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Freshwater Salinization Syndrome Alters Retention and Release of 'Chemical Cocktails' along Flowpaths: from Stormwater Management to Urban Streams

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Abstract

We investigate impacts of Freshwater Salinization Syndrome (FSS) on mobilization of salts, nutrients, and metals in urban streams and stormwater BMPs by analyzing original data on concentrations and fluxes of salts, nutrients, and metals from 7 urban watersheds in the Mid-Atlantic U.S. and synthesizing literature data. We also explore future critical research needs through a survey of practitioners and scientists. Our original data 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 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 loads of Cl^-, SO_4^{2-}, Br^-, F^-, and I^- along flowpaths through urban streams, and P release from urban stormwater BMPs in response to salinization, and (7) a significant annual reduction (> 50%) in Na^+ concentrations in an urban stream when road salt applications were dramatically reduced, which suggests potential for ecosystem recovery. We compared our original results to published metrics of contaminant retention and release across a broad range of stormwater management BMPs from North America and Europe. Overall, urban streams and stormwater management BMPs consistently retain Na^+ and Cl^- but mobilize multiple contaminants based on salt types and salinity levels. Finally, we present our top 10 research questions regarding FSS impacts on urban streams and stormwater management BMPs. Reducing diverse 'chemical cocktails' of contaminants mobilized by freshwater salinization is now a priority for effectively and holistically restoring urban waters.

Introduction

Freshwater salinization represents a growing risk to source water protection, infrastructure, biodiversity, and can increasingly contribute to mobilization of chemical cocktails containing nutrients and metals from watersheds to streams and rivers (Löfgren 2001, Bäckström et al. 2004, Kaushal et al. 2005, 2018, 2019). The synergistic impacts of freshwater salinization on mobilization of multiple mixtures of nutrients, metals, and salts or 'chemical cocktails' and coinciding changes in pH and buffering capacity have been called Freshwater Salinization Syndrome (FSS) (Kaushal et al. 2018, 2019). FSS can negatively affect freshwater as well as estuarine systems, thereby affecting local economies dependent upon healthy aquatic ecosystems. Despite growing environmental impacts of FSS, relatively little is known regarding the effects of different salt ions from various sources (*e.g.*, road deicers, fertilizers, weathering of urban infrastructure, *etc.*) on contaminant mobilization, the magnitude and duration of mobilization of chemical cocktails seasonally, or the variability of environmental impacts across urban streams and rivers (Kaushal et al. 2021, Kaushal et al. in press).

Certain BMPs can enhance "hot spots" or "hot moments" of both retention and release of nutrients, salts, metals, and organics along hydrologic flowpaths (Groffman et al. 2005, Vidon et al. 2010, Weitzman et al. 2021), and this can complicate efforts to improve urban water quality. There is a growing need to better understand FSS impacts within the context of stormwater management BMPs and stream-riparian restoration projects (Cooper et al. 2014, Szota et al. 2015, Snodgrass et al. 2017, Kratky et al. 2017, Lam et al. 2020, Burgis et al. 2020). The dilemma is that, while some types of stormwater management may be effective at attenuating salt pulses that accompany stormwater runoff, salinity remains a stressor in many urban restored streams (Cooper et al. 2014, Fanelli et al. 2019) and the longevity of restoration effectiveness can be relatively short despite expensive efforts (Mayer et al. 2022). Restoration itself does not always produce desired outcomes (Cockerill and Anderson 2014) and can sometimes produce unintended consequences and tradeoffs such as salt retention and contaminant release (*e.g.*, Wood et al. 2022).

Aims and Scope

In this paper, we investigate and document environmental impacts of FSS on retention and mobilization of salts, nutrients, and metals in urban streams and stormwater BMPs by: (1) analyzing original data from our long-term study sites, and (2) synthesizing information from published sources, which shows direct and indirect effects on multiple contaminants. These contaminants represent novel combinations of elements formed from watershed biogeochemical processes (Kaushal et al. 2018, 2019, 2020, in press). We provide new monitoring information from our previously unpublished data on changes in concentrations and fluxes of salts, nutrients, and metals in urban streams and stormwater BMPs during winter deicing events and other times of year. Our original data regarding impacts of FSS on biogeochemical patterns and processes along stormwater flowpaths is presented in case studies from 7 urban watersheds in the Baltimore-Washington D.C. metropolitan region, which have been intensively studied through long-term monitoring. However, we acknowledge that there are limitations in our inferences given the apparent small geographic area of the data we present. Therefore, we also placed our data within the context of other studies of contaminant retention and release in stormwater management BMPs in North America and Europe.

Based on our growing understanding of FSS risks, we explore 3 themes: (1) Is FSS threatening attempts to restore or mitigate for negative effects of stormwaters? (2) How do flowpaths created for stormwater BMPs influence biogeochemical processes related to FSS? and (3) What are the current knowledge gaps and research frontiers regarding impacts of FSS and efficacy of stormwater BMPs in the context of FSS? Much of the basic biogeochemistry and geochemistry of FSS and its impacts on urban stream and stormwater management flowpaths is either currently not clearly documented or poorly synthesized. Otherwise, FSS would be explicitly and comprehensively considered in many watershed restoration strategies.

The sections of our paper addressing our three themes are intended to inform growing interest in developing strategies for monitoring, modeling, and managing different levels and forms of salt pollution (Kaushal et al. 2021). Our intention is to provide insight (though, not recommendations) on the potential retention and release of salt ions and multiple contaminants across urban streams and stormwater BMPs and to identify thresholds of ranges in salt concentrations and types of salts that have the greatest impacts on urban water quality. Our paper also points to priority research directions from interactions with stakeholders such as characterizing sediment characteristics in different stormwater BMPs and experimental retention and mobilization of salts, nutrients, and metals. This research can provide information on which stormwater BMPs and sediment characteristics retain salts and has implications for enhancing designs of stormwater BMPs and improving identification of risks for contaminant release. Our paper is intended to present new results and catalyze further research on these topics, as a first step in determining critical ranges in salt concentrations. Our paper may also contribute to improved selection of deicers based on contaminant mobilization potential, and identify which types of urban streams and stormwater BMPs may be most impacted by salt pollution.

