

Evaluating impacts of freshwater salinization syndrome on mobilization of nutrients and metals from stormwater best management practices

A Report Submitted to the Chesapeake Bay Trust

by

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Introduction and Key Restoration Questions

Salinization is increasingly affecting many watersheds, significantly impacting drinking water resources and infrastructure, reducing stability and resilience of aquatic ecosystems, and potentially hindering stream and river restoration efforts (Kaushal *et al* 2005, 2018, 2021). Salinization is related to deicer use on roadways with additional contributions from accelerated weathering of impervious surfaces, water softeners, and sewage inputs. The concentrations of chloride observed in many urban streams in Maryland now exceed the limit of 250 mg/L established by the U.S. EPA for chronic toxicity to freshwater life. These observed ranges and extreme fluctuations in salinity can mobilize nitrogen, phosphorus, base cations, and toxic metals from sediments to streams due to enhanced ion exchange and solubility (*e.g.*, Duan and Kaushal 2015, Haq *et al.* 2018, Kaushal *et al.* 2019).

In spite of many years of research on rising chloride concentrations in Maryland and elsewhere, extensive laboratory and field data to evaluate the water quality impacts of salinization are still missing, especially within the context of stormwater management BMPs and stream-riparian restoration projects. This mismatch between extensive research on effects of freshwater salinization on water quality, the effects of different ions in deicers, and potentially different effects across BMPs and stream restoration is necessary to guide management. Our work analyzing the effects of different salt ions on contaminant retention and release in urban streams and stormwater BMPs can help inform salt reduction levels below critical threshold levels for mobilizing nutrients and metals (established from our experiments and monitoring). Here, we present results that can also allow agencies involved in watershed and stream restoration to better account for the effects of different road salts on mobilization of other nutrient and metal ions and secondary water quality impacts of freshwater salinization. More detailed information is presented in (Kaushal *et al* 2022a, Kaushal *et al* 2022b, Galella *et al* In Preparation) and will also be presented at the Chesapeake Bay Trust Restoration Research Symposium.

Our project addressed the following 2 questions:

- 1) What are critical thresholds in concentrations of different road salt ions (Na^+ , Ca^{2+} , and Mg^{2+}) which can mobilize nutrients and metals to surface waters across varying stormwater BMPs?
- 2) What are the concentrations of different road salt ions and associated metals and nutrients in nearby stream outfalls before, during, and after deicing events?

Our overall objectives of this study were to: (1) assess the effects of freshwater salinization from different forms of salt deicers on mobilization of nutrients and metals in various stormwater management best management practices (BMPs); and (2) characterize changes in concentrations of salts, nutrients, and metals in tributaries of the Anacostia River near the University of Maryland campus in response to deicing events linking lab experiments and field observations.

Results of this study provide comparison of environmental impacts of different road salt ions known as Freshwater Salinization Syndrome (FSS) on retention and mobilization of salts, nutrients, and metals in urban stormwater BMPs (Kaushal *et al* 2019). Our results also monitored changes in concentrations of salts, nutrients, and metals in nearby urban stream outfalls during winter deicing events. This information can inform growing regional interest in developing monitoring programs and strategies for managing different levels and forms of salt

pollution. Results can also provide environmental managers with guidance on the potential retention of salts across stormwater BMPs and threshold salt concentrations and types of salt deicers, which have the most impacts on urban water quality. We also investigated the potential to which BMPs retain salt ions and risks for contaminant exchange and release. Finally, we investigated the potential for urban streams to recover from Freshwater Salinization Syndrome's impacts on water quality by comparing concentrations of salt ions and metals in years with minimal road salt application vs. years with typical or high applications of road salts.

Methods

Overall Study Design

Briefly, we collected data involving both field monitoring and salinization experiments from watersheds in the Anacostia watershed; these sites have been intensively studied through our long-term monitoring and also allow comparisons pre and post stream restoration. Data from these sites consists of: (1) routine monitoring data from urban streams over annual time scales and during and after winter road salt events, (2) synoptic surveys of longitudinal changes in concentrations and fluxes of chemicals along urban streams and stormwater BMP flowpaths and (3) experimental salinization studies manipulating levels and types of salt ions in incubations with sediments from urban streams and stormwater BMPs. All study sites are in urban watersheds where road salt is applied. All watersheds have been the subject of previous studies spanning multiple years (*e.g.*, Kaushal *et al* 2019). Monitoring for this study spanned over hourly, daily, weekly, and bi-weekly and annual time scales at our long-term study sites. Salinization experiments to quantify mobilization of contaminants from sediments to stream water were conducted similarly to our previous work (Duan and Kaushal 2015, Haq *et al* 2018a, Kaushal *et al* 2019). Further details on methods of chemical analysis can be found in our previous studies (Mayer *et al* 2010, Newcomer *et al* 2012, Cooper *et al* 2014, Pennino *et al* 2016, Haq *et al* 2018, Kaushal *et al* 2019, Galella *et al* 2021), and descriptions of methods are also provided below. More detailed results will also be available in publications from this work (Kaushal *et al* 2022a, Kaushal *et al* 2022b, Galella *et al* In Preparation) and also be presented at the Chesapeake Bay Trust Restoration Research Symposium.

