035	0.71
DRKR	**1.162 ± 0.154**	0.002	0.93	**2.149 ± 0.415**	0.007	0.87	**0.564 ± 0.176**	0.033	0.72
GRGF	**3.117 ± 0.873**	0.023	0.76	**5.665 ± 0.583**	0.001	0.96	**2.352 ± 0.508**	0.010	0.84
CC	**1.575 ± 0.280**	0.005	0.89	**2.483 ± 0.309**	0.001	0.94	**0.529 ± 0.129**	0.015	0.81
PB	**2.038 ± 0.170**	3.E-04	0.97	**4.748 ± 0.721**	0.003	0.92	**0.541 ± 0.057**	0.001	0.96
NERP	**3.964 ± 0.366**	4.E-04	0.97	**7.597 ± 0.535**	1.E-04	0.98	**1.169 ± 0.176**	0.003	0.92
SLIG	**2.498 ± 0.253**	0.001	0.96	**5.367 ± 0.205**	1.E-05	0.99	**0.848 ± 0.111**	0.002	0.94

Table 5: Results of a linear regression analysis of the base cation response at each incubation site to sodium chloride additions. Units for calcium slopes are mg-Ca per g-NaCl, potassium slopes are mg-K per g-NaCl, and magnesium slopes are mg-Mg per g-NaCl. Bold slopes are significant at the $p<0.05$ level.

Site	<---------- TDN ---------->			<---------- SRP ---------->			<---------- DIC ---------->			<---------- DOC ---------->			<---------- Si ---------->		
	Slope	p-value	r^2	Slope	p-value	r^2	Slope	p-value	r^2	Slope	p-value	r^2	Slope	p-value	r^2
POBR	**0.049 ± 0.014**	0.023	0.77	0.087 ± 0.036	0.074	0.59	0.048 ± 0.032	0.200	0.37	0.013 ± 0.030	0.698	0.04	**-0.012 ± 0.004**	0.034	0.71
BARN	**-0.074 ± 0.021**	0.026	0.75	**0.300 ± 0.084**	0.023	0.76	**-0.301 ± 0.072**	0.014	0.81	-0.029 ± 0.025	0.317	0.25	0.043 ± 0.040	0.344	0.22
MCDN	**0.065 ± 0.014**	0.009	0.85	**1.346 ± 0.333**	0.016	0.80	**-0.395 ± 0.083**	0.009	0.85	-0.007 ± 0.037	0.864	0.01	-0.078 ± 0.068	0.318	0.25
GFGL	**0.051 ± 0.005**	0.001	0.96	**5.634 ± 1.221**	0.010	0.84	**0.323 ± 0.073**	0.011	0.83	**0.069 ± 0.024**	0.042	0.69	0.031 ± 0.041	0.499	0.12
GFGB	**0.026 ± 0.001**	3.E-05	0.99	**2.1082 ± 0.195**	4.E-04	0.97	**0.158 ± 0.042**	0.019	0.78	**0.190 ± 0.013**	0.000	0.98	0.008 ± 0.014	0.588	0.08
GFVN	**0.043 ± 0.011**	0.019	0.78	**1.752 ± 0.201**	0.001	0.95	0.097 ± 0.073	0.256	0.31	0.055 ± 0.023	0.077	0.58	-0.039 ± 0.018	0.095	0.54
DRKR	**0.127 ± 0.012**	4.E-04	0.97	**1.074 ± 0.227**	0.009	0.85	**0.282 ± 0.097**	0.044	0.68	-0.006 ± 0.017	0.720	0.04	-0.003 ± 0.026	0.903	0.01
GRGF	**0.070 ± 0.012**	0.004	0.89	1.491 ± 0.712	0.104	0.52	-0.012 ± 0.026	0.681	0.05	-0.024 ± 0.010	0.067	0.61	0.015 ± 0.008	0.130	0.48
CC	**0.029 ± 0.003**	0.001	0.96	**4.180 ± 0.712**	0.004	0.90	-0.005 ± 0.037	0.890	0.01	0.075 ± 0.030	0.069	0.60	0.013 ± 0.005	0.068	0.61
PB	0.021 ± 0.031	0.537	0.10	0.329 ± 0.405	0.462	0.14	0.032 ± 0.173	0.862	0.01	0.041 ± 0.059	0.527	0.11	0.012 ± 0.008	0.183	0.39
NERP	**0.131 ± 0.018**	0.002	0.93	0.106 ± 0.147	0.509	0.12	0.113 ± 0.059	0.127	0.48	**0.071 ± 0.016**	0.010	0.84	0.012 ± 0.005	0.075	0.59
SLIG	0.005 ± 0.006	0.404	0.18	2.424 ± 2.256	0.343	0.22	**0.065 ± 0.019**	0.029	0.74	0.049 ± 0.028	0.159	0.43	0.017 ± 0.007	0.071	0.60

Table 6: Results of a linear regression analysis of the nutrient response at each incubation site to sodium chloride additions. Units for TDN slopes are mg-N per g-NaCl, SRP slopes are µg-P per g-NaCl, DIC and DOC slopes are mg-C per g-NaCl, and silica slopes are mg-Si per g-NaCl. Bold slopes are significant at the p<0.05 level.

Site	<---------- Mn ---------->			<---------- Zn ---------->			<---------- Sr ---------->			<---------- Cu ---------->		
	Slope	p-value	r^2	Slope	p-value	r^2	Slope	p-value	r^2	Slope	p-value	r^2
POBR	**0.008 ± 0.002**	0.030	0.73	**0.008 ± 0.003**	0.043	0.68	**0.042 ± 0.002**	6E-05	0.99	**0.020 ± 0.001**	3E-05	0.99
BARN	**0.013 ± 0.002**	0.001	0.94	**0.009 ± 0.001**	9E-05	0.98	0.001 ± 0.003	0.692	0.04	**0.020 ± 0.003**	0.002	0.93
MCDN	**0.010 ± 0.003**	0.024	0.76	**0.011 ± 0.003**	0.021	0.77	**0.037 ± 0.003**	1E-04	0.98	**0.029 ± 0.001**	3E-06	1.00
GFGL	**0.003 ± 0.000**	2E-04	0.98	**0.003 ± 0.001**	0.003	0.91	**0.015 ± 0.000**	5E-07	1.00	**0.037 ± 0.001**	1E-06	1.00
GFGB	**0.011 ± 0.001**	0.001	0.95	**0.010 ± 0.001**	1E-04	0.98	**0.012 ± 0.001**	7E-05	0.99	**0.034 ± 0.000**	3E-08	1.00
GFVN	**0.011 ± 0.001**	0.001	0.94	**0.10 ± 0.001**	0.001	0.95	**0.016 ± 0.002**	0.001	0.94	**0.028 ± 0.001**	3E-06	1.00
DRKR	**0.011 ± 0.002**	0.003	0.91	**0.009 ± 0.002**	0.005	0.88	**0.020 ± 0.001**	6E-06	1.00	**0.043 ± 0.004**	4E-04	0.97
GRGF	**0.006 ± 0.001**	0.005	0.89	**0.009 ± 0.001**	0.001	0.94	**0.014 ± 0.003**	0.010	0.84	**0.024 ± 0.000**	8E-07	1.00
CC	**0.003 ± 0.000**	0.001	0.94	**0.003 ± 0.001**	0.041	0.69	**0.006 ± 0.000**	3E-05	0.99	**0.038 ± 0.002**	1E-05	0.99
PB	**0.011 ± 0.001**	0.001	0.94	**0.007 ± 0.002**	0.027	0.75	**0.017 ± 0.000**	1E-06	1.00	**0.058 ± 0.001**	2E-06	1.00
NERP	**0.009 ± 0.002**	0.005	0.88	**0.011 ± 0.002**	0.003	0.91	**0.016 ± 0.003**	0.004	0.90	**0.164 ± 0.003**	9E-07	1.00
SLIG	**0.007 ± 0.001**	0.003	0.92	**0.008 ± 0.000**	3E-05	0.99	**0.016 ± 0.003**	0.004	0.90	**0.161 ± 0.006**	1E-05	0.99

Table 7: Results of a linear regression analysis of the trace metal response at each incubation site to sodium chloride additions. Units for manganese slopes are mg-Mn per g-NaCl, zinc slopes are mg-Zn per g-NaCl, strontium slopes are mg-Sr per g-NaCl, and copper slopes are mg-Cu per g-NaCl. Bold slopes are significant at the $p<0.05$ level.

Chapter 5: Discussion

Effects of Salinization on the Biogeochemistry and Fluxes of Base Cations (Ca, K, Mg)

In the incubation experiments, we observed consistent mobilization of base cations from the sediment into the water column in response to episodic salinization (Fig. 2-4). Rates of increase for calcium and potassium were greater in the Anacostia watershed than in the Baltimore watersheds (Table 3), which could be attributed to differences in the underlying lithology and sediment as most of the Anacostia watershed is within the Atlantic Coastal Plain physiographic region, while the Baltimore watersheds are within the Piedmont physiographic region. However, ambient stream chemistry was not a good predictor of the response of base cations to salinization.

Our results are consistent with a previous study evaluating the effect of experimental salinity on wetland sediment biogeochemistry, which reported increased levels of magnesium, potassium, sodium, calcium, and decreased pH with long-term salinization (Kim and Koretsky 2013). The authors concluded that ion exchange would result in a greater release of cations with a greater salinity treatment, and that pH was suppressed due to the interactive effects of carbonate precipitation, oxidation, and ion exchange reactions (which would affect iron and manganese cycling). We suggest similar mechanisms in our results, although we evaluated the potential effects of episodic salinization on stream water quality.