Part 1. Is FSS threatening attempts to restore or mitigate for negative effects of stormwaters?

In response to significant urban stream degradation, many cities have implemented stream restoration projects and stormwater management (Bernhardt et al. 2005, Collins et al. 2010, Passeport et al. 2013, Newcomer Johnson et al. 2016, Hawley 2018, 2021). Frequently used restoration strategies implement a variety of approaches incorporating geomorphic, hydrological, biogeochemical, aesthetic, and/or habitat-based designs, focusing on channel stability, flood prevention, and enhancing urban water quality (*sensu* Bernhardt et al. 2005, Kaushal et al. 2008, Craig et al. 2008, Mayer et al. 2010). Project objectives include infrastructure protection, preventing erosion that may damage adjacent property or degrade sewer systems, reducing stormwater flows, and enhancing biogeochemical functions that improve water quality. Significant financial resources have been committed to many stream restoration projects that integrate stream-floodplain reconnection and innovative stormwater management (Mayer et al. 2022, Hopkins et al. 2022). These more recent stream restoration strategies may affect carbon, nitrogen, and metal fluxes through various approaches including artificial wetland creation (Palta et al. 2017, Maas et al. 2021), channel manipulation (Doheny et al. 2012, Harrison et al. 2014), woody debris structures (Lazar et al. 2014), replacing riparian vegetation, “daylighting” streams (Beaulieu et al. 2014, Pennino et al. 2014), and increasing hydrologic connectivity between streams and floodplains and hydrologic residence times (Bukaveckas 2007, Forshay et al. in review). Although less considered, these stream restoration and stormwater management approaches have the potential to retain not only nutrients but also salt ions (*e.g.*, Cooper et al. 2014, Snodgrass et al. 2017, Burgis et al. 2020) and magnify the emerging water quality impacts of FSS based on location, size, and type of restoration (*e.g.*, Newcomer Johnson et al. 2014, Maas et al. 2021).

There may be both retention and release of novel elemental combinations, also referred to as ‘chemical cocktails’ (*sensu* Kaushal et al. 2020), along hydrologic flowpaths through urban streams and various forms of stormwater management. Retention and release mechanisms can vary for different chemical cocktails (see Figure 1, a conceptualization of such mechanisms based on Flanagan et al. 2019; Duan et al. 2019; Williams et al. 2016; Cizek et al. 2018; Barbier et al. 2018; Semadeni-Davies 2006). For example, there can be pulses in concentrations of salt ions during winter months in restored streams and pulses in elemental concentrations during the stream restoration process often due to construction disturbances, similarly to the way concentrations increase during other soil disturbance activities (Figure 2). However, there is relatively lesser work documenting unintended water quality impacts during the stream restoration process. Conversely, there can also be rapid and significant year-round reductions in Na^+ concentrations (> 50%) in urban restored streams during low road salt application years (Figure 2), which suggests the potential for recovery from FSS impacts.

Interactions between FSS and retention and mobilization of contaminants in restoration features are poorly understood and represent a research frontier in urban watershed management. Instead, much more work has focused on the effects of stormwater BMPs on reducing runoff and retention of nutrients. Stormwater BMPs also retain road salt

(Snodgrass et al. 2017). Stream-floodplain reconnection can accumulate salt ions in shallow groundwater (Cooper et al. 2014, Mayer et al. 2022). There can be retention of Cl^- ions in restored floodplains following stream-floodplain reconnection due to increased hydrologic connectivity designed to promote denitrification (Kaushal et al. 2008, Mayer et al. 2010) (Figure 3). Infiltration-based BMPs are also common in modern developments and may have higher salt accumulation rates because higher volumes of water are directed through these landscape features (Kratky et al. 2017). Thus, stormwater management BMPs and stream restoration features have the potential to accumulate different salt ions, which can lead to contaminant mobilization. The specific types of salt ions (*e.g.*, Na^+, Ca^{2+}, Mg^{2+}) may preferentially mobilize certain contaminants (*e.g.* Cu). However, relatively less is known how the retention of FSS salt ions along urban flowpaths impacts diverse biogeochemical processes.

Part 2. How do flowpaths created for stormwater BMPs influence biogeochemical processes related to FSS?

In this section, we investigate how flowpaths created for stormwater BMPs influence different biogeochemical processes related to FSS. We document different biogeochemical patterns and processes using both analysis of our own original data and synthesizing published literature. In our case studies, we provide examples of FSS impacts on stormwater BMPs and urban streams using our original data from 7 long-term study sites in the Mid-Atlantic U.S. We then place our data within the context of other studies of contaminant retention and release in stormwater management BMPs in North America and Europe. Overall, our case studies and literature synthesis demonstrate how FSS triggers synergistic changes in pH, ionic strength, *etc*, which contribute to changes to solubility, biological transformation, degradation, and sorption potential of elements, as they are retained and released along urban stormwater flowpaths (Figure 1).

Study Design for Case Studies from the Mid-Atlantic U.S.