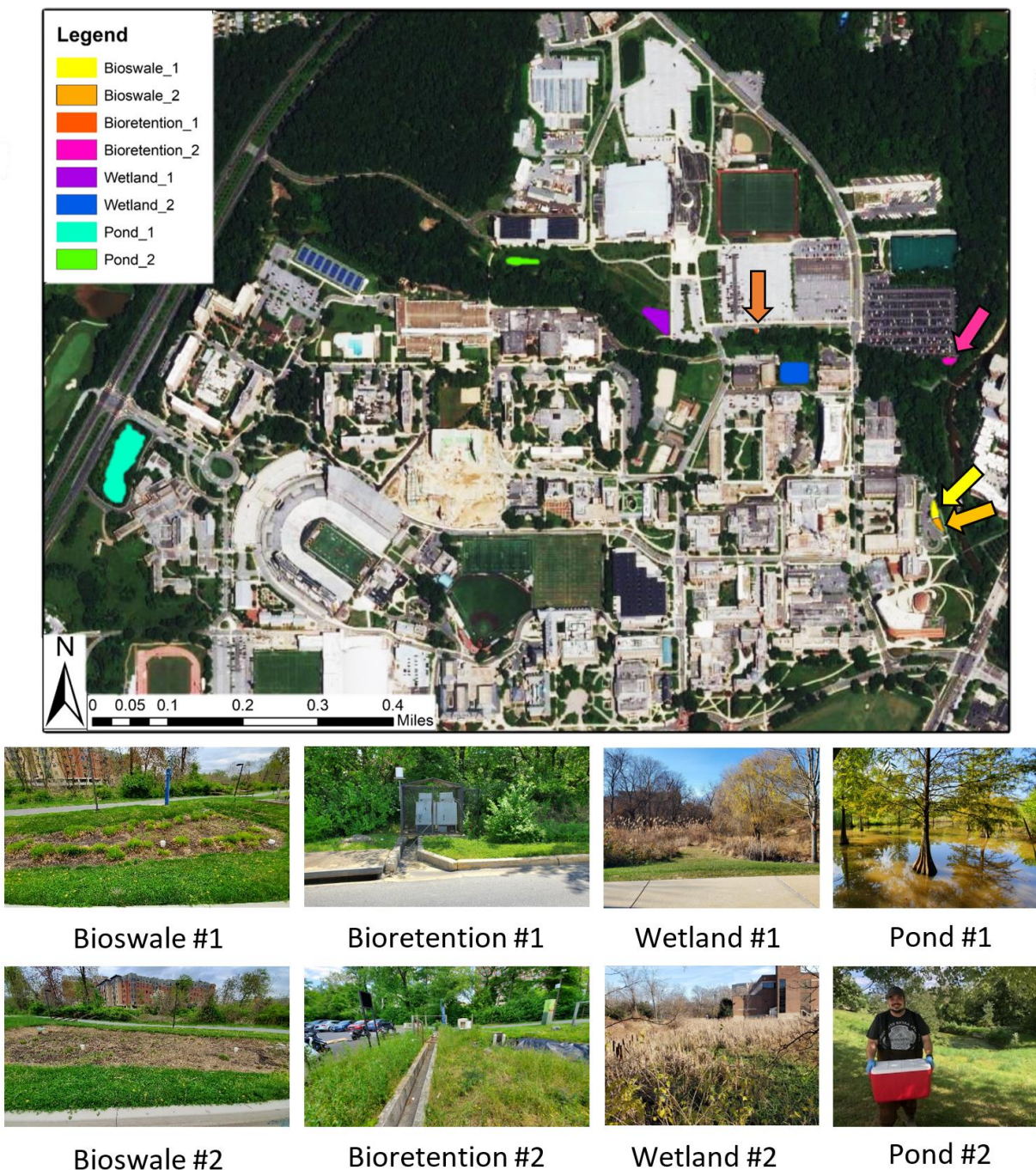


Figure 1. A map of the stormwater management BMPs sampled for this study within the University of Maryland College Park campus. Replicate Bioswale, Bioretention, Wetland and Pond sites were sampled (Galella *et al* In Prep).

Site Descriptions for Stormwater Management BMPs:

All stormwater management BMPs were located on the campus of the University of Maryland College Park, which is within the Anacostia River watershed. This location was chosen due to the wide variety of stormwater management features available as well as the availability of duplicate features. A total of 8 stormwater BMPs were studied: replicate bioswale (Bioswale #1 and #2), bioretention (Bioretention #1 and #2), wetland (Wetland #1 and #2), and pond (Pond #1 and #2) sites shared similar site characteristics among replicates. Half of the sites (*i.e.*, Bioswales #1 and #2, and Bioretention #1 and #2) had no freestanding water, so water for experimental salinization studies were procured from nearby Paint Branch stream and Campus Creek respectively (Further details on site selection are in Galella *et al* In Prep).

Bioswale #1 and #2 were constructed in 2017 to help manage runoff from a building on the UMD campus as well as an approximately 2,500 square meter parking lot adjacent to the stormwater management features. A total of three Bioswale cells were constructed with the two shown in Figure #1 being sampled. The cells are comprised of a top layer (3-8 cm) of mulch overlaying a porous soil matrix (Davis *et al* n.d.). A wide variety of water tolerant plant species were planted to promote evapotranspiration and slow overland flow.

Information regarding Bioretention site #1 appears to be scarce, but it is first clearly visible in satellite picture in 2006. It is a conduit to help drain the approximately 30,000 square meter parking lots adjacent to the feature which serve as student parking. There site is comprised of a 10-meter-long concrete inlet facing the parking lot with an outlet discharging into campus creek. There is 5-10 cm of organic rich soil present at this site with a large concentration of earthworms. Grasses are present overlaying the soil but to a lesser degree than the vegetation present at other sites.

Bioretention #2 was constructed in 2003 with two separate parallel cells in order to capture and treat runoff water from an adjacent half-acre asphalt parking lot (Davis *et al* n.d.). Though decomposition has altered the composition over time, the cell originally was filled with porous soil covered with a 3-8 cm layer of hardwood mulch (Davis *et al* n.d.). In order to promote evapotranspiration, increase biological diversity and encourage the uptake of some pollutants grasses, shrubs and small trees were planted therein (Davis *et al* n.d.). Stormwater is directed at the bioretention cells through an inlet and allowed to infiltrate through the biological material in order to provide water treatment (Davis *et al* n.d.). It should be noted that this site is in a current state of disrepair and looks to not have been maintained for a number of years, perhaps since its installation.

Wetland #1 was constructed between 2001 and 2002, concurrently with the construction of the Xfinity center. It captures runoff water not only from that 17,000 square meter facility but also an adjacent 8,500 square meter parking lot. The wetland contains two parallel cells with individual water inlets from the parking lot. They have an area of open water with boulders and cobbles present to help decelerate incoming flow during high discharge events followed by a shallower wetland area with wetland flora.

Wetland #2 was constructed sometime between 1989 and 1994 and was originally a shallow runoff pond which gradually infilled through slackwater sediment deposition. Over time as the water level became shallower, wetland species began to naturally infill until presently there is only a small area of open water, taking up <10% of its surface area. Wetland #2 is centrally located and drains the impervious surfaces created by at least 4 buildings and 3 small parking lots. The main inlet structure is adjacent to the Natural Buoyancy Research Facility and the outlet drains to Paint Branch stream.

Pond #1 was constructed between 2002 and 2005 in order to drain the University of Maryland's 25,000 square meter School of Music building complex. Near the end of its construction a riparian buffer was also planted around the lake's border to lower its temperature and reduce the speed of overland flow. Hydrophilic cypress trees were also planted in the pond itself, growing with their roots submerged for the majority of the year.

Pond #2 is the oldest site sampled in this study, being constructed sometime prior to 1988 and being altered during construction of the 5,000 square meter Terrapin Trail Garage in 2001. This site has high banks and a deep-water level with some limited wetland species present around its bank. Faunal activity was high during sample collection with a large concentration of frogs being observed.

Stream Monitoring Sites: Salts, Nutrients, and Metals in Response to Deicing Events

We monitored salts, nutrients, and metals in stream outfalls of the Anacostia watershed near the UMD campus in response to deicing events. Throughout snowmelt, samples were collected daily, and at peak snowmelt, samples were collected hourly or at least twice a day (similar to Kaushal *et al.* 2019). Samples were acidified with 0.5% high-purity nitric acid and analyzed for dissolved base cation concentrations (sodium, calcium, magnesium) and trace metals (copper, manganese) in an acidified matrix on an ICP-OES (see methodology for chemical analyses below). In this report, two main focal sites were Paint Branch and Campus Creek as examples, but more sites are presented in Galella *et al.* (2021). For example, Paint Branch, a tributary of the Anacostia River and the Chesapeake Bay, is located approximately 5 miles outside of Washington DC and has a drainage basin area of 30.5 square miles, basin slope of 0.0652 feet/foot, impervious surface land coverage of 31.7%, urban development land coverage of 67.5%, and forested land coverage of 25.4%. This sampling station is located near the University of Maryland Campus (38° 59' 20.8" N, 76° 56' 07.23" W). Campus Creek is a small stream running through the UMD campus, which experienced stream restoration using regenerative stormwater conveyance.