Positive relationships between salinization and base cations have also been demonstrated in the soil literature. Column leaching experiments of salinizing urban and forested soils in Sweden and central USA have indicated that sodium preferentially displaces calcium, potassium, and magnesium during ion exchange reactions, leading to the mobilization of these base cations (Norrstrom and Bergstedt 2001; Lofgren 2001; Robinson et al. 2017). Polyvalent elements, such as calcium and magnesium were 18-51 times higher in the salt solution leachate, while the monovalent cations, such as potassium and sodium, were 2-6 times higher in the salt solution leachate (Lofgren 2001). Furthermore, the increased ionic strength caused by chloride was found to easily release hydrogen ions leading to an initial decrease in the pH of the soil. Decreases in pH can affect the edge charge on clay minerals, and at high salinity levels, can cause organic matter-cation colloid dispersal (Norrstrom and Bergstedt 2001). At lower salt concentrations, a suppressed pH can stabilize organic matter-cation colloid dispersal, however, limiting the mobilization of base cations (Norrstrom and Bergstedt 2001). Surface soils receiving salt applications have been shown to be enhanced in sodium and depleted in calcium relative to their surroundings when subjected to sodium chloride road salting, or enhanced in magnesium and depleted in sodium when subjected to magnesium chloride road salting – both of which are further evidence for ion exchange, complexation or sorption of organic matter, or dispersal of colloids (Backstrom et al. 2004; Cunningham et al. 2008).

The mobilization of base cations from soils and sediments to streamwater due to episodic salinization and freshwater salinization syndrome could further enhance the base cation loads of streams and rivers (Norrstrom and Bergstedt 2001; Robinson et al. 2017). In our study, the increases in base cations could be due to the mobile anion effect as the presence of anions (*i.e.,* nitrate, chloride) enable the leaching of base cations from exchange sites on the sediment into the water column, and we suggest this could increase the base cation loads of streams and rivers. This is consistent with stream monitoring work in small forested watersheds showing 14% of the magnesium and 19% of the calcium flux (*i.e.,* roughly a 20% increase) was attributed to mobilizations induced by salt inputs (Price and Szymanski 2014). In stream monitoring studies of medium sized watersheds, road salt inputs increased the net calcium and magnesium flux each by 44% above respective background, increased the total solute flux in streamflow by 120%, and caused a net flushing (*e.g.*, loss) of sodium from the watershed (Shanley 1994). Finally in long-term monitoring studies, Kaushal et al (2017) measured long-term increases in base cation concentrations at some of these same sites in our study (which were on average up to 60 times greater than a nearby forested reference), which suggested mobilization of base cations by salinization.

Effects of Salinization on the Biogeochemistry and Fluxes of Nutrients (N, P, Si)

The variability in the response of TDN concentrations to salinization between the Baltimore sites (where 88% of sites exhibited a positive response) and Anacostia watershed sites (where 50% of sites exhibited a positive response) could be due to the sediment conditions and stream concentrations during the sample grab. The 2 sites that did not show a significant effect of salinity in the Anacostia watershed had nearly twice the ambient TDN concentrations than the other 2 Anacostia sites. This potentially indicated that the sediment at these two sites is already low in nitrogen content, perhaps due to prior leaching from prior exposure to chloride (as discussed in Hale and Groffman 2006). Broadly across all sites, the ambient stream chemistry was not a good predictor of the response of nitrogen in the incubations (*i.e.,* the presence or strength of a salinization effect on nitrogen).

Our results of episodic salinization affecting nitrogen dynamics are consistent with previous salinization studies of stream sediments (Duan and Kaushal 2015), wetland sediments (Kim and Koretsky 2013), and soils (Green et al. 2008; Compton and Church 2011; Duckworth and Cresser 1991). Similarly, our results could be interpreted within the context of these studies. First, ammonium, an important TDN species, can be mobilized by salinization due to sodium dispersion and ion exchange. (Duckworth and Cresser 1991; Green et al. 2008; Compton and Church 2011; Kim and Koretsky 2011). As a positively charged ion, ammonium can easily be adsorped on negatively charged particles of soils and sediments (Nieder et al. 2011). Once retained on the sediment particle's cation exchange sites, ammonium can exchange with sodium ions, which could cause flushing of ammonium induced by salinization (Duckworth and Cresser 1991; Kim and Koretsky 2011). Furthermore, salinization has been shown to increase net mineralization in both roadside soils (Compton and Church 2011; Green et al. 2008) and forested debris dams in a lab environment (Hale and Groffman 2006), which could further contribute to elevated ammonium concentrations. Finally, several previous studies have also shown appreciable leaching of dissolved organic nitrogen (DON; another important TDN species) from plant litter or soils along with DOC upon increased salinization (Steele and Aitkenhead-Peterson 2013; Green et al. 2009).

Unlike ammonium or DON, the effects of salinization on nitrate fluxes varied considerably in previous studies, potentially due to the competing processes of nitrification (due to the enhanced ammonium availability) and nitrate removal via denitrification. Duckworth and Cresser (1991) concluded that salinization has no effect on nitrate release in forested soils, however, these soils were highly organic. Although Compton and Church (2011) reported increases in nitrogen mineralization in response to salinity, they discuss how the extent of nitrification (or immobilization) of the released ammonium depends heavily on the response of DOC to salinity, and thus the implications for nitrate concentrations are unclear. Duan and Kaushal (2015) reported net nitrate retention with increasing salinization in sediments and net nitrate release with salinization in soils, after conducting experiments from a subset of the exact sites used in this study. However, they also identified ammonium and DON to be the dominant sources of nitrogen that were leached out of sediments or soil during the experiments, which could account for our observed result of increases in TDN concentrations with salinization. Interestingly, at some of the same sites as this study there were consistent positive relationships between in-stream nitrate and chloride concentrations in the long-term stream chemistry data at the Baltimore LTER site (Kaushal et al. 2017).

The results of our incubation experiments can be used to interpret the significant linear relationships between *in-situ* nitrate and chloride at 2 high-frequency sensors sites. The mean rate of increase for the 9 experiments that showed a statistically significant increase in TDN concentrations with increasing salinization was 0.11 mg N per g Cl (with a standard deviation of 0.06). The mean slope for the experiments is within the same order of magnitude as the slope from the Rock Creek high-frequency sensor, and an order of magnitude smaller than the slope from the Difficult Run high-frequency sensor.

Despite the statistically significant positive relationship between specific conductance (or chloride) and nitrate concentrations, the relationship was weak, the goodness of fit is low, and the model has no predictive power. There are many hydrological and biogeochemical factors that mask the in-situ response of nitrate concentration to increases in salinity, and it is unlikely that the underlying factors in the experimental incubations would be exactly the same as a stream channel. For example, the type of salt additions used in our experiment (lab grade sodium chloride) is not the same type of salt-sand mixtures used on pavements (magnesium chloride, calcium chloride, potassium chloride, organic deicers). There are also differences in the relative abundance of nitrogen species in the incubation experiments and the stream (only TDN was measured in our experiments, only *in-situ* nitrate was measured by the sensor).

Salinization may cause increases in TDN (including nitrate) in the stream, potentially due to the mobilization of nitrogen from sediments to stream water, coupled with enhancements in net nitrification, or due to the leaching of nitrogen from soils throughout the watershed and the subsequent flushing to streams during storm flow. Although urban watersheds are hydrologically connected to impervious surfaces (Kaushal and Belt 2012), a major nitrogen source is sewage leaks (Pennino et al. 2016; Newcomer-Johnson et al. 2014; Kaushal et al. 2011), and so it is more likely that the nitrate is generated from flow-path biogeochemical processes (*e.g.,* nitrification*)* than from being washed-in into the channel during snowstorms. Furthermore, because both nitrate and chloride concentrations in these watersheds can be higher in groundwater than streamwater (Mayer et al. 2010; Kaushal et al. 2005), it is also possible that the in-situ positive relationships are due to nitrogen and chloride being derived from the same groundwater hotspot in the riparian zone near the sensors.

The mobilization of SRP from sediments in this study seems to contradict previous studies in soils showing that salinization reduces SRP concentrations (Jun et al. 2013; Compton and Church 2011; Duan and Kaushal 2015). The reduction of SRP upon salinization can be attributed to the reduced stability of colloidal humic iron-aluminum phosphate complexes with increasing ionic strength and decreasing pH (Bunn et al. 2002; Saiers et al. 2003), both of which can be caused by salinization (Green et al. 2008). Iron complexes in colloidal organic matter can bind phosphorus from the water column. The reduction of SRP with salinization could also be due to biotic perturbations, such as the temporary inhibition of microbial activity at higher salinity or the rapid uptake of any released phosphate (Srividya et al. 2009, Oren 2001).

Our results of increasing SRP with salinization are more consistent with investigations of stream, wetland, and marine sediments. Although Duan and Kaushal (2015) determined SRP release from stream sediments to decrease with salinization at five of the same sites in this study, they also reported that releases of SRP from sediments increased at two urban sites. They suggested that these SRP increases were coupled with the release of large amounts of labile DOC, which could result in redox conditions that are favorable for SRP release. However, in our study, there was no observable relationship between the responses of SRP and DOC. Furthermore, increased salinity has been associated with increases in streamwater phosphate concentrations and net watershed phosphorus export in a recent study (Merrikhpour and Jalali 2013). Experimental studies of wetland sediments indicated both releases of phosphate with salinization, attributed to enhanced anaerobic organic matter (and phosphorus) mineralization (Kim and Koretsky 2013), or the retention of phosphorus on sediments with salinization, attributed to the formation and precipitation of insoluble iron-phosphate complexes (Baldwin et al. 2006). In marine and estuarine sediments, phosphate was mobilized (*i.e.,* decreased sorption) linearly with increasing salinity, and the magnitude of release depended heavily upon the sediment's exchangeable phosphorus content (Zhang and Huang 2011; Clavero et al. 1990; Spiteri et al. 2008). These releases of phosphorus in coastal environments were attributed to a combination of desorption from iron and aluminum oxides with increasing salinity, increased aqueous complexation of phosphate with cations, and enhancements in anoxic microbial sulfate reduction (Spiteri et al. 2008). Changes in

SRP dynamics between sediments and streamwater with salinization are complex and warrant further evaluation, especially within the context of redox changes.