As mentioned previously, we present new, previously unpublished results from 7 watersheds in the Baltimore-Washington D.C. metropolitan region in the Mid-Atlantic U.S.; these sites have been intensively studied through our long-term monitoring (Table 1). Five of these watersheds experienced some form of stream restoration (Table 2). Original data from these sites consists of: (1) routine monitoring data from urban streams both 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 different levels and types of salt ions in incubations with sediments from urban streams and stormwater BMPs. All study sites were in urban watersheds where road salt is applied. All watersheds have been the subject of our previous studies spanning multiple years (*e.g.*, 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). Monitoring for this present study spanned over multiple time scales: daily, weekly, bi-weekly, seasonal, annual, and decadal time scales at these long-term study sites in Maryland, USA. Salinization experiments to quantify mobilization of contaminants from sediments to stream water were conducted similarly to our previous work at other sites (Duan and Kaushal 2015, Haq et al. 2018a, Kaushal et al. 2019). Details on methods of chemical analyses can be found in our previous studies and is also described further below (*e.g.*, 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), but we describe them briefly below.

Site Descriptions for Case Studies in the Mid-Atlantic U.S.—Site descriptions of our 7 study sites representing various stormwater BMPs and urban streams are below. Results from each of these study sites is mentioned throughout our different case studies regarding FSS impacts on different biogeochemical patterns and processes along flowpaths in storwmater BMPs and urban streams.

Campus Creek and Paint Branch Stream—Stream water and sediment samples were collected from Paint Branch Stream and one of its tributaries, Campus Creek, both of which are tributaries of the Anacostia River and the Chesapeake Bay. The sampling sites are located near the University of Maryland campus in College Park, MD, USA (38°59’20.8” N, 76°56’7.23” W), approximately five miles northeast of Washington, DC. Paint Branch Stream has a drainage area of 79 square kilometers and contains 31.7% impervious cover, while Campus Creek has a drainage area of 1.76 square kilometers and is 26.5% impervious. The sampled portion of Paint Branch Stream was restored in 2015 through stabilization efforts, floodplain reconnection, and habitat improvements. Campus Creek was restored in 2019 using Regenerative Stormwater Conveyance (RSC), designed to slow the flow of water and increase nutrient retention (Duan et al. 2019). Further details on site description can be found in Haq et al. (2018).

Minebank Run—Ground water and surface water samples were collected from Minebank Run, an urban stream located in the Gunpowder Falls Watershed near Baltimore, MD, USA (39°24’41.4” N, 76°33’15.8” W). The downstream section of the Minebank Run Watershed, restored in early 2005, has a drainage area of 5.3 km^2 and contains 21% impervious cover. The restoration goals included stream channel stabilization, protection of buried sewer lines and other city infrastructure, re-vegetation of riparian zones, and floodplain reconnection. Further details on site description can be found elsewhere (*e.g.*, Kaushal et al. 2008, Mayer et al. 2010, 2022).

Herring Run—Herring Run is an unrestored, channelized stream located in Baltimore, MD, USA and discharges into the Back River (39°19’4.7” N, 76°33’18.5” W). Herring Run has a drainage area of 5.5 km^2 and the land cover is 25% impervious. Further details on site description can be found in Reisinger et al. (2019).

Scotts Level Branch—Scotts Level Branch, a suburban stream with a narrow riparian buffer located northwest of Baltimore, MD, USA (39°21’41.7” N, 76°45’42.3” W), has a drainage area of one km^2 and contains 29% impervious cover. In 2014, a portion of the stream was restored through the installation of several control structures including cross vanes and j-hook vanes to direct flow, boulders and bank protection measures to prevent erosion, and woody debris to slow water flow and provide habitat for wildlife. The streambank, floodplain, and channel were also regraded. Further details on site description can be found in Newcomer et al. (2012) and Wood et al. (2022).

Stony Run—Stony Run, located in north central Baltimore (39°20'22.2" N, 76°37'32.5" W), has a drainage area of two km^2, with 28% impervious cover. A reach on the mainstem of the stream was restored between 2008 and 2009 through the addition of step pools, mild stream meanders, and hardened stream banks designed to slow the flow of water. Further details on site description can be found in Harrison et al. (2011) and Reisinger et al. (2019).

Red Run—Red Run is a stream northwest of Baltimore City with a drainage area of 19.1 km^2 and 29.2% impervious cover, containing extensive upland stormwater management systems (39°24'16.6" N, 76°46'46.6" W). The stormwater management infrastructure includes primarily infiltration-based designs such as stream buffer zones, wetlands, bioretention cells, detention ponds, and sand filters. Further details on site description can be found in Pennino et al. (2016).

Methods for Salinization Experiments Used in Case Studies from the Mid-Atlantic U.S.

The purpose of these experiments was to determine critical patterns and processes associated with different road salt ions that mobilize nutrients and metals. 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 plastic bag. Two liters of nearby surface water was also collected into acid-washed HPDE Nalgene bottles leaving no headspace. Sediments 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 sediments 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, $MgCl_2$, and $CaCl_2$. Different concentrations of salt ions were chosen for each salt based upon peak salinity readings within the Baltimore-Washington DC metropolitan area (Table 1). To represent salt inputs to rivers (snowmelt with road salt), pure lab-grade NaCl was dissolved into 100 mL unfiltered streamwater in a separate volumetric flask before being pipetted onto sediment in the Erlenmeyer flask. To isolate the sediment-water interaction, a control flask of only unfiltered streamwater was also incubated along with the treatment flasks. 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 containing 0.5% high-purity nitric acid for base cation analysis.

Methods for Water Chemistry Analyses Used in Case Studies from the Mid-Atlantic U.S.

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, MD, 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 with analytical guidelines for surface water analysis issued by the US Environmental Protection Agency such as APHA (1998) and USEPA (1983).

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 0.5 g Cl/L. Samples from stream monitoring during snow events were also analyzed by fluorescence spectroscopy to characterize dissolved organic matter sources and quality. Analytical work took place in the Biogeochemistry Laboratory at the University of Maryland, Department of Geology. All laboratory and field collection methods followed those described in Galella et al. (2021) and Mayer et al. (2022) and QA/QC protocols were documented in Quality Assurance Project Plans (QAPP) archived at USEPA/ORD, Corvallis, OR, USA (available upon request).