Incubation Experiments: Determining critical thresholds of different road salt ions that mobilize nutrients and metals to surface waters across stormwater BMPs

We collected sediment samples along the flowpath through stormwater BMPs, composited the samples, and then later subdivide into replicate batches in the laboratory after homogenization for use in salinization experiments. As described in Haq *et al.* (2018) and Duan and Kaushal (2015), roughly 1 kg of sediment was collected from the stormwater BMPs per site using a clean shovel and a new Ziploc bag. Two liters of nearby surface water was also collected (*via* acid-washed HPDE Nalgene bottles; no headspace). The sediment and surface water were transported in a chilled cooler to the laboratory, and kept cool and moist during the experimental set-up (Haq *et al.* 2018, Duan and Kaushal 2016). In order to homogenize the samples for particle size, the sediment were sieved in the lab with a 2 mm sieve and the fine fraction (<2 mm) was used for incubation studies (Haq *et al.* 2018, Duan and Kaushal 2015). The sediments were separated into batches for use in experiments. Sixty grams of homogenized sediment from each batch was 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. Aqueous salt treatments, normalized to the concentration of Cl⁻ in solution were applied to the sediment aliquots. Common road salts were selected to be used in this analysis including NaCl, MgCl₂, and CaCl₂. Concentrations of 1, 2.5, 5, and 10 g Cl/L were chosen for each salt based

upon peak salinity readings within the DC and Baltimore metropolitan areas (Table 1). 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; regression models have suggested even higher concentrations of salinity (*e.g.* 14,000 $\mu\text{S}/\text{cm}$) following road salt applications at our Anacostia watershed sites.

In order to represent salt inputs to rivers (snowmelt with road salt), pure lab-grade sodium chloride was dissolved into 100 mL unfiltered streamwater in a separate volumetric flask before being pipetted onto sediment in the Erlenmeyer flask. 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 hours 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 hours 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 or frozen 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. For each site, the incubation experiments were conducted in duplicates (using the same sediments and streamwater grab samples), the resulting dissolved concentrations were averaged (Haq *et al.* 2018, Kaushal *et al.* 2018).

Table 1. Quantity of NaCl, CaCl₂, and MgCl₂ added to unfiltered stream water for each incubation concentration. Incubation concentrations are normalized to 1, 2.5, 5, and 10 grams of chloride per liter (Galella et al. In Prep).

Salt Introduced	0 g Cl/L	1 g Cl/L	2.5 g Cl/L	5 g Cl/L	10 g Cl/L
NaCl (g)	0.0	1.6	4.1	8.2	16.5
CaCl ₂ (g)	0.0	1.6	3.9	7.8	15.7
MgCl ₂ (g)	0.0	1.3	3.4	6.7	13.4

Water Chemistry Analyses

Base cation (calcium, potassium, magnesium) and trace metals (manganese, zinc, strontium, copper) concentrations in the acidified water samples were measured *via* inductively coupled plasma optical emission spectrometry in an acidified (0.5% high-purity nitric acid) analytical matrix on a Shimadzu Elemental Spectrometer (ICPE-9800; Shimadzu, Columbia, Maryland, USA). For base cation measurements, the acidified sample were nebulized in radial mode (across a plasma flame). For trace metals measurements, the acidified sample were nebulized in axial mode (down plasma flame). The instrument was calibrated to the range of trace metals that are commonly observed in urban streams in accordance to analytical guidelines for surface water analysis issued by the US Environmental Protection Agency.

Dissolved organic carbon (DOC), measured as non-purgeable organic carbon, dissolved inorganic carbon (DIC) and total dissolved nitrogen (TDN) were measured using a Shimadzu

Total Organic Carbon Analyzer (TOC-V CPH/CPN) total nitrogen module, TNM-1 (Haq *et al* 2018). This instrument uses a chemiluminescence to derive TDN (Haq *et al* 2018). DOC and DIC are derived from a high temperature catalytic oxidation method (Duan and Kaushal 2013). Samples are diluted before analyzation so that their chloride concentration does not exceed 0.5g Cl/L.

Samples from stream monitoring during snow events were also analyzed by fluorescence spectroscopy to characterize dissolved organic matter sources and chemical composition. Analytical work took place in the Biogeochemistry Laboratory at the UMD Department of Geology.

Statistical Approaches

We evaluated differences in mobilization of salts, nutrients, and metals in laboratory experiments across stormwater BMP type (bioretention, wetlands, ponds, *etc.*), road salt type (Na^+ , Ca^{2+} , Mg^{2+}), and different dosing levels of salt ions. Analysis of Variance (ANOVA) was used to determine if mobilization of elements differed significantly in response to site type, dosing with different salt ions, and across varying concentration levels. For this analysis, data were divided into site types (wetlands, ponds, bioretention). Three-way ANOVAs with independent variables salt type, site type, and concentration level (including interactions) were performed for each of the chemical constituents (DIC, DOC, TDN, B, Ca, Cu, Fe, K, Mg, Mn, Na, S, *etc.*) as the dependent variable. ANOVAs were performed on all data from salinization experiments. We performed pair-wise comparisons of means among salt types to determine salt type effects on mobilization (with Tukey's Honestly-Significant-Difference Test). Linear regressions were used to investigate dose-response relationships and trends in mobilization of elements in response to dosing with different concentration levels of salt types (NaCl , MgCl_2 , and CaCl_2). A p-value of 0.05 or less was considered statistically significant.

Results:

Results: Significant Differences in Salinization Impacts Based on Salt Concentrations and Types

Table 2. ANOVA analysis data comparing site type, salt type and salt concentration. Dissolved Inorganic Carbon (DIC), Dissolved Organic Carbon as non-purgeable organic carbon (DOC), and Total Dissolved Nitrogen (TDN) data analysis is ongoing so site type could not be used as a variable in the analysis (Galella *et al.* In Prep).

Variable	Site Type			Salt Type			Salt Concentration		
	N	F-ratio	p-value	N	F-ratio	p-value	N	F-ratio	p-value
B	248	10.675	0.000	248	1.989	0.139	248	2.722	0.021
Ba	248	22.458	0.000	248	10.523	0.000	248	26.294	0.000
Ca	248	0.416	0.868	248	69.988	0.000	248	28.744	0.000
Cu	241	0.318	0.927	241	72.073	0.000	241	25.260	0.000
Fe	182	1.784	0.105	182	2.917	0.057	182	2.771	0.020
K	248	41.476	0.000	248	21.122	0.000	248	176.314	0.000
Mg	248	0.420	0.866	248	73.466	0.000	248	23.883	0.000
Mn	245	53.566	0.000	245	3.889	0.022	245	5.324	0.000
Na	248	0.106	0.996	248	77.882	0.000	248	24.069	0.000
Sr	248	6.264	0.000	248	79.050	0.000	248	66.406	0.000
DIC	X	X	X	36	21.301	0.000	36	4.220	0.006
DOC	X	X	X	36	22.903	0.000	36	12.346	0.000
TDN	X	X	X	36	14.548	0.000	36	21.124	0.000

Table 3. Tukey's Honestly-Significant-Difference test was used to better classify how different salts behaved in terms of elemental mobilization. Mean mobilization rates for a given major or trace element share a common letter in the post-hoc column when they are not statistically different from one another ($p > 0.05$) (Galella *et al.* In Prep).