Relative to nitrogen or phosphorus, the effects of salinization on silica transformations are relatively less known and unstudied. There were no clear trends in silica concentrations between salinity treatments or sites in our experimental incubations. Previous geochemical studies have reported that sodium chloride causes a release of silicate from quartz particles (*e.g.,* Dove and Elston 1992), potentially indicating that silica could be released with salinization in quartz-rich soils and sediments. Some wetland sediments have also shown to release silicate upon experimental salinity intrusion (*e.g.,* Weston et al. 2006). However, our results suggest that silica is much more stable under enhanced salinity in stream sediments. This stability is consistent with the relatively conservative behavior of silica across salinity gradients in many estuarine environments. The response of silica to salinization may be of interest as silica can alleviate salinity stress and salt toxicity in a wide range of plants (*e.g.,* Romero-Aranda et al. 2006; Shi et al. 2013). Thus, a release of silica on a watershed scale in response to salinization could potentially limit the ecosystem impacts of episodic salinization. Nonetheless, the effect on silica warrants further study and investigation.

In-situ Patterns of Nitrate and Salinity During and Post-Snowstorm Events

The loading patterns of both nitrate and salinity during and after snowstorms are highly complex and warrant further investigation. Our exploration of high-frequency sensor data at Rock Creek and Difficult Run revealed a cyclical pattern at these sites between nitrate concentrations and specific conductance during and immediately after a winter snowstorm. Although this relationship could potentially be indicative of concurrent flushing of road salts (salinity) and nitrate or flowpath ion-exchange processes, the nitrate concentrations and specific conductance were not discharge-weighted, and therefore it is also possible that this relationship is driven by variable discharge (typical of urban streams) during the storm event.

Furthermore, the timeseries of specific conductance during the snowstorm week was consistently bell-shaped, similar in shape to a storm hydrograph, with a distinguishable baseline, a steep rising limb, and peak, and a shallow receding limb. The specific conductance peak was slightly out of phase with the peak in discharge, potentially indicating some lag time (or travel time) for the salinity (i.e. episodic pulse) to reach the stream channel. The timeseries of specific conductance was consistent across all the winter snowstorms assessed on record for the two high-frequency nitrate sites.

On the other hand, the timeseries for nitrate varied between the sites and the snowstorms. For some storms, the nitrate timeseries was the opposite of specific conductance as it decreased during the snowstorm event (potentially due to dilution), but quickly increased slightly above baseline in the hours to days following the event, before returning to baseline (i.e. pre-storm) concentrations. Other timeseries of nitrate increased with a steep rising limb to a peak (similar to discharge and specific conductance), but then sharply declined below baseline (i.e. pre-storm) concentrations for a few days before returning to baseline.

An example of this observed pattern is presented in figure 11 for the Rock Creek in-situ high-frequency sensor during a snowstorm from January 7th 2017 to January 21st 2017. During this snowstorm event, the nitrate timeseries is consistent with specific conductance. When nitrate from this storm (measured in 15 minute intervals) is plotted against specific conductance from this storm (also measured in 15 minute intervals), a cyclical clockwise pattern is revealed (Fig. 11). Nitrate initially increases sharply with specific conductance, then nitrate is constant at higher levels of specific conductance, before decreasing sharply at the highest levels of specific conductance. This could potentially suggest a source-limited system and all of the exchange-able nitrate has been leached out with the early increases in ionic strength (i.e. first pulse).

Although the cyclical pattern between nitrate and specific conductance during a snowstorm event is consistent across all of the events on record at both sites with nitrate sensors, the direction (i.e. clockwise or counter-clockwise) varies between storm and site. Previous studies have documented a clockwise hysteresis relationship of both nitrate concentrations with discharge during a rainfall storm events (Lloyd et al 2016), and average nitrogen concentrations with yearly runoff (Kaushal et al 2008).

Effects of Salinization on the Biogeochemistry and Fluxes of Carbon (DIC, DOC)

The response of carbon to episodic salinization varied largely across sites and across salinity treatment levels (Fig. 7). Our results agree with a recent sediment salinization study, which indicated that salinization can increase sediment releases of

DOC at some sites but not others potentially based on organic matter quality (Duan and Kaushal 2015). Although our study did not characterize the quality of DOC, Duan and Kaushal (2015) found that salinization consistently and considerably increased net releases of the protein-like fluorophore, but the effects of salinization on humic-like fluorophore releases were not consistent. This difference was attributed to variations in the effect of salinization on humic *versus* protein fractions of organic carbon. Increasing ionic strength caused by salinization can enhance the solubility of the proteinaceous materials *via* sodium dispersion processes (Green et al., 2008, 2009) or through nonspecific electrostatic interactions at low salinities (*e.g.,* a "salting-in" effect) (Tanford 1961; Chen et al. 1989).

Humic fractions of organic carbon, which are larger hydrophobic molecules that occur in the colloidal size range (*e.g.*, Aiken et al. 1985), can experience an array of effects when subjected to increasing ionic strength or salinization. For example, humic molecules can flocculate (*e.g.*, Sholkovitz 1976) or undergo sorption to mineral surfaces (Fox 1991; Hedges and Keil 1999), depending on the magnitude of the pH suppression caused by salinity (Kipton et al. 1992; Li et al. 2007, 2013). Because stream sediments are generally enriched in labile, proteinaceous materials that are derived from biofilms (algae and microbes), or wastewater organics in urban watersheds (*e.g.,* Daniel et al. 2002), it is reasonable that salinization has potential to mobilize a significant amount of DOC from some stream sediments.

Amrhein et. al. (1992) also argued that decreases in pH and increases in ionic strength of the streamwater, induced by salinization, could pull DOC-metal colloid complexes from the benthic surface into the water column where they could remain suspended due to their interaction with the other charged particles or due the hydrology. Steele and Aitkenhead-Petersen (2012) suggest that the solubility of DOC and other nutrients substantially increases with increased salinity (sodium absorption ratio) in urban soils throughout the state of Texas, USA. However, Compton and Church (2011) conducted short and long-term soil incubations with low salinity treatment levels and concluded that increasing salinity removes DOC from solution *via* flocculation and sorption to mineral surfaces, and thus prevents its leaching to streams. As a result of variations in organic matter content and sorption capacity across sites, the effect of salinization on DOC releases varies but tends to be driven by a combination of the array of mechanisms mentioned above (Amrhein et al. 1992; Evans et al. 1998; Green et al. 2008, 2009; Compton and Church 2011; Ondrašek et al. 2012).

Relative to prior sediment salinization experiments, our study examined the effects of salinization across wider ranges; 0, 0.5, 1.0, 2.5, 5.0, and 10.0 g/L sodium chloride (*i.e.,* 0 to 6 g/L chloride). Some studies suggest that there may be a specific threshold salinity level between which salts stabilize colloids (low salinity) or mobilize colloids (high salinity) (Norrstrom and Bergstedt 2001; Green et el. 2008; Kim and Korestsky 2013). We found that the effects of salinization on DOC release from sediment are more complicated across larger salinization ranges. For example, at 5 of our 12 sites (suburban and urban: GFGL, GFGB, GFVN, NERP, CC), salinization consistently increased net releases of DOC from sediment (Table 4). These sites were all suburban and urban sites. Here, we can still invoke the same conceptual model and biogeochemical mechanisms proposed by Duan and Kaushal (2015) to interpret the positive salinization effect on DOC release. That is, organic matter at these suburban and urban sites was probably more labile (containing more protein-like components) and salinization consistently and considerably increased net releases of the protein-like fluorophore (Duan and Kaushal 2015). At other sites, the effect of salinization on DOC varied within these salinity ranges, probably reflecting combined effects that we have discussed above on humic substances or total DOC. For example, at a few sites (DRKR, GRGF, BARN), we found that salinization increased DOC concentrations at the lower salinity treatments, but then decreased concentrations at the higher salinity treatments (Fig. 7 and Supporting Fig. S2) Sediments from all 12 sites had an estimated organic matter content of less than 1% at the time of sample collection (Table 2), however, the extent of prior salt exposure of the sediment at each site could also impact the response of DOC (Green et al. 2009).

For DIC, the response to episodic salinization also varied largely across sites. The effects of episodic salinization on DIC releases from sediments to streamwater may involve changes in the dissolution of carbonate minerals, or changes in the organic carbon mineralization process and subsequent carbon dioxide efflux, which may be coupled with DOC biogeochemistry. On one hand, the solubility of carbonate minerals increases with salinization (Akin and Lagerwerff 1965). On the other hand, the solubility coefficient for carbon dioxide decreases with salinity (Weiss et al. 1974; Duan and Sun 2003). Duan and Kaushal (2015) observed that salinization increased DIC releases from sediment at lower salinity levels due to the dominance of the former effect, but decreased DIC releases at higher salinity levels due to the dominance of the latter effect. Duan and Kaushal (2015) reported sites showing a consistent positive response of DIC to salinization (increasing DIC concentration) or a consistent negative response (decreasing DIC concentration). Although our study had a wider range of salinity treatments, our results are consistent with Duan and Kaushal (2015) and their conceptual model as DIC concentrations increased in 4 of the 12 incubation sites and decreased in 2 sites (Table 4). Moreover, elevated salinity for long periods may suppress microbial transformations of carbon in the sediment and pore-water, which could alter in-stream DIC concentrations (Oren 2001). Similar to DOC, our study showed that the effect of salinization on DIC dynamics is more complicated, if we extend salinity to a wider and more realistic range of salinization for urban sites.

Effects of Salinization on the Biogeochemistry and Fluxes of Trace Metals (Mn, Zn, Sr, Cu)

Several synthesis publications have associated freshwater salinity changes with increases in inorganic pollutants such as arsenic and lead (Norrstrom 2005, Palmer et al. 2010), and several studies have empirically linked elevated salinity in freshwater with elevated concentrations of trace metals at specific river sites throughout the world (Novotny et al. 2008, Mason et al. 1999). However, because these studies do not postulate a geochemical, biological, or hydrological mechanism, the empirical linkage is uncharacterized. Trace metals could be generated from in-channel processes or they could simply be transported alongside the salts during a storm from the watershed into the river. Few studies have attempted to identify and test mechanisms that could explain the relationship between salinity and trace metals in rivers, and the factors that control such a relationship.

In the soil literature, column leaching experiments with solutions of NaCl (to simulate salty water runoff from pavements) have demonstrated increases in dissolved Cr, Pb, Ni, Fe, Cd, and Cu with increased salinity (Amrhein et al. 1993). In lab experiments, urban soils (e.g. infiltration pond soils) responded with increases of several order of magnitude above background of mobile Pb, Cu, As, and Hg when treated with NaCl and MgCl2 (Nelson et al. 2009; Sun et al. 2015). Although divalent cations (e.g. Ca) can induce a stronger mobilization effect than monovalent cations (e.g. Na), mobilization in urban soils depends more so on redox conditions, DOC content, and source minerals than on the composition of salinity (Sun et al. 2015).