Methods for Statistical Analyses for Case Studies from the Mid-Atlantic U.S.

We performed linear regressions to determine relationships across salt concentrations among mobilized elemental variables from field and laboratory data. Linear regressions were used to investigate relationships and trends in mobilization of elements in response to freshwater salinization. Alpha = 0.05 was used to indicate statistical significance. All statistical analyses were conducted using R and Systat.

Study Design and Methods for Literature Synthesis on FSS Contaminant Retention and Release

We placed our case study data within the context of other published studies of contaminant retention and release in stormwater management BMPs in North America and Europe (Table 2). We completed a systematic search using Google Scholar^{tm} to identify and compile relevant studies. These studies included literature reviews and case study articles. The initial search had key words from each of the following: (1) stormwater management categories such as “constructed wetland”, “permeable pavement”, *etc*.; (2) process-oriented terms such as “retention” and “release”; (3) salt ion types associated with stormwater management BMPs, including base cations, trace metals, and nutrients. The key words were grouped together based on the stormwater BMP typology and the salt ion of interest. Information from each study, such as location, period of study, and sampling locations are located in Supplementary Table 1.

In each article, we calculated retention and release metrics for loads from the inflow and outflow concentrations where raw data was provided, or we used author-generated estimates of changes in concentrations. In some cases, we simply reported increases or decreases in concentrations or loads of contaminants in stormwater BMPs. In other cases, we reported changes in load removal efficiencies when sufficient inflow and outflow data were available. Positive removal efficiencies indicate net retention of a contaminant within a stormwater BMP. Negative removal efficiencies indicate net contaminant release from a stormwater BMP. If calculations of reduction percentages for loads were not given in a citation, they were estimated using: $[1-(\text{Outflow}/\text{Inflow})] \times 100$. In order to address the hydrological and biogeochemical mechanisms, we classified mechanisms based on the authors’ conclusions and mechanisms highlighted in Figure 1. We excluded papers that did not provide enough information on inflow and outflow metrics for each stormwater BMP type. Studies are from the United States and Europe. Some arid climates are not represented, and most of the studies focus on stormwater management features in urban areas. Further details regarding methods and descriptions of study sites including locations, periods of study, and number of study sites can be found in the Supporting Information.

Results and Discussion for Case Study 1: FSS Can Mobilize Major Ions and Nutrients along Urban Streams and Stormwater Management Flowpaths in the Mid-Atlantic U.S.

Road salts are linked to the mobilization of major ions and nutrients, and our monitoring work at our Campus Creek study site shows large pulses during winter months (Figure 2). Specific conductance is a measure of the ability to conduct electrical current and is often related to concentrations of major ions such as Na^+ and Cl^- (Kaushal et al. 2018, 2021). In streams of the Mid-Atlantic U.S., we observed relationships between specific conductance and a variety of base cations and total dissolved N, suggesting co-mobilization of chemical cocktails at our Herring Run, Minebank Run, Stony Run, and Scotts Level Branch study sites (Figure 4). Only K^+ does not show these relationships at our study sites likely due to strong biotic demand in terrestrial watersheds as a limiting nutrient (Tripler et al. 2006). Co-mobilization and formation of chemical cocktails has been demonstrated in salinization experiments in soil and stream sediments from this region (Duan and Kaushal 2016, Haq et al. 2018). Our experimental data from our Scotts Level Branch study site also showed that salinization with a variety of salt ions and deicers can mobilize N from sediments to streamwater (Figure 5). Na^+ can displace NH_4^+ from exchange sites, Cl^- can displace NO_3^- from exchange sites, and long-term increases in ionic strength and pH from road salts can increase the solubility of organic N (Green and Cresser 2008, Green et al. 2008, Duan and Kaushal 2015, Haq et al. 2018a).

Changes in retention and release are often related to cation exchange capacity (CEC), the capacity of soil particles to hold on to positively charged ions (Table 2). Yukselen and Kaya (2006) found that the soil property that accounted for the most variability in CEC was specific surface area, which can be linked to the amount of clay and organic matter in the sediment sample High concentrations of Na^+ ions can displace Ca^{2+} and Mg^{2+} in roadside soils, leading to soil structure disruption (Norrström and Bergstedt 2001, Bäckström et al. 2004, Cooper et al. 2014), which is another mechanism by which base cations, metals, nitrate, and ammonium can be mobilized. Furthermore, increased Na^+ retention in groundwater reservoirs may also lead to the exchange of Mg^{2+} and Ca^{2+} ions in soils (Shanley 1994, Löfgren 2001, Norrström and Bergstedt 2001). Thus, the elevated levels of Na^+ and Cl^- due to road salt inputs enhance ion exchange and displace Mg^{2+} and Ca^{2+} and NO_3^- and NH_4^+ from exchange sites on sediments and soils.

Stormwater BMPs can potentially retain and reduce concentrations of nutrients, such as nitrogen (N), phosphorus (P), and potassium (K), and metals and organic matter along flowpaths (Table 2). However, an effect of FSS might be the retention of unwanted chemicals and the release of dissolved ions, organics, and metals along hydrologic flowpaths, which could impact water quality (Table 2). Experimental salt additions show enhanced mobilization of N from soils and stream sediments to stream water at our Scotts Level Branch study site (Figure 5), and there can also be release of other nutrients and ions (Duan and Kaushal 2015). For example, as Na^+ is retained along flowpaths, there can be downstream release of P, and loads of multiple ions can increase longitudinally along urban watersheds draining stormwater management such as at our Campus Creek study site (Figure 6). Chemical cocktails of N and base cations in urban streams can also be related to hydrological, geochemical, and biological factors leading to close relationships among base cations, N, and specific conductance in urban restored streams (Figure 4). These relationships can be due to similarities in: (1) hydrologic flowpaths (groundwater) (2) anthropogenic sources and inputs (road salts, sewage, *etc*) and (3) geochemical processes (*e.g.*, ion exchange) contributing to transport. More experimental work is necessary to investigate the relative importance of hydrological *vs*. geochemical controls on nitrogen in urban streams, as most research has focused on biological controls on N in restored streams (Newcomer Johnson et al. 2016). In addition, more work is needed to conduct a detailed grain size analysis and determination of organic matter content to understand the influence on ion exchange processes along hydrologic flowpaths.