	Barium			Boron			Calcium		
	Mean	SE	Post-hoc	Mean	SE	Post-hoc	Mean	SE	Post-hoc
NaCl	0.417	0.031	a	1.055	0.301	a	93.086	8.575	a
CaCl ₂	0.686	0.056	b	0.814	0.272	a	1266.5 26	158.7 74	b
MgCl ₂	0.593	0.034	ab	0.201	0.082	b	176.52 3	17.90 3	a
	Copper			Iron			Potassium		
NaCl	1.302	0.168	a	0.304	0.034	a	15.713	1.290	a
CaCl ₂	0.061	0.009	b	1.835	1.021	a	11.768	0.959	b
MgCl ₂	0.078	0.009	b	0.275	0.046	a	13.327	1.089	ab
	Magnesium			Manganese			Sodium		
NaCl	14.498	1.063	a	1.009	0.283	a	1295.0 94	165.5 26	a
CaCl ₂	35.191	3.958	a	2.485	0.781	b	51.849	4.911	b
MgCl ₂	758.162	101.219	b	1.727	0.532	ab	52.132	4.907	b
	Strontium			DIC			DOC		
NaCl	0.259	0.022	a	20.83 6	2.650	a	26.267	3.438	a
CaCl ₂	1.109	0.113	b	17.41 8	0.610	b	5.737	0.601	b
MgCl ₂	0.407	0.045	a	16	1.144	b	14.922	1.706	a
	TDN								
NaCl	6.394	0.792	a						
CaCl ₂	3.896	0.361	b						
MgCl ₂	7.164	0.871	a						

We observed significant differences in mobilization of salt ions, metals and nitrogen based on different salt concentrations and salt types (Table 2). There were consistent significantly increasing responses in increased mobilization of metals and nutrients, with increasing salinity from nearly all salt types (Figure 3 and Table 3). Salt concentrations and salt type showed the main treatment effects. Only B, and Fe didn't show significant positive effects from salt type, and all other elements were significantly affected by salt type (Table 2). Salt concentration significantly affected mobilization of all elements across all sites with no exceptions. There were statistically significant site differences among BMP types. There were sometimes statistically significant differences among site replicates (even within a BMP type, there was sometimes large variation in mobilization response). This could have been due to differences in organic matter, clay content, soil type, or anthropogenic pollution sources. For

example, Mn was far higher in Pond 1 than in Pond 2, and K was far more mobile in Bioretention 1 than Bioretention 2 regardless of the salt used during the incubation. Table 3 illustrates that NaCl, being monovalent, often mobilizes major and trace elements differently from divalent CaCl_2 and MgCl_2 . CaCl_2 and MgCl_2 are often more variable with less of a clear pattern between them. In general, there were much smaller effects of site type than salt concentration and salt type on mobilization of metals and nutrients. Regardless of stormwater management BMP, the amount and type of road salt applied is the important factor controlling major and trace element mobilization.

Retention of Ions across Salt Concentrations, Salt Types and Stormwater Management BMPs

We can calculate retention of Na^+ , Mg^{2+} and Ca^{2+} by comparing a known amount added with actual measured values in overlying incubation water. Patterns of retention appeared to be generally similar across the same site with different salt types, but there were exceptions. In some cases, retention increased up to a certain limit in concentration, and then plateaued and/or decreased. In a very few cases, percent retention kept increasing with increasing cation concentration added for Ca and Mg (*i.e.*, Bioretention #2). The response in percent cation retention was often not linear with increasing salinity (cation added). There were some thresholds in the retention potential for each site likely based on differences in substrate type and/or site history in anthropogenic metal and cation loadings and available cation exchange sites on soils and sediments. Retention of Na, Ca, and Mg varies based on the salt added, salt concentration and the stormwater management feature tested. The majority of sites varied between 5% and 44% retention of base cations. There were a few sites that went higher at 78-96%, with the highest retention occurring at the lowest salt concentration added. In general, retention results also showed a negative relationship with increasing salt ion concentration; this indicates that cation exchange sites can eventually become saturated, and this threshold of saturation occurred at different concentrations for different salt types and stormwater management BMPs. For example, all pond sites appeared to follow this trend of decreasing retention as salinity treatments increased. In general, there was a relatively high level of retention of ions ranging from up to 40, 78, and 96% for Na^+ , Ca^{2+} , and Mg^{2+} respectively (Figure 2). This may have not just been due to differences in organic matter content of the sediments, but it could also be based on differences in cation exchange capacity of the soils and related to clay content.