Although less characterized, in-situ monitoring of roadside soils have also demonstrated a positive linkage between salinity and trace metals content. A study in Sweden observed increases in conductivity and dissolved Na and Ca, and decreases in pH and DOC concentrations following road salting events. These salinity enhancements were significantly aligned with increases in Cd, Zn, Cu, and Pb (Backstrom et al. 2004). Another study noted consistent exponential decreases in heavy metals; Pb, Cd, Cu, Zn, Ni, and Cr in a 10m band from the road. The decrease in trace metal concentrations was well associated with a decrease in Na, and the study concluded road salting induced soil leaching to be the contributing factor (Zehetner et al. 2009). An additional study indicated downward (i.e. vertically towards groundwater, along flowpath) increases of Cd, Pb, Cu, Zinc, and PAHs – up to 34 times higher than the average trace metal concentration in the surrounding soil (Norrstrom 1998). Novotny et al. (1998), also consistently observed lead concentrations exceeding the drinking water quality limit in the groundwater directly beneath (4.5 m) a runoff infiltration pond, with lead concentration being strongly correlated with sodium concentrations (Norrstrom and Jacks 1998).

According to the literature, organic matter ligand formation and dispersal, DOC complexation, and proton ion exchange can affect trace metals mobility (Norrstrom 2005). Through ion exchange processes, river salinity inputs could lead to decreased pH of water, and alter the ionic strength of the water (e.g. mobile anion affect). This in turn, could potentially alter DOC sorption, coagulation, and colloid dispersal (Norrstrom and Bergstedt 2001). The pH and ionic strength of the water could leach DOC-metal colloid complexes from the benthic surface into the water column, mobilizing chloride-Cu, chloride-Fe, chloride-Pb, or chloride-Cd into the water column (Amrhein et al. 1993). With respect to their movement, Pb and Zn have been shown to be linked with the oxide and carbonate fractions of water, while Cu was coupled with the organic fractions (Norrstrom and Jacks 1998). Furthermore, CMA (a common road salt additive) decomposition increases the concentration of Pb and Zn carbonates. Interestingly, during periods of episodic salinization, supersaturation of calcite (from CMA) may occur, removing dissolved metals as co-precipitates with calcite. The behavior of CMA is heavily linked with redox conditions of soils (Amrhein et al. 1994).

The Role of Climate and Biology in Driving Long-term and Episodic Salinization

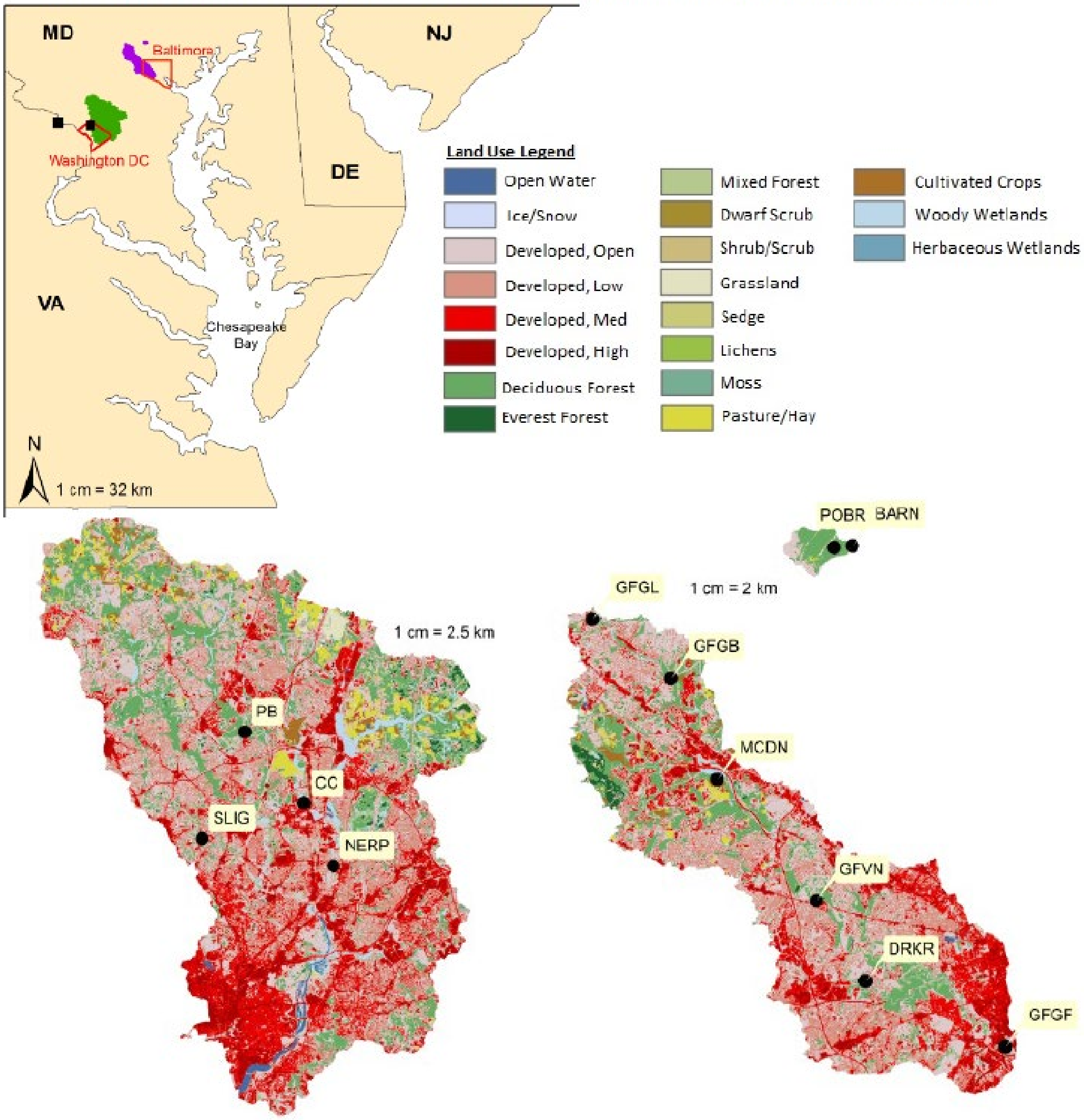
Changes in the chemistry of freshwater waterbodies are largely governed by biology and climate. In specific, the long-term salinization of freshwater, especially lentic waters, can be coupled with shell-forming organisms and evaporation dynamics as they drive changes in the freshwater carbonate buffer system (Charles and Smol, 1994). Evaporation dynamics can initiative concentration-dilution, hydrolysis, and precipitation reactions and can cause a significant loss or accumulation of carbon (Kilham 1990). Biology can initiate redox reactions, and complex and unfavorable metabolic-dependent transformations which controls the saturation index of calcium carbonate (Prescott et al 2014). In addition, the stratigraphic remains of aquatic biota serve as an record of past dissolved chemical conditions of water and are often used to create historical and paleo reconstructions (Charles and Smol, 1994). Although bedrock is an important source of elements and alkalinity to freshwater, the lithographic regulation is relatively constant over long time periods (i.e. bedrock changes over geologic time intervals). However, recent studies have indicated that anthropogenic material inputs can induce changes in lentic water similar to ones expected from change in lithology, such as increased salinity and alkalinity (e.g. Dugan et al 2017).

Mussels, as an example of organisms that can potentially drive changes of freshwater salinization, are hyper-sensitive to changes in salinity, pH, and temperature. Over the past decades there has been a freshwater mussel decline (with reported species loss of up to 40%) in the US and Canada (Gillis 2011). Mussels are relatively immobile filter feeders, and as such, they are subjected to a higher salinity concentration than other lentic organisms as chloride contributes to densimetric stratification of receiving waters which results in a layer of high-chloride concentrations just above the sediment-water interface (Gillis 2011), and subsequent depletions of mussel populations. Mussels are calcium-carbonate shell-forming organisms, and a decline in their population could lead to an accumulation of dissolved calcium in lentic waters (Prescott et al 2014), and subsequently long-term increases in calcium concentrations (Chapra et al 2012). Such long-term increases in calcium would be out-of-phase with increases in other base cations, and could be evidenced by tracking calcium-to-magnesium ratios. Changes in salinity from evaporation would affect all base cations consistently and could also be evidenced by tracking ratio of concentration of base cations. Previous studies have hypothesized invasive mussel species in the Great Lakes region could survive high-salinity conditions, outcompeting native species for resources, and driving long-term decreases in calcium concentrations (Chapra et al 2012). Interestingly, water hardness has an ameliorating effect on mussel chloride toxicity as the EC50 is almost directly proportional to water hardness for a certain range (Gillis 2011). Furthermore, most chloride inputs to lentic waters of colder and temperate regions occur in the winter (due to road salt application), while mussels are most active in the water column during the summer (Gillis 2011), and so the exact interaction between mussels, salinity, and base cation chemistry is complex.

Unlike lentic waterbodies, changes in the salinity of lotic waters (e.g. rivers) are less driven by evaporation and are more influenced by watershed chemical inputs, carbonate equilibrium, and watershed microbial chemical transformations via flowpath, riparian, hyporheic, or transient-hydrodynamic processes. These microbial transformations are sensitive to altered channel and watershed hydrology, and as described in previous sections, could be impacted by changes in ionic strength or pH induced by the increased salinization of lotic waters. Nonetheless, long-term increases in salinization of lotic waters are likely due to increases in the salt inputs (e.g. Kaushal et al 2018). Likewise, episodic salinization could is likely due to a combination of post-storm road salt inputs and flashy and altered hydrology (e.g. Haq et al 2018). Interestingly, climate could exacerbate episodic salinization, as for example, increased snowfall, and decreased land surface temperature (i.e. increased pavement ice formation) could lead to the increased use of road salts and thereby, an increased magnitude of episodic salinization on a seasonal basis.