Results and Discussion for Case Study 2: FSS Can Mobilize Metals along Urban Streams and Stormwater Management Flowpaths in the Mid-Atlantic U.S.

Over annual periods, concentrations of metals and base cations at our Paint Branch study site increase significantly as water temperatures decline and road salt is applied during winter months (Figure 7). During winter road salt events, original data from our Campus

Creek study site show that there can be pulses in metals concentrations (Figure 8). Our data from experimental salinization from our Paint Branch and Campus Creek study sites also show that ~30–40% of Na^+ is retained on exchange sites in sediments from different streams and stormwater management features and mobilizes metals such as Cu, Sr, and base cations through ion exchange (Figure 9). In addition, experimental work at our Paint Branch and Campus Creek study sites show that the types of salt ions involved in FSS can play a significant role in the specific types of metals mobilized (Figures 10 and 11). 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.

FSS enhances retention and release of metals through multiple mechanisms such as cation exchange, organic matter complexation, and oxidation-reduction conditions (*e.g.*, Kim and Koretsky 2013, Kaushal et al. 2019, 2020, Wilhelm et al. 2019). Many studies suggest a link between increased road salt input and the mobilization of trace metals such as Cd, Cu, Pb, Hg, and Zn in watersheds in the northeast US, Europe, and Canada (Amrhein and Strong 1990, Bauske and Goetz 1993, Amrhein et al. 1994, Norrström and Jacks 1998, Bäckström et al. 2004, Kelly et al. 2008, Nelson et al. 2009). Heavy metals accumulate in roadside soils primarily due to automobile traffic (Schuler and Relyea 2018), but can be readily released into solution in contact with road salt. Violante et al. (2010) found that heavy metals that are not readily bioavailable can be mobilized and transformed into more bioavailable species by salts. Road salts can drive the mobilization of elements into the water column through accelerated ion exchange and complexation reactions with Cl^- and organic materials (Amrhein et al. 1994, Lumsdon et al. 1995). In a study by Sun et al. (2015), increased NaCl concentrations in soils were linked to the increase of Pb and Hg in the interstitial water. Their data suggested that the release of certain metals into the dissolved phase not only depends on salt concentrations, but also redox conditions, dissolved organic matter content, competition for exchange sites, and source bedrock material. These conditions can change seasonally with freshwater salinization along hydrologic flowpaths through stormwater BMPs and affect retention processes.

Results and Discussion for Case Study 3: FSS Can Alter Alkalinization and Acidification in Urban Streams and Stormwater Management Flowpaths in the Mid-Atlantic U.S.

During winter road salt events, our original monitoring data at our Campus Creek study site demonstrate sharp declines in pH (acidification) in response to road salt applications likely due to mobilization of H^+ from soil exchange sites by Na^+ (Figure 8). Similarly, our complementary results from experimental salt additions involving our Scotts Level Branch study site show acidification and rapid increases in H^+ ion concentrations due to H^+ mobilization from sediments (Figure 5). Short term responses to salinization events can yield episodic acidification events due to mobilization of H^+ and strong acid anions like Cl^- (*e.g.*, Figure 5), which could enhance solubility of metals. For example, changes in pH based on ionic strengths and compositions influence the solubility of dissolved organic C and associated metal complexes (*e.g.*, Cu, Pb, Cd, Zn) (Löfgren 2001, Bäckström et al.

2004, Kaushal et al. 2019, 2020). Metal solubility can also be enhanced due to increased complexation with dissolved Cl^-, SO_4^{2-}, OH^-, and/or CO_3^{2-}.

Salinization can also contribute to alkalinization of urban waters over longer time scales (*sensu* Kaushal et al. 2018), particularly as H^+ is displaced from ion exchange sites in soils from Na^+ and other base cations. There can also be strong relationships between base cations and dissolved inorganic carbon (DIC) in restored streams (Kaushal et al. 2017). Previous work in urban watersheds suggests that chemical weathering of impervious surfaces can enhance river alkalinization by increased concentrations of base cations, bicarbonate, and acid neutralizing capacity in urban streams (Kaushal et al. 2017). These relationships across stream restoration are influenced by road salts on base cation exchange and mobilization of Ca^{2+} and Mg^{2+} in soils (Cooper et al. 2014) or elevated concentrations of Ca^{2+} and Mg^{2+} from impervious surfaces (Sivirichi et al. 2011). Alkaline conditions caused by long-term salinization with base cations favor the release of P from oxyhydroxides in sediments and soils, which contributes to freshwater eutrophication (Duan and Kaushal 2015, Haq et al. 2018a). Microbial nitrification is stimulated at slightly alkaline pH in soils and sediments affected by road salts (Green and Cresser 2008, Green et al. 2008), which contributes to N transformations and coastal eutrophication.

Results and Discussion for Case Study 4: FSS Can Alter Quantity and Quality of Organic Matter in Urban Streams and Stormwater Management Flowpaths in the Mid-Atlantic U.S.

Monitoring results from our Campus Creek study site 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 8). Interestingly concentrations of dissolved organic carbon and total dissolve nitrogen didn’t appear to show strong responses during and after the road salt event at our Campus Creek study site; this suggests that salinization can significantly impact the sources of organic matter, but impacts on total quantity can sometimes be more complex (Figure 8). Overall, our monitoring data show that salinization can have an important effect on the lability and quality of organic matter transported in urban streams.