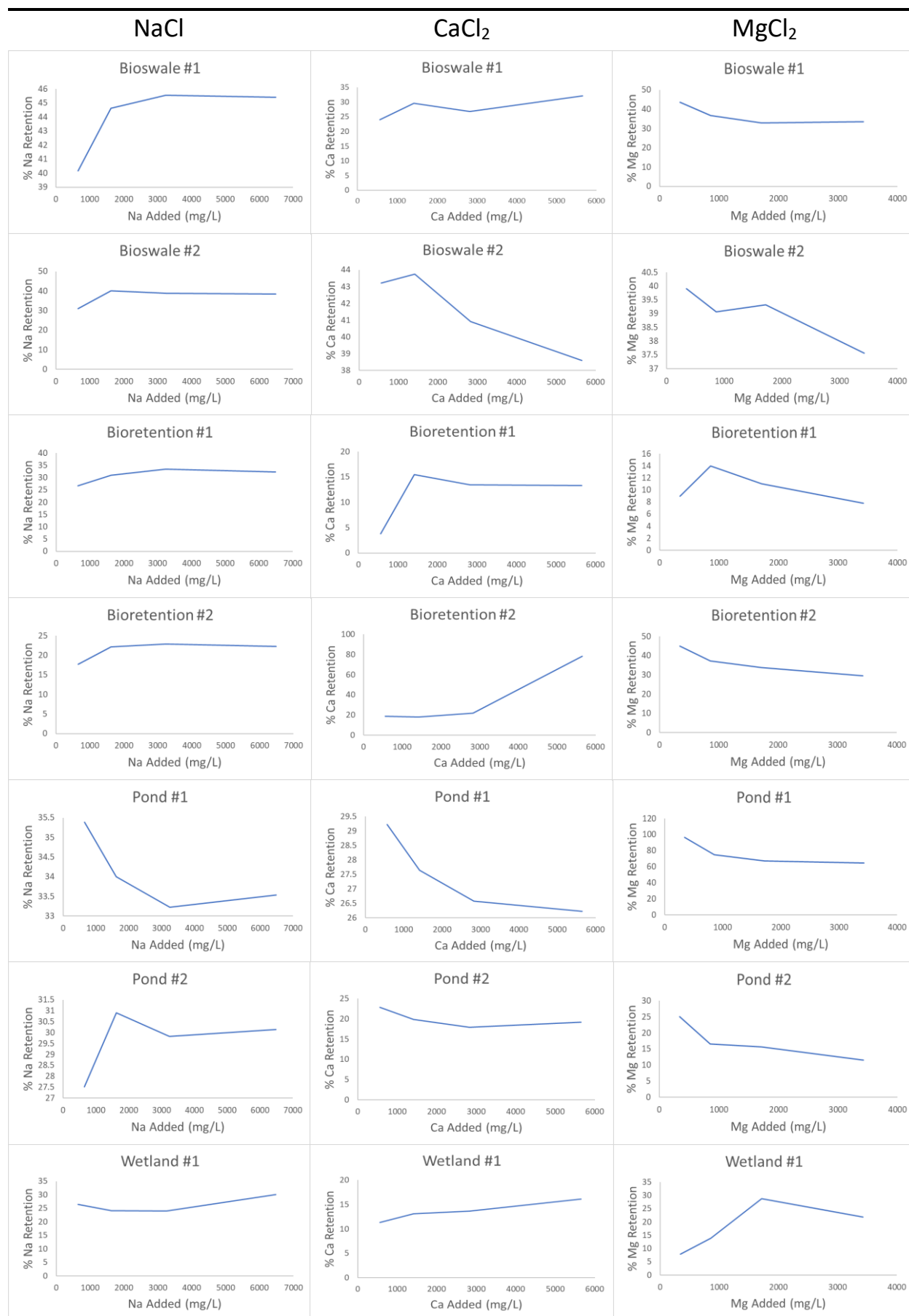


Figure 2. Sodium, calcium, and magnesium retention after NaCl, CaCl₂, and MgCl₂ incubations. Concentrations are measured in milligrams per liter (Galella et al. In Prep).

Salinization Dose-Response Relationships

There were consistent increasing dose response curves for nearly all elements, with mobilization generally occurring in a statistically significant linear manner in response to the quantity of salt ions added. All salts studied had positive relationships between concentrations of salt ions added with concentrations of Ca, Cu, Ba, K, Mg, Mn, Na, S, and Sr (all major and trace elements except for Fe and B) in overlying water as shown in Table 2. Certain types of salt ions were able to preferentially mobilize certain metals and ions. For example, Ca mobilized greater Sr than the other salt types. NaCl was able to mobilize significantly greater concentrations of Cu than either CaCl₂ or MgCl₂. This is quite important as aquatic species can suffer from Cu toxicity if levels become too high (Grosell *et al* 2007). Interestingly, negative relationships with increasing salinity were observed with Fe and to a lesser degree B. Overall, there were statistically significant increasing trends for major and trace elements based on salt concentrations. Variability in dose-response functions was also observed among major and trace elements based on salt type.

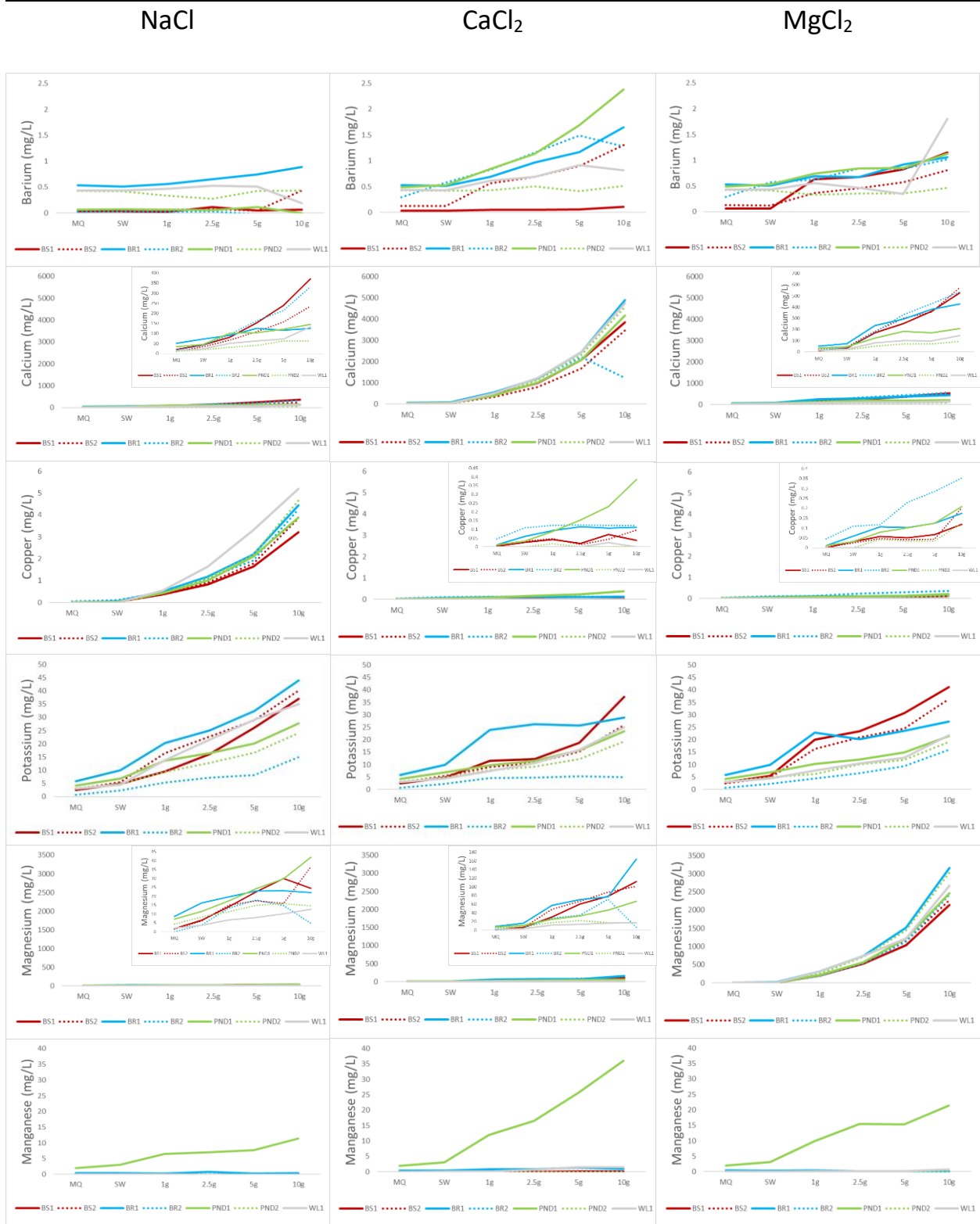


Figure 3. Elements mobilized by salt type and concentration. Y axis is normalized between salt types to better illustrate changes in mobilization by salt type. Inserts in the upper right corner of select graphs better show mobilization in otherwise flattened curves. X axis is plotted as a function of discrete salt treatment levels and not continuous concentrations (Galella et al. In Prep).