Figures

Figure 1: Maps of the study area, with different spatial scales for each map. The high-frequency nitrate sensors are denoted as black squares in the Chesapeake Bay map (Rock Creek sensor is in Washington DC; Difficult Run sensor is in VA). Land use maps for Gwynns Falls and Baisman Run (Baltimore) watersheds and Anacostia (Washington DC) watershed are based on the National Land Cover Database 2011 (Homer et al. 2015). Figure from Haq et al. 2018.



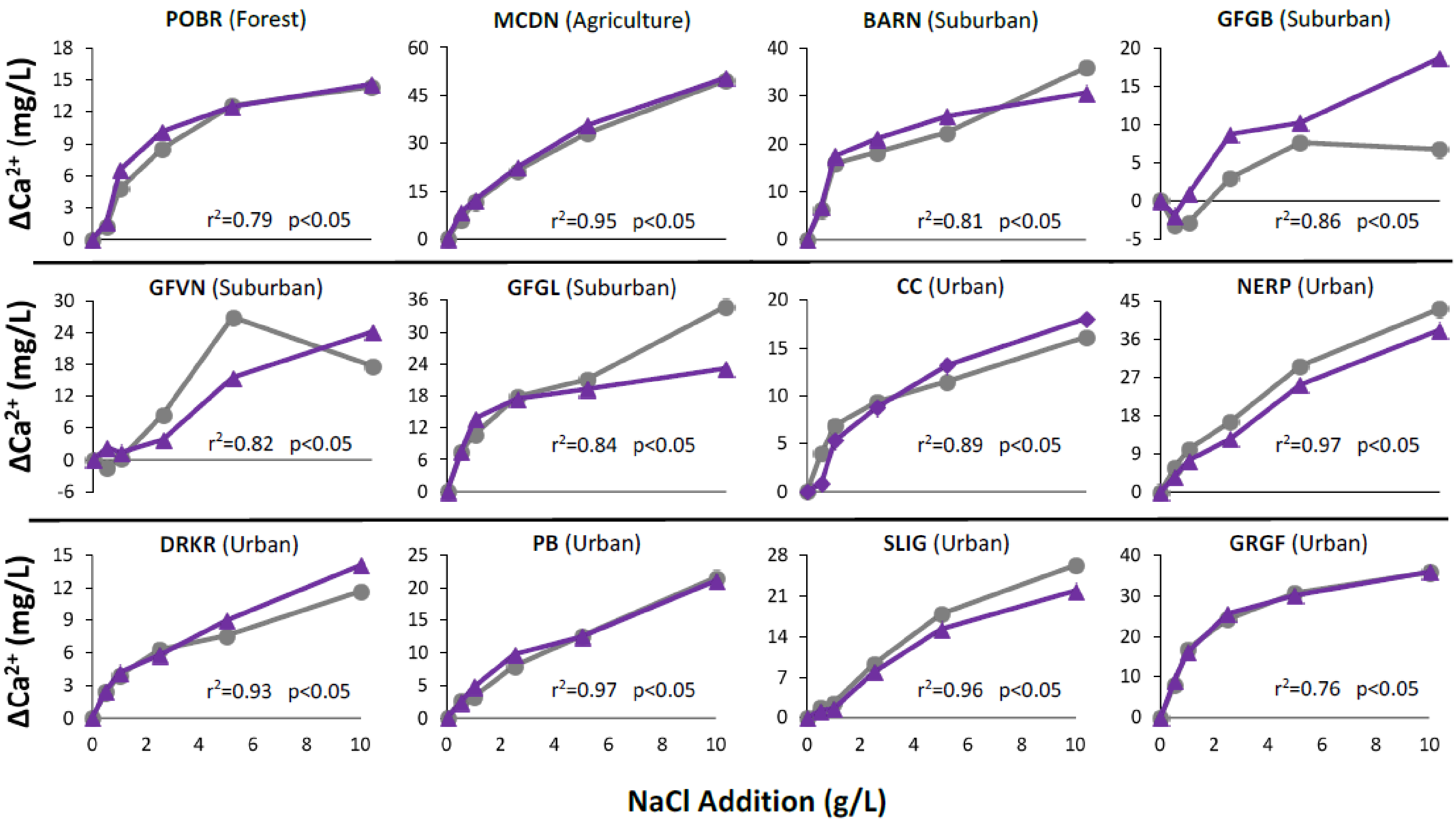


Figure 2: Responses of dissolved calcium to experimental salinization (relative to an untreated control incubation). We observed significant linear mobilization of calcium at all 12 sites. The results from trial 1 are displayed as gray lines with circular data points, while the results from trial 2 are displayed as purple lines with triangular data points. The sites are ordered by watershed impervious surface coverage from top left to bottom right, and the average of both trails was used to obtain the r2 and p-values. Figure from Haq et al. 2018.

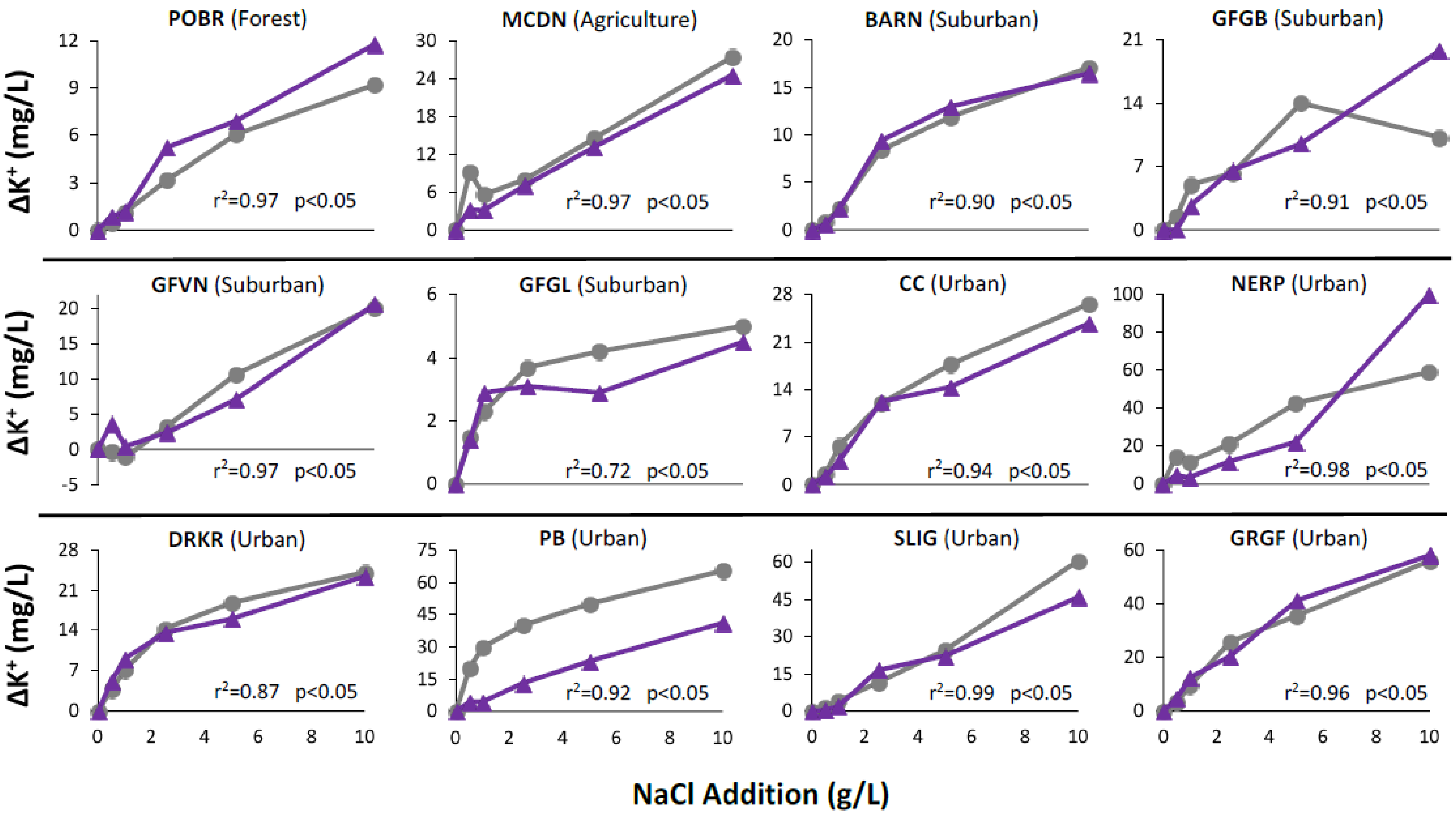


Figure 3: Responses of dissolved potassium to experimental salinization (relative to an untreated control incubation). We observed significant linear mobilization of potassium at all 12 sites. The results from trial 1 are displayed as gray lines with circular data points, while the results from trial 2 are displayed as purple lines with triangular data points. The sites are ordered by watershed impervious surface coverage from top left to bottom right, and the average of both trails was used to obtain the r2 and p-values. Figure from Haq et al. 2018.