Changes in the salt concentration, total dissolved solids, specific conductivity, and ionic strength (a measure of ion concentrations in solution given as sum of the molar concentrations of ions multiplied by the valence squared) of freshwater sources has been correlated with changes in quantity and quality of dissolved organic matter (DOM) (Gabor et al. 2015, Gao et al. 2015, Duan and Kaushal 2015, Zhu et al. 2020). Studies suggest that hydrophobic DOM sorption processes are directly affected by changes in salinity (Brunk et al. 1997). Sorption onto particulate matter is one of the primary forms of transformation/transport of hydrophobic DOM in the environment (Brunk et al. 1997). Increases in salinity increase the ionic strength of water resulting in an increase in the sorption coefficients of hydrophobic DOM. Two specific salt ions thought to be important in this process are Ca^{2+} and Mg^{2+} (Brunk et al. 1997) because the introduction of these two positively charged cations into solution increases the transformation of dissolved DOM into particulate form through sorption processes (Brunk et al. 1997). As a result of an increase in sorption, the amount of DOM in particulate phase, specifically the amount covering suspended sediments in the water column has the potential to increase significantly (Brunk et al. 1997). As freshwater sources continue to experience a rise in salinity, more particulate DOM may be mobilized in the form of suspended sediments, potentially affecting freshwater quality because of an overall increase in sediments containing large amounts of known and larger amounts of unknown and uncharacterized DOM compounds.

“Salting in” and “salting out” effects can also influence the concentration and quality of DOM in stormwater management BMPs. “Salting in” refers to the positive correlation between ionic strength and the solubility of organic matter such as proteins, for example. Salting in tends to occur at lower ionic strength when the addition of salt ions can increase the solubility of proteins. “Salting out” refers to the process by which water molecules will attach themselves to salt ions, which decreases the number of attachments water can make with proteins. Salting out tends to occur at higher ionic strengths when proteins can form protein-to-protein bonds that become hydrophobic. The proteins then precipitate out of the water column. At higher ionic strengths, salting out can decrease the concentrations of DOM in solution. The difference between salting in and salting out is controlled by the ionic strength of the solution and the concentration of various salt ions. At low salt concentrations, proteins will dissolve more easily with increases in ionic strength. At high salt concentrations protein will precipitate out with increases in ionic strength. The Hofmeister series is a classification of ions in order of their ability to salt in or salt out proteins. The Hofmeister series for anions and cations is presented below (the order is from highest to lowest ability to salt in proteins (Hyde et al. 2017): *Anions:* $CO_3^{2-} > SO_4^{2-} > S_2O_3^{2-} > H_2PO^{4-} > F^- > Cl^- > Br^- \approx NO_3^- > I^- > ClO_4^- > SCN^-$; *Cations:* $(CH_3)_4N^+ > Cs^+ > Rb^+ > NH_4^+ > K^+ > Na^+ > Li^+ > Mg^{2+} > Ca^{2+}$. FSS from different sources increases the concentrations of some of these anions and cations in urban waters and can affect the solubility of organic matter and therefore, its quantity and quality.

Results and Discussion for Case Studies from the Literature: Evidence for Retention and Release of Multiple Contaminants along Stormwater Flowpaths

Our synthesis of case studies from North America and Europe showed similar findings to our original data and results from the Mid-Atlantic U.S. Although outflow retention metrics differed among elements within a particular stormwater BMP, the dominant mechanisms of retention and release were similar across all stormwater BMPs. In some cases, we simply reported increases or decreases in concentrations or loads of contaminants in stormwater BMPs (Table 2). In other cases, we reported changes in load removal efficiencies and positive removal efficiencies indicate net retention of a contaminant within a stormwater BMP. Negative removal efficiencies indicate net contaminant release from a stormwater BMP. For example, chloride ranged from −130% Cl^- export to a 94% decline along flowpaths from inflow to outflow, with a 38.25% average retention. The primary mechanisms for the declines in Cl^- concentrations were infiltration and storage. Sodium showed significant retention along flowpaths compared with the rest of the base cations

(Mg^{2+}, Ca^{2+}, and K^+), similarly to our results from the Mid-Atlantic U.S. (Supporting Information). Na^+ retention measured in a stormwater management pond, bioretention cell, and a bioswale showed consistent decreases in concentrations from 10 to 47% due to storage and infiltration. Mg^{2+}, Ca^{2+}, and K^+ all showed patterns of increasing concentrations along stormwater management flowpaths due to cation exchange processes. Instead of retention, these elements typically showed patterns of release with values of −63% - 1230%, −6%-152%, and −22% - 211% for Mg^{2+}, Ca^{2+}, and K^+, respectively. In the stormwater management pond, these elements showed patterns of retention. Interestingly, bioswales showed the highest values of release for Mg^{2+}, Ca^{2+}, and K^+. Nutrients, including N and P, primarily showed retention. N concentrations ranged from 16–100% retention, with an average value of 33.5% retention. On the other hand, P showed variable retention and/or release in the constructed wetland and bioretention. The primary retention mechanisms for N and P were denitrification and microbial uptake respectively along the stormwater management flowpaths.

Part 3. Knowledge Gaps and Emerging Research Frontiers

What are the current knowledge gaps and research frontiers?