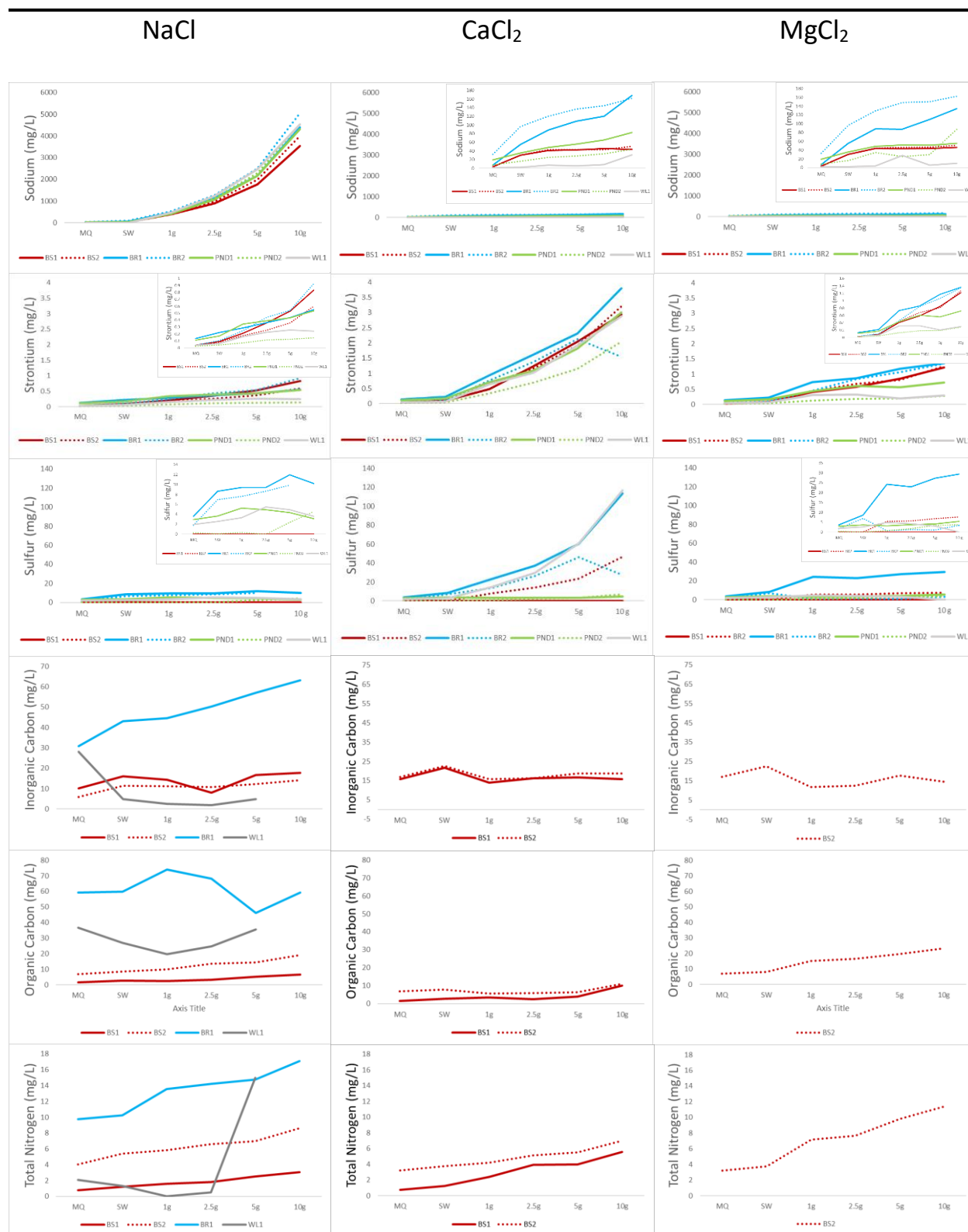


Figure 3 (Continued). Elements mobilized by salt type and concentration. Y axis is normalized between salt types to better illustrate changes in mobilization by salt type. Inserts in the upper right corner of select graphs better show mobilization in otherwise flattened curves. X axis is plotted as a function of discrete salt treatment levels and not continuous concentrations (Galella et al. In Prep).

Consistent Results between Salinization Experiments with Stream Chemistry Monitoring