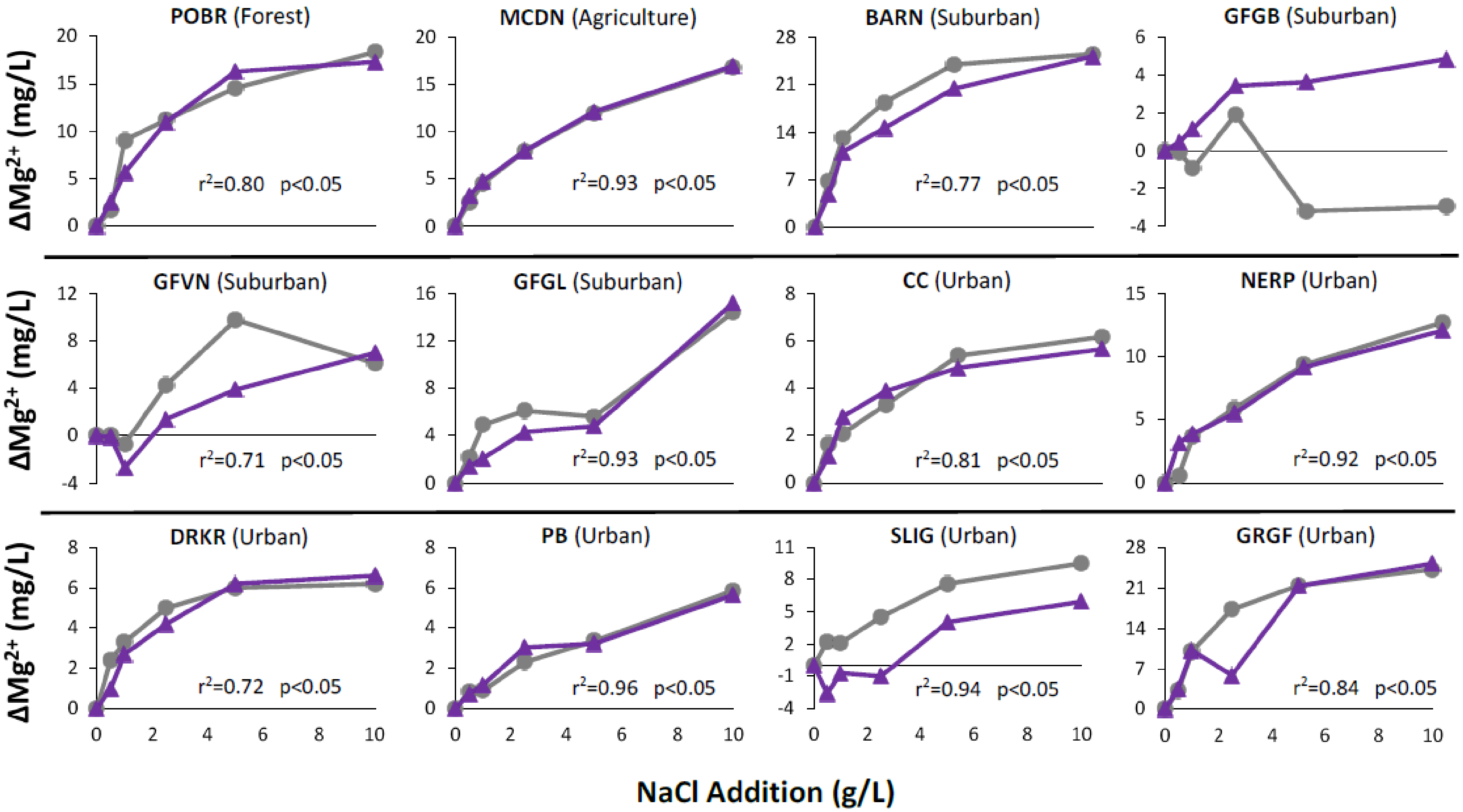


Figure 4: Responses of dissolved magnesium to experimental salinization (relative to an untreated control incubation). We observed significant linear mobilization of magnesium at 11 of the 12 sites. The results from trial 1 are displayed as gray lines with circular data points, while the results from trial 2 are displayed as purple lines with triangular data points. The sites are ordered by watershed impervious surface coverage from top left to bottom right, and the average of both trails was used to obtain the r2 and p-values. Figure from Haq et al. 2018.

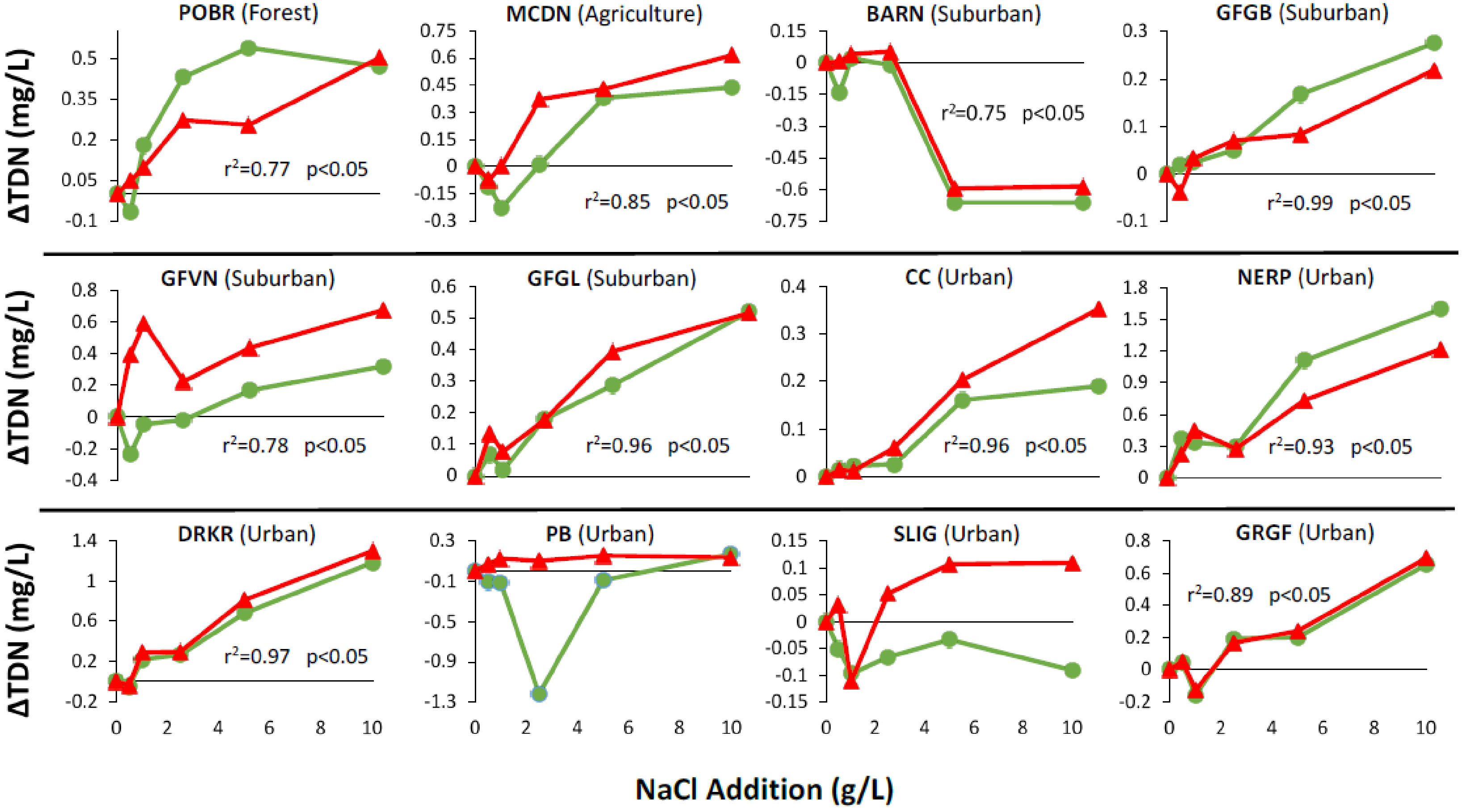


Figure 5: Responses of dissolved nitrogen to experimental salinization for (relative to an untreated control incubation. We observed significant linear mobilization of TDN at 9 of the 12 sites. The results from trial 1 are displayed as green lines with circular data points, while the results from trial 2 are displayed as red lines with triangular data points. The sites are ordered by watershed impervious surface coverage from top left to bottom right, and the average of both trails was used to obtain the r2 and p-values. Figure from Haq et al. 2018.

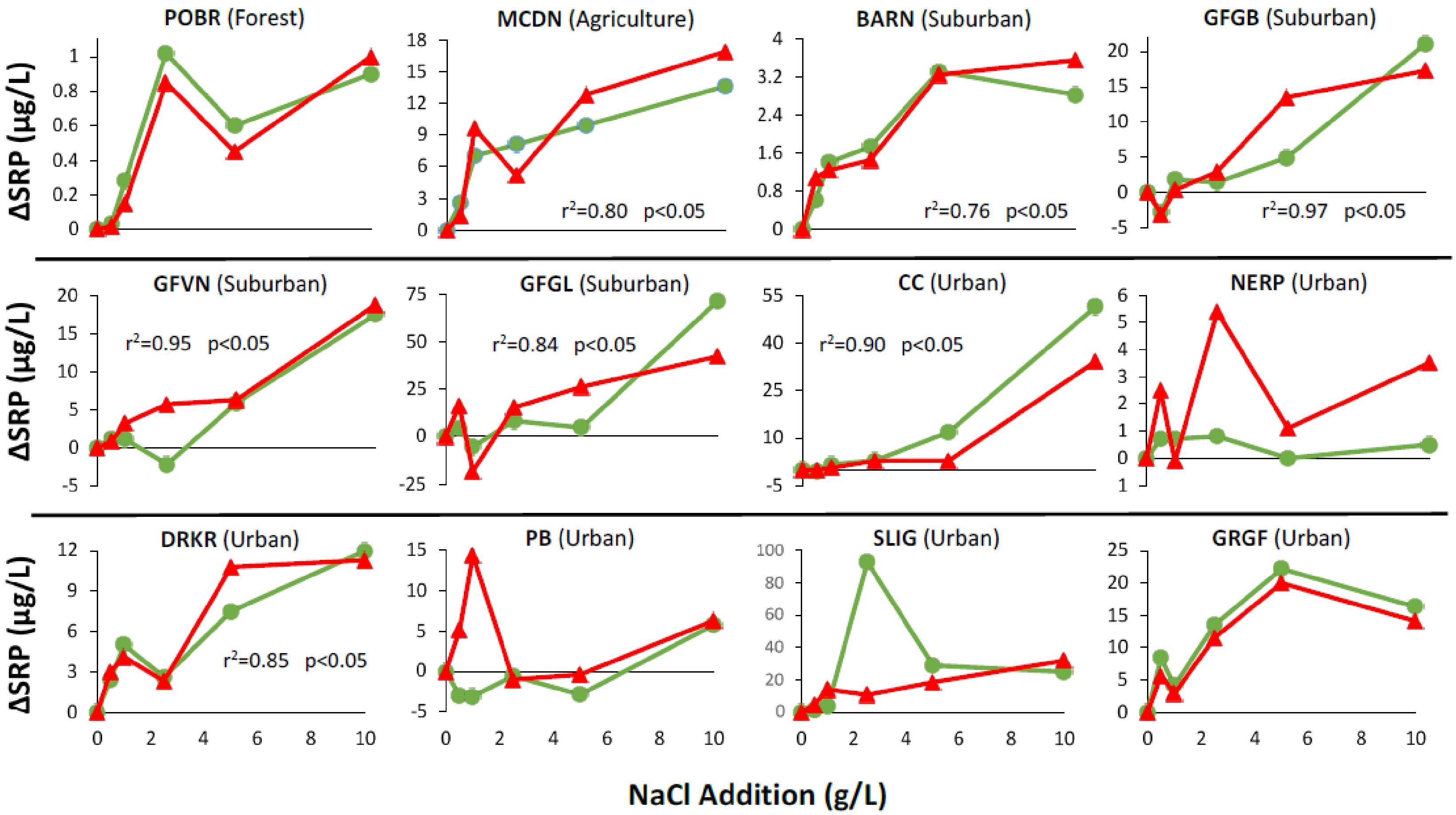


Figure 6: Responses of dissolved phosphorus to experimental salinization for (relative to an untreated control incubation). We observed significant linear mobilization of SRP at 7 of the 12 sites. The results from trial 1 are displayed as green lines with circular data points, while the results from trial 2 are displayed as red lines with triangular data points. The sites are ordered by watershed impervious surface coverage from top left to bottom right, and the average of both trails was used to obtain the r2 and p-values. Figure from Haq et al. 2018.