More work is necessary to evaluate the effects of reduced applications of road salt on decreased concentrations of Na^+ and other ions in urban streams and the potential for ecosystem recovery (Figure 2). More work is also needed to elucidate the impacts of FSS on restored ecosystems and stormwater management features and whether stormwater management is either impaired by FSS or can be implemented as a BMP to ameliorate the effects of FSS. For example, salt accumulation in restored floodplains (Figure 3) can impact the efficacy of stream restoration on enhancing water quality; in a stream restored to repair and reduce erosion and improve nitrogen uptake via reconnected banks (Kaushal et al. 2008), high Cl^- concentrations from salt runoff from a major highway accumulated in the groundwater and sustained elevated salinity year-round (Cooper et al. 2014). Other stormwater management approaches like regenerative stormwater conveyance systems (RSC), designed to reduce flashy runoff, increase groundwater infiltration, and improve nitrogen uptake (Duan et al. 2019), can contribute to Cl^- storage in groundwater water or shallow surface pools (Figure 3), thereby contributing to chronic, elevated Cl^- concentrations in the stream (Fanelli et al. 2019). Such hydrologic storage of Cl^- inputs has been shown to occur in groundwater beneath detention ponds (Snodgrass et al. 2017) and in urban restored stream-floodplain systems (Ledford et al. 2016), suggesting that stormwater management may contribute to chronic salinity. Streams draining watersheds with stormwater management ponds had consistently higher specific conductance and Cl^- concentrations during base flow conditions, suggesting that stormwater management can contribute to groundwater plumes of Cl^- and Na^+ that sustain elevated salinity in streams throughout the year (Snodgrass et al. 2017). The relationship between salt inputs and elevated salinities may be obscured by this groundwater retention (Reisinger et al. 2019), making it more difficult to assess impacts from various sources. However, there can be increased concentrations of salt ions and loads in streams draining stormwater management BMPs, suggesting the importance of retention and release of salt ions along hydrologic flowpaths (Figure 6). Furthermore, there may be associated effects on contaminant mobilization of elements like P along hydrologic flowpaths (Figure 6), which warrants further study.

While salinity may be chronically elevated due to groundwater retention, severe peaks of salts may be attenuated by stormwater features by shifting salt pulses to “press regimes” in urban streams where salinity peaks are muted but levels remain chronic (Fanelli et al. 2019). These peaks can occur in winter due to road salt use, and there can be significant relationships between lower stream water temperatures during winter and concentrations of ions and metals (in addition to conductivity as a proxy for salinity, temperature may be another proxy in some cases) (Figure 7). It is important to note that these pulses in salt ions associated with road salting events also are characterized by elevated levels of other mobilized contaminants (Figure 8). Whether these chemical cocktails or pulses are more or less stressful for aquatic organisms remains a subject for assessment (Mount et al. 1997, Cormier et al. 2013). Nevertheless, stormwater management may be effective at reducing salinity peaks to some extent. For example, wetlands that formed naturally in stormwater features created conditions that reduced the timing and peaks of salinity pulses from road salts while also reducing peak temperatures in an urban ecosystem in North Carolina, USA (Maas et al. 2021). Peak salinities were reduced by 94% and pulses were delayed by 45 days due to storage of salt-laden water in the ground and subsequent slow release over time (Maas et al. 2021) (Table 2).

Hydrologic disconnection between streams and floodplains exacerbates Cl^- pulses. Daley et al. (2009) recommended reducing first-flush Cl^- pulses often seen in flashy urban systems (Cooper et al. 2014) by engineering stormwater management that increases hydrologic residence and reconnects surface water and groundwater. Slossen et al. (2021) showed that channelized streams with armored banks and limited ground water connection effectively delivered Cl^- from road salts downstream, whereas streams with higher surface water-ground water connection delivered 50% less Cl^- than the channelized streams. Extreme disconnection such as occurs when streams are placed in pipes and conduits (buried), significantly increases stream velocity and discharge (Pennino et al. 2014), leading to more rapid downstream transport of pollutants, and reducing stream functions such as microbial activity and respiration, N uptake, and algal abundance (Beaulieu et al. 2014, Pennino et al. 2014, Arango et al. 2017). Conversely, “daylighting” streams, whereby buried streams are released from conduits and allowed to interact with groundwater, may significantly improve stream function (Beaulieu et al. 2015) and potentially help attenuate the effects of FSS.

Stormwater management features may dilute elevated Cl^- concentrations by increasing groundwater-surface water interaction (Fanelli et al. 2019). Ledford and Lautz (2015) found that degraded urbanized channels were impacted by road salt runoff whereas, downstream, connected stream reaches were buffered by groundwater discharge lower in Cl^- concentration. Therefore, the authors suggested that restored streams that reconnect floodplains may attenuate seasonal Cl^- fluctuations by storing high salinity runoff in the ground and discharging water throughout the year. It is unknown whether such chronic releases from groundwater to streams are less stressful to aquatic life than highly flashy, pulses of water that contain extreme salt concentrations that may otherwise flush through the system to downstream waters (Kaushal et al. 2014). However, in either situation, salt loads accumulate in receiving waters, including estuaries, where increasing salinity trends cause unique stresses on aquatic life such as increased alkalinity (Kaushal et al. 2017).

More directed restoration efforts may be necessary to address salinization. Lessons may be taken from restoration of urban streams where re-establishing functional riparian zones is key to improving ecological function of degraded streams. Studies at urban riparian ecosystems suggest that, effectively restoring riparian soils is dependent upon establishing deep-rooted vegetation to increase the depth of the microbially active zone (Gift et al. 2010). For example, denitrification, nitrification, and C mineralization are dependent upon microbial populations and soil respiration (Weitzman et al. 2014). Therefore, re-establishing connected water tables with highly organic soils is key to functional restoration (Gift et al. 2010). In agricultural systems where long-term irrigation with saline waters and/or poor crop management produces sodic soils, more active management is necessary. Sodic soils suffer structural problems from excess Na^+ including slaking, swelling and dispersion of clay, surface crusting and hardsetting that affect water and air movement in soils, reduce water holding capacity, root penetration, seedling emergence, and increase runoff and erosion and, ultimately, cause imbalances in plant nutrient availability (Qadir and Oster 2004). Restoration of sodic and saline-sodic soil systems is promoted by providing calcium (Ca^{2+}) to replace excess Na^+ from the cation exchange sites, often through costly gypsum amendments which can reduce sodicity by up to 62% (Qadir and Oster 2004). Vegetative bioremediation can be effective (up to 52% reduction of sodicity) but is often highly variable. Salt tolerant plants such as sesbania (*Sesbania bispinosa*), Sudan grass (*Sorghum* X *drummondii*) or Kallar grass (*Laptochloa fusca*) are grown and cropped to uptake and remove excess soil salts. A benefit of growing these grasses is that soil availability of nutrients like P, Zn, and Cu may increase (Qadir and Oster 2004). Efficacy of vegetative bioremediation may be limited under conditions of very high levels of salinity and/or sodicity where crop growth is variable and patchy (Qadir and Oster 2004). However, long-term (50 yr) implementation of forest management practices were found to significantly improve soil sodicity and increase soil organic C content and Ca^{2+} while decreasing soil pH (Pandey et al. 2011).

Organic mulching is a key to effective management of sodic soils because it provides organic matter that can be a source of Ca^{2+} and Mg^{2+} that enhances exchange of Na^+ from soils and improves soil porosity thereby allowing for better leaching of Na^+ (Saifullah et al. 2018). Applying manure and pyrite increases soil methanotrophs in saline rice fields, thereby reducing methane (CH_4) production (Pandey et al. 2011). In some cases, biochar soil amendments may help remediate salt contaminated soil, but effectiveness is dependent upon tailoring biochars to contaminants of concern (Saifullah et al. 2018). A limitation of biochar use is feedstock sourcing and cost-effective production of biochars. Understanding soil bacterial communities and rhizosphere ecology, and how to apply various cyanobacteria, salt tolerant bacteria, and methanotrophs to remediate salty and sodic soils will be critical to restoring ecosystem function, especially in agricultural systems (Pandey et al. 2011). Ultimately, preventing salt damage is dependent upon water managers, stakeholders, and scientists collaborating to identify cost-benefits of best management practices (Canedo-Arguelles et al. 2016).

Critical questions remain about which stormwater features, including detention and retention ponds, rain gardens, natural or accidental wetlands, bioswales, and other green infrastructure, effectively address salinized runoff (Passeport et al. 2013) and how to identify optimal site selection for each approach (Martin-Mikle et al. 2015). Little is known about how ions and/or associated chemical cocktails are captured or released across stormwater management features or why features may have different mobilization rates. These processes are likely dependent upon hydrogeologic process such as surface water-groundwater interactions, bank storage, precipitation, and discharge/recharge (Ledford et al. 2016) along with soil type and organic matter availability (Kincaid and Findlay 2009, Gustavsson et al. 2012). Estimates of the capacity of stormwater systems for subsurface salt storage range across orders of magnitude (Ledford et al. 2016) and must be improved to understand the capacity for salt attenuation among various BMPs. Stormwater management in predominantly lake systems may be at particular risk of salt contamination as accumulation is likely to far exceed flushing rates (Dugan et al. 2017, McGuire and Judd 2020). Ancillary or unexpected consequences of stormwater management must also be considered such as accumulation of salts in soils and groundwater, mobilization of various ions and metals (Galella et al. 2021), longevity of the project, and trade-offs in outcomes (Wood et al. 2022). Stormwater management BMP's may accumulate ions or metals and, in turn, may require remediation (*e.g.*, phytoremediation) or disposal of contaminated soils.

Top 10 Questions for Future Research

As described above, many questions remain regarding the impacts of FSS on water quality, ecosystem functions, and services associated with stormwater BMPs and green infrastructure. To better understand critical research and information needs, we have been synthesizing questions from a wide range of stakeholders, practitioners, environmental managers, and researchers. Recently, we communicated with these broader groups in a US Environmental Protection Agency webinar on freshwater salinization and chemical cocktails https://www.epa.gov/water-research/water-research-webinar-series (Mayer et al. 2021). We received approximately 130 questions covering a wide range of science and management issues from among 1,600 attendees representing all 50 US States (and Washington DC, Guam, and Puerto Rico) and 21 countries. What follows is a list of the top 10 emerging research questions, based on frequency of inquiry from the audience and overlap of topics, related to investigating potential FSS impacts on the environment and human health, and how to better manage FSS to avoid contaminant risks.

1. What role does seasonality play in the impacts of FSS on stormwater BMPs? Are water quality impacts heightened during winter months when salt is applied for road safety, or does it seem like there are significant impacts year-round?

2. What types of land-use patterns make stormwater BMPs more vulnerable to FSS? Is FSS primarily important in areas where there is increased urbanization/developed land-use where runoff is flashy or can it also impact the function and services of green infrastructure in rural areas?

3. How does FSS impact groundwater concentrations of contaminants over time? What are long-term trends in salts, hardness, and metals in groundwater

flowpaths underneath stormwater BMPs (particularly more infiltration-based approaches)?

4. In treatment technologies such as bioretention, are salts, nutrients, metals, and other contaminants temporarily stored in sediments and then released to groundwater flowpaths later (internal loading from sediments) during the stormwater BMP life cycle?
5. What are the long-term impacts of salinization on soil formation and fertility in stormwater BMPs and on accumulation of major ions, nutrients, and metals? Will changes in organic matter cause shifts in ecosystem functions and services and potential toxicity to certain forms of aquatic life?
6. Are there any risks to public health owing to salt impairment of groundwater and do stormwater BMPs contribute to or ameliorate this risk?
7. Which has greater impacts on water quality and ecosystem functions and services associated with stormwater BMPs: acute salt pulses to stormwater BMPs and urban streams during flashy runoff or chronic and prolonged delivery of salt ions in streamflow (potentially exceeding threshold