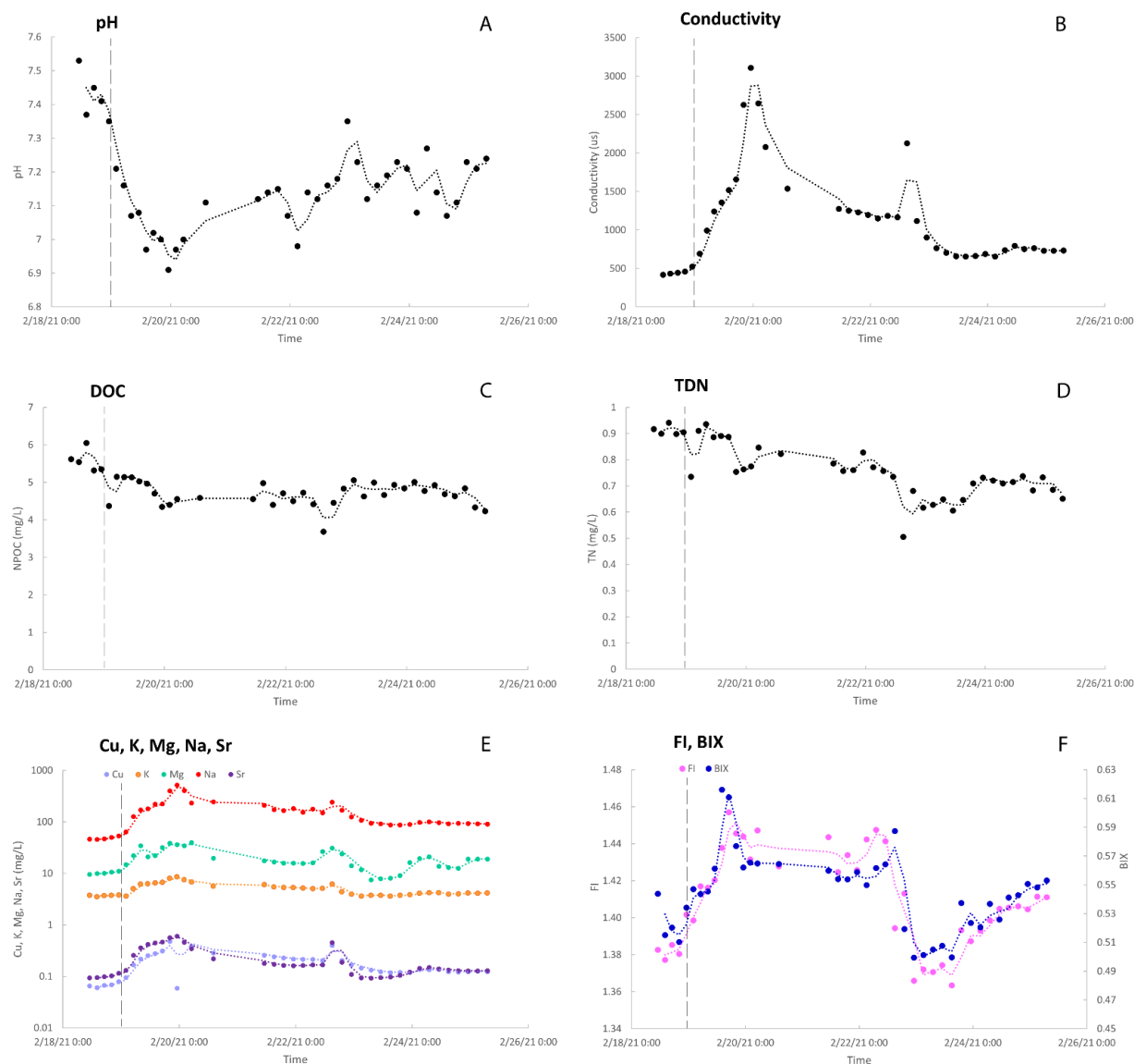


Figure 4. Pulses in water quality impacts during a winter road salt event in Campus Creek, an urban stream in College Park, Maryland, USA, restored using regenerative stormwater conveyance; further details on this study site can be found in our methods and elsewhere (Kaushal et al. 2019, 2020, 2021). Vertical line represents the onset of a snow event and road salting. We observed sharp pulses in concentrations of salt ions and metals in Campus Creek during and after road salt events. We also observed sharp declines in pH (acidification) in response to road salt applications likely due to mobilization of H^+ from soil exchange sites by Na^+ . There were sharp increases in organic matter from microbial and algal sources; this was based on fluorescence spectroscopy and the fluorescence index (FI) and biological index (BIX) in response to road salt applications likely due to lysing cells and/or changes in solubility.

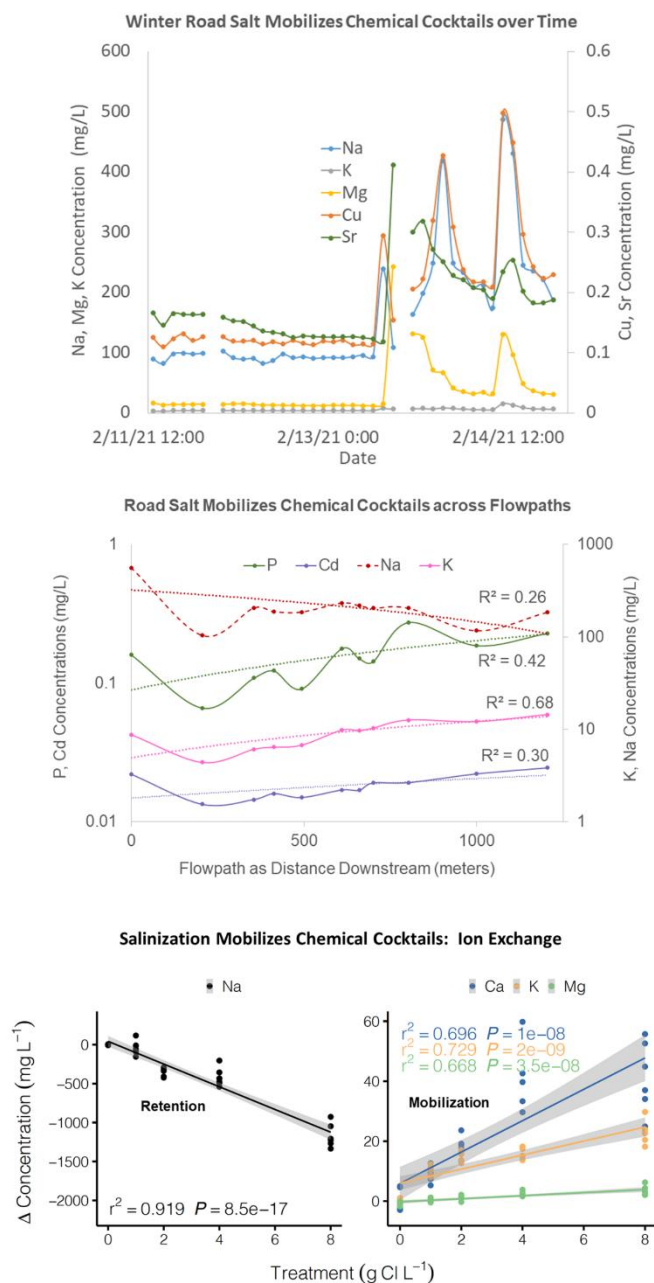


Figure 5. Freshwater Salinization Syndrome mobilizes chemical cocktails across space and time in Campus Creek, a small urban stream in College Park, Maryland. Campus Creek has undergone a type of stream restoration known as regenerative stormwater conveyance, which dramatically enhances floodplain reconnection through the creation of a series of step pools. (Top Panel) In Campus Creek, there are peaks in ion concentrations during a winter road salt event illustrating the importance of mobilization of multiple elements over time in response to deicer applications and winter climate. (Middle Panel) Along the longitudinal flowpath of Campus Creek, Na concentrations decline during winter after a road salt event, as other elemental concentrations increase; this suggests the importance of ion exchange and/or shifts in sources along the flowpath (Bottom Panel) Laboratory salinization experiments with sediments from Campus Creek demonstrates the importance of Na retention as NaCl is added at increasing concentrations (using experimental methods similar to Haq *et al.* 2018 and Kaushal *et al.* 2019);

other elements are mobilized and released from sediments of Campus Creek due to ion exchange and geochemical processes.