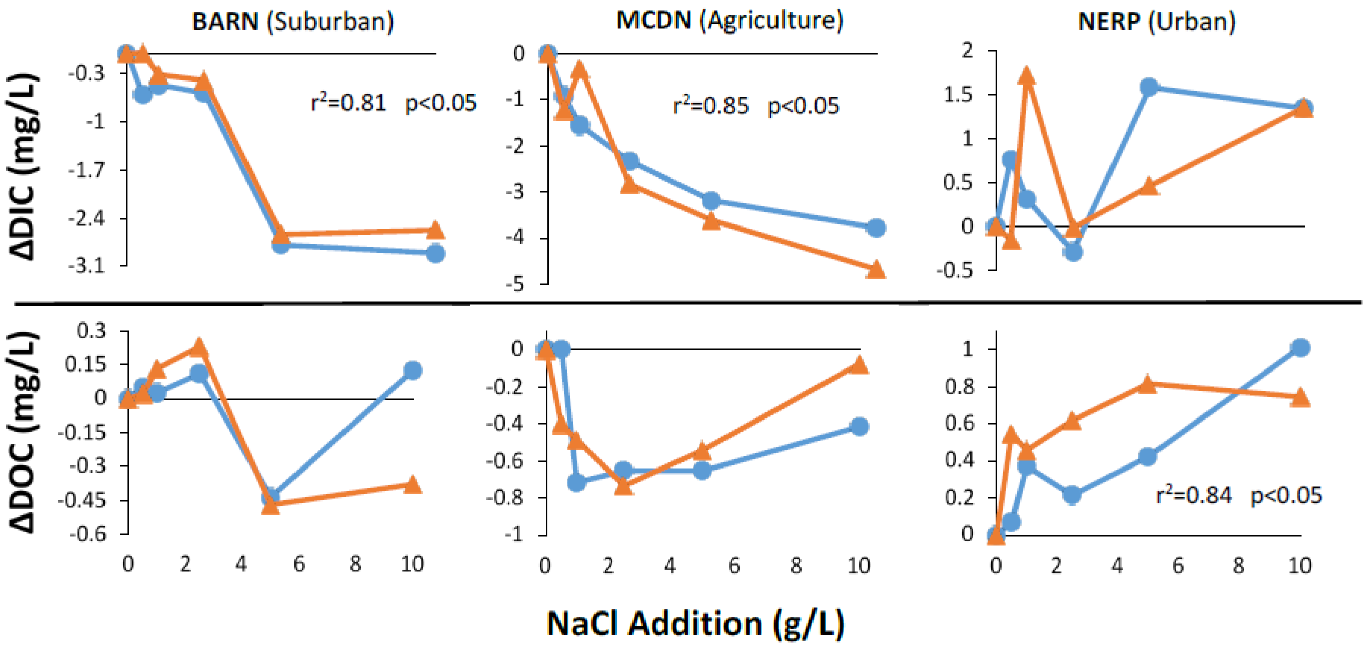


Figure 7: Responses of DIC and DOC to experimental salinization for 3 of the 12 sites. The effects of salinization on carbon was variable, and this subset of sites was selected to demonstrate the variability. For each treatment level, a positive value indicates carbon was released from the sediment into the water column relative to an untreated control incubation, while a negative value indicates carbon was removed from the water column. The results from trial 1 are displayed as blue lines with circular data points, while the results from trial 2 are displayed as orange lines with triangular data points, and the average of both trails was used to obtain the r2 and p-values. Figure from Haq et al. 2018.

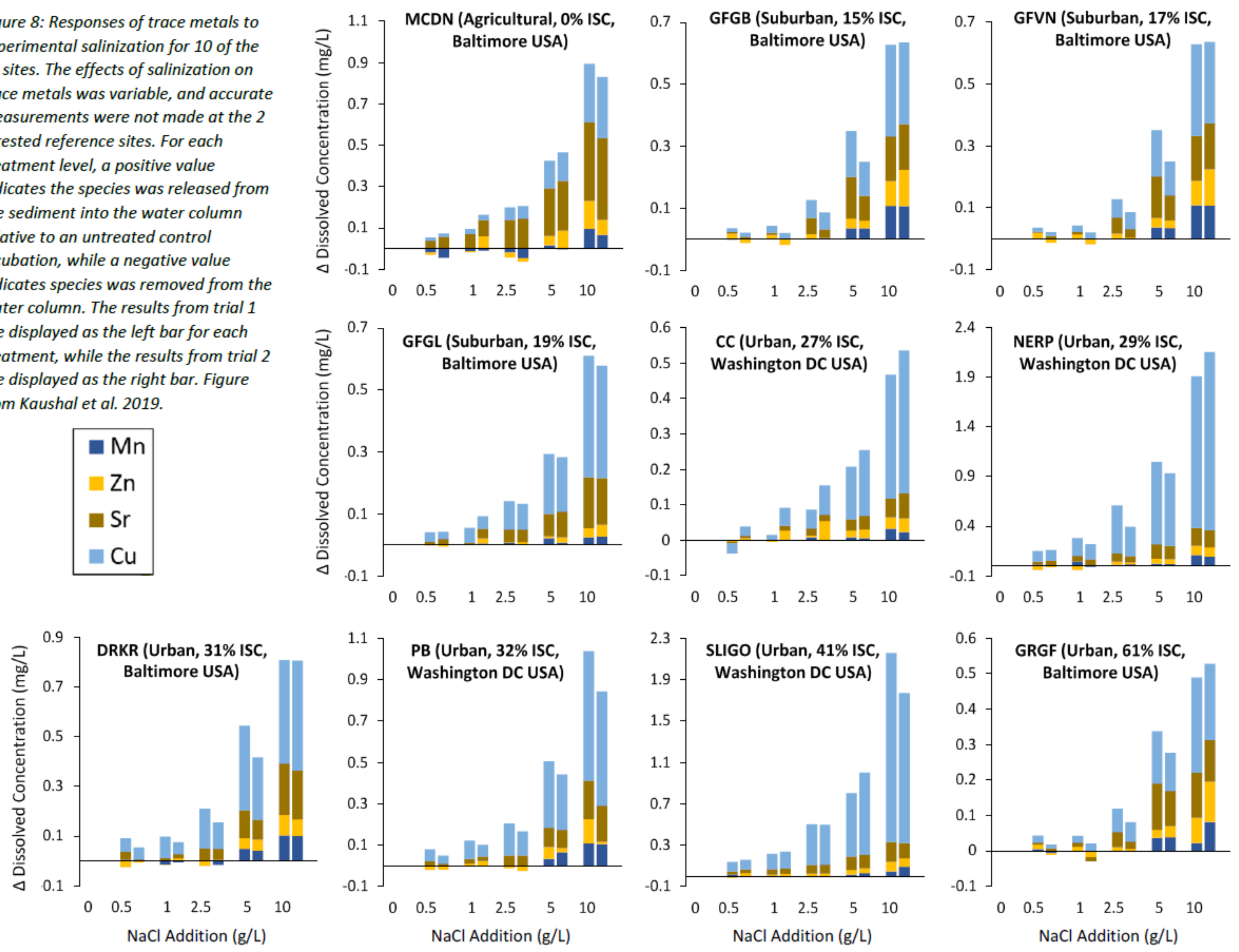


Figure 8: Responses of trace metals to experimental salinization for 10 of the 12 sites. The effects of salinization on trace metals was variable, and accurate measurements were not made at the 2 forested reference sites. For each treatment level, a positive value indicates the species was released from the sediment into the water column relative to an untreated control incubation, while a negative value indicates species was removed from the water column. The results from trial 1 are displayed as the left bar for each treatment, while the results from trial 2 are displayed as the right bar. Figure from Kaushal et al. 2019.