Mobilizing Chemical Cocktails: Comparison by Year and Season

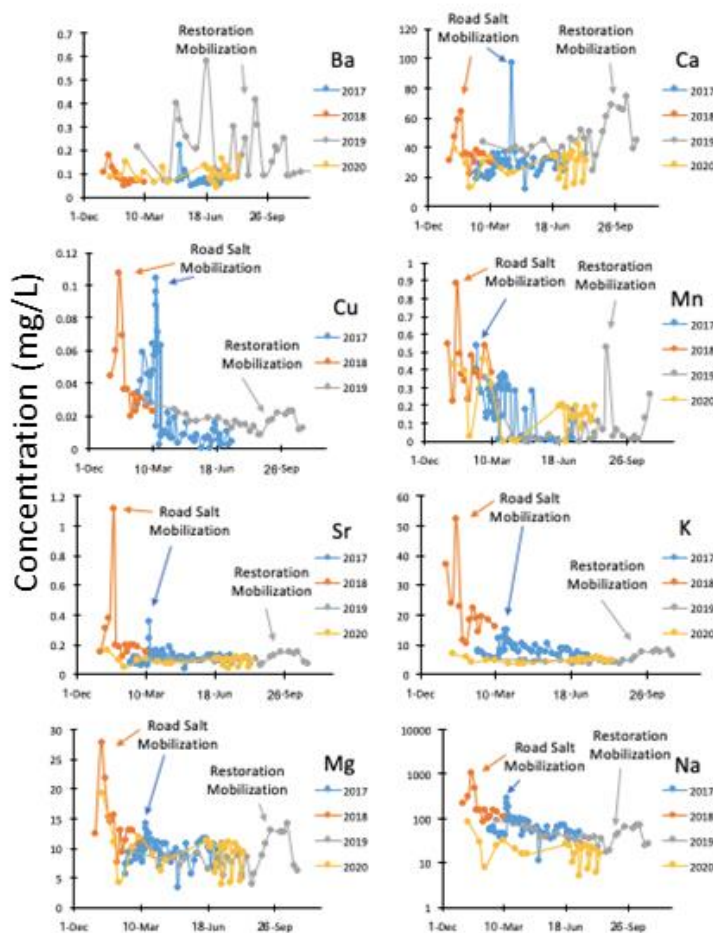


Figure 6. Variations in elemental concentrations in Campus Creek, a stream undergoing stream restoration and conversion to regenerative stormwater conveyance. There were pulses (large changes in chemical concentrations over relatively short time scales) in elemental concentrations during road salt events and also during the year 2019 when stream restoration was occurring. 2020 was a year with low or no road salt application and Na^+ concentrations were lower throughout the whole year compared to previous years.

Effects on Salt Ions and Metals Mobilization

During winter road salt events, our stream monitoring data showed that there was a wide range in water quality impacts beyond just increases in salt ions themselves; these changes in water quality from monitoring data were also similar and consistent with results from experimental salinization in the laboratory. Our stream monitoring results showed that road salt

events coincided with sharp winter peaks in specific conductance, concentrations of salt ions and metals, rapid declines in pH, and changes in organic matters sources (Figure 4). In addition, experimental work at these sites showed that the types of salt ions involved in FSS can play a significant role in the specific types of metals mobilized. The specific effects of different ions on mobilization of other ions and metals may be related to similarities in valence states and charges of ions, atomic masses, and/or shared affinities for ion exchange sites in soils and sediments (Figure 5, Table 3).

Retention and Release of Contaminants along Stormwater BMP and Stream Flowpaths

During winter, there were longitudinal changes in concentrations of salt ions and metals in an urban restored stream after concentrations of salt ions and metals peaked during road salt applications (Figure 5). Concentrations of Na declined along longitudinal flowpaths whereas concentrations of P and metals increased. This was likely due to ion exchange reactions where Na was retained on sediment and soil exchange sites and other elements were displaced and mobilized into the water column.

Effects on pH and Acidification

During winter road salt events, our stream monitoring data show sharp declines in pH (acidification) in response to road salt applications (Figure 4), which is likely due to mobilization of H^+ from soil exchange sites by Na^+ (Kaushal *et al* 2022a). During short term responses to salinization events, salinization can yield episodic acidification events due to mobilization of H^+ and strong acid anions like Cl^- (e.g., Figure 4), which could enhance solubility of certain metals (Kaushal *et al* 2022a).

Effects on Dissolved Organic Matter

Our monitoring results also showed sharp increases in organic matter from microbial and algal sources in response to road salt applications likely due to lysing cells and/or changes in solubility (Figure 4). Interestingly concentrations of dissolved organic carbon and total dissolved nitrogen didn't appear to show strong responses during and after the road salt event (Figure 4). Thus, our stream monitoring data show that salinization can have an important effect on the lability and quality of organic matter transported in urban streams. The solubility of dissolved organic matter is influenced by the ionic strength of solutions and the concentration of various salt ions. Within certain salinity ranges, proteins will dissolve more easily with increases in ionic strength (Kaushal *et al* 2022a). At very high ranges of salinity, proteins can precipitate out with increases in ionic strength (Kaushal *et al* 2022a).

Monitoring Recovery from Freshwater Salinization Syndrome

Over the long-term, our stream monitoring results suggest that there can be peaks in major ions and metals during road salting events (Figure 6). Interestingly, our monitoring has also found that there can be peaks major and trace elements which also occur during the stream restoration process (Figure 6). For example, Campus Creek, is an urban stream on the UMD campus that was restored using regenerative stormwater conveyance. We observed sharp peaks in elemental concentrations during the stream restoration process similar to road salt events (similar to the way concentrations increase during other soil disturbance activities). Our results also showed that there was a significant decrease in concentrations of Na^+ and other ions during 2020, which was a year with minimal or no snow (Figure 6). The reduction in concentrations of

Na^+ was up to greater than 50% compared to other years when more substantial amounts of road salt were applied (Figure 6). Our results suggest that reduced applications of road salt can reduce peaks in concentrations of elements of concern with rapid recovery responses within some urban streams. Overall, our stream monitoring results were consistent with results from incubation experiments, which show that the contaminant mobilization response is strongly dependent on the concentrations and types of salt ions added. Thus, reducing salt applications in the environment below certain thresholds can reduce contaminant mobilization observed in both laboratory and field studies. In addition, the types of salt ions matter in terms of their contaminant mobilization potential.

Summary and Future Questions

Overall, our results show: (1) sharp pulses in concentrations of salt ions and metals in urban streams directly following both road salt events and stream restoration construction (*e.g.*, similar to the way concentrations increase during other soil disturbance activities); (2) sharp declines in pH (acidification) in response to road salt applications likely due to mobilization of H^+ from soil exchange sites by Na^+ ; (3) sharp increases in organic matter from microbial and algal sources (based on fluorescence spectroscopy) in response to road salt applications likely due to lysing cells and/or changes in solubility; (4) significant retention (~30-40%) of Na^+ in stormwater BMP sediments and floodplains in response to salinization; (5) increased ion exchange and mobilization of diverse salt ions (Na^+ , Ca^{2+} , K^+ , Mg^{2+}), nutrients (N, P), and trace metals (Cu, Sr) from stormwater BMPs and restored streams in response to FSS; (6) downstream increasing P release from stormwater BMPs in response to salinization, and (7) a significant annual reduction (up to over 50%) in Na^+ concentrations in an urban stream when road salt applications were dramatically reduced, which suggests the potential for short-term recovery. Urban streams and stormwater management BMPs can retain sodium and chloride but mobilize different elemental contaminants based on salt types and salinity thresholds. In fact, our work showed that there was a relatively high level of retention of ions in stormwater management BMPs ranging from up to 40, 78, and 96% for Na^+ , Ca^{2+} , and Mg^{2+} respectively. Our work also raises further questions, however. For example, our monitoring shows that the stream restoration process can impact mobilization of contaminants in pulses in concentrations, but it is unclear how long these pulses from construction last and whether they are important compared to contaminant retention over longer time scales? Finally, our work suggests that reductions in applications of salt ions can significantly reduce mobilization of chemical cocktails, but more work is necessary to explore spatial and temporal responses across watersheds. Our work addresses the questions originally posed in the proposal, and we are currently working on related manuscripts (Kaushal *et al* 2022a, Kaushal *et al* 2022b, Galella *et al* In Prep). We will also present results at the Chesapeake Bay Trust Restoration Research Symposium.

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