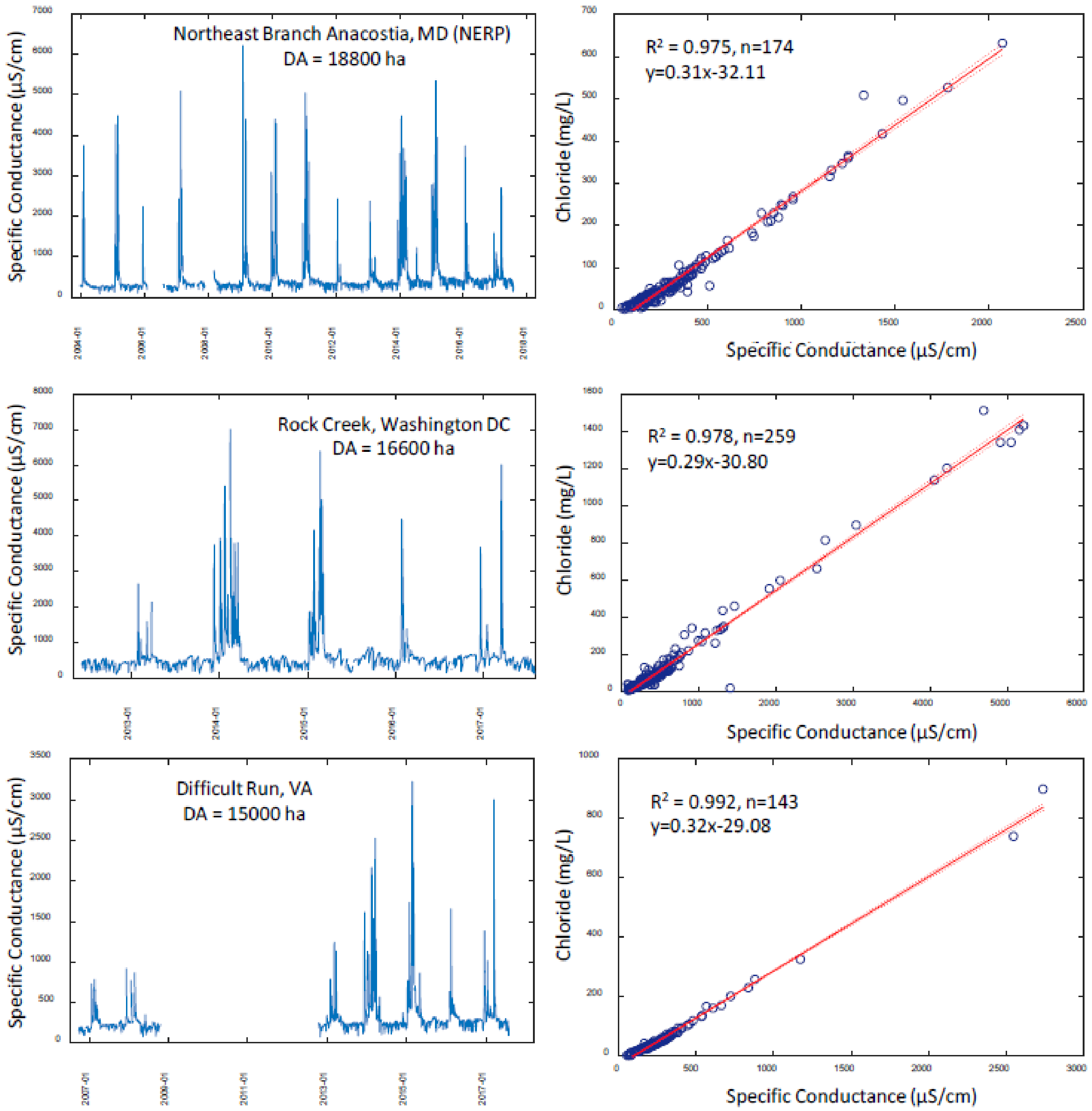


Figure 9: (Left panel) Timeseries of daily average values of specific conductance. Episodic salinization manifests in the high-frequency sensor record as a pulse in specific conductance in the hours to days following a snowstorm. Experiments were conducted to determine potential effects of the salinization pulse on sediment biogeochemistry. (Right panel) Relationship between dissolved chloride from grab samples and the nearest instantaneous specific conductance measurement. There was a strong, positive, linear relationship between specific conductance and chloride concentrations. Dotted red line is the 95% confidence bounds for the regression. NERP is also an incubation experiment site. Difficult Run and Rock Creek are nearby to the incubation experiment sites, and the in-situ relationships between salinity and nitrate were assessed at these sites. Figure from Haq et al. 2018.

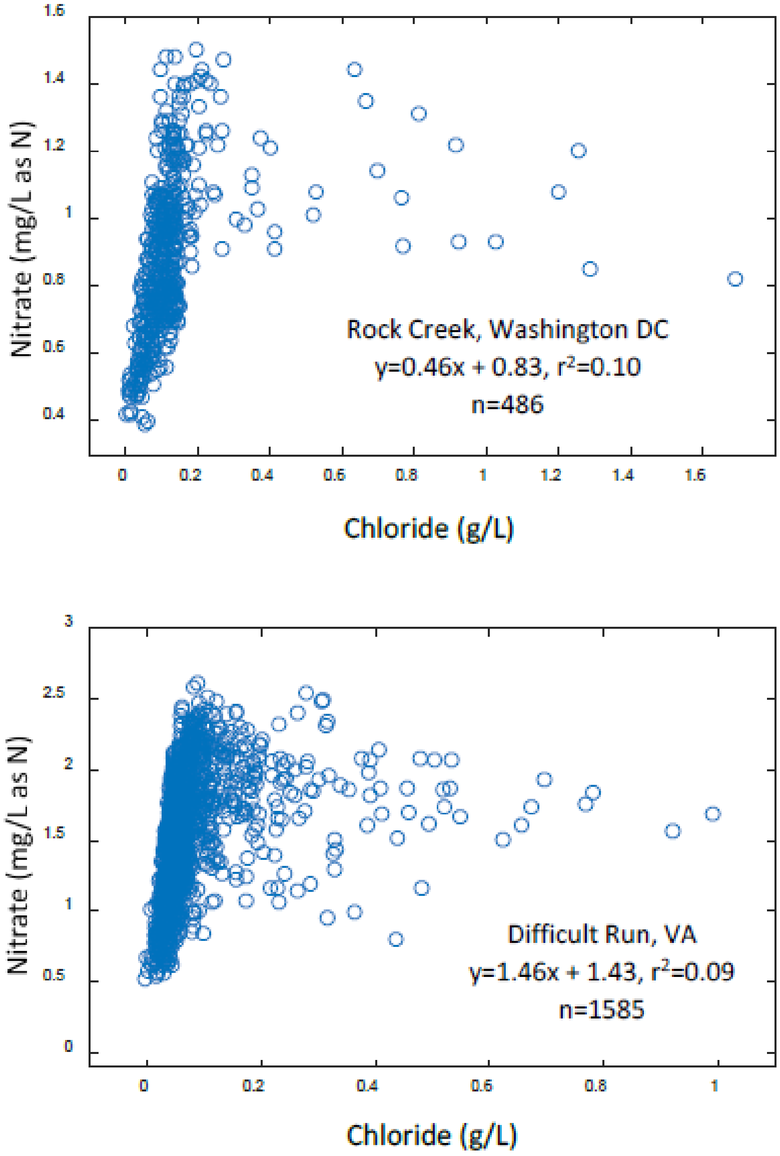


Figure 10: Linear relationships between chloride (as estimated from daily average values of specific conductance) and nitrate in the high-frequency sensor record. The slope from the Rock Creek sensor (top panel) is within the same order of magnitude as the mean slope from the experiments, while the slope from the Difficult Run sensor (bottom panel) is an order of magnitude larger (contrasted in units of mg N per g Cl). The NERP sensor lacks nitrate measuring capabilities. Figure from Haq et al. 2018.

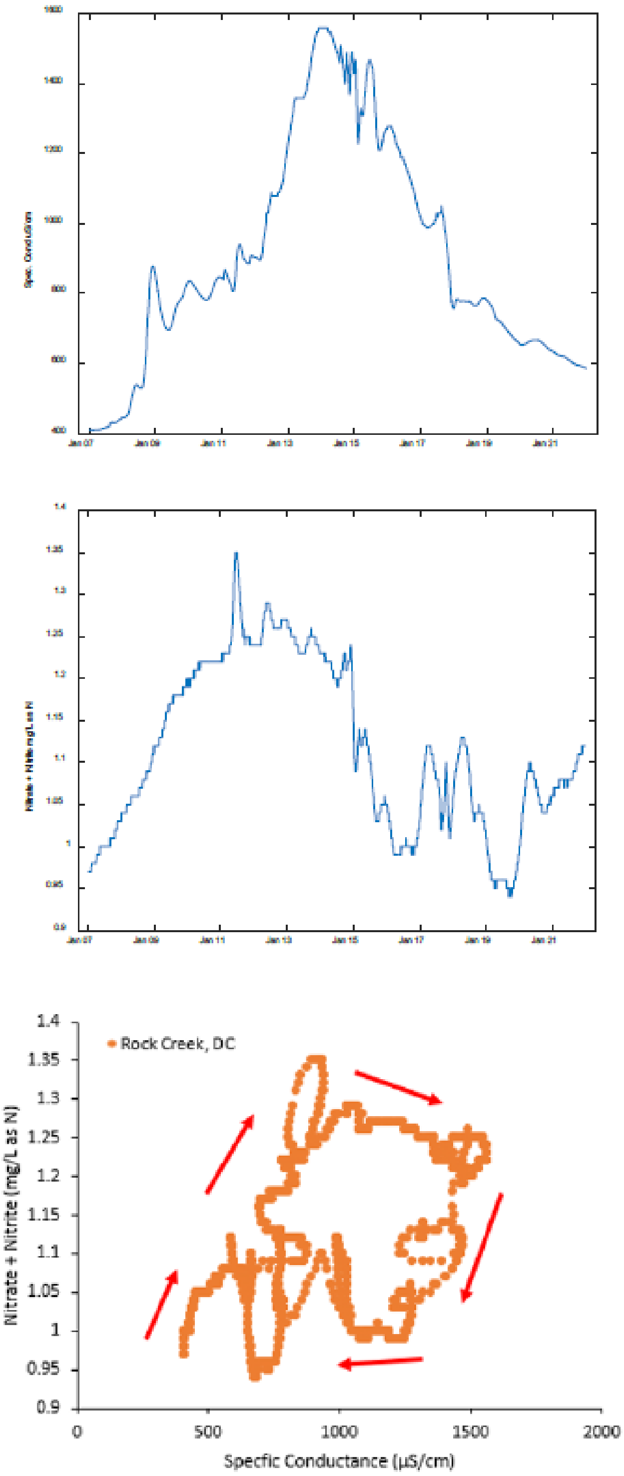


Figure 11: Example of specific conductance and nitrate concentration timeseries patterns during a snowstorm event in January 2017 at the Rock Creek high-frequency sensor site, and the corresponding hysteresis relationship. The in-storm concentration patterns of specific conductance and nitrate, along with their relationship, varied between each site and each snowstorm event on record. Bottom panel appears from Kaushal et al. 2019.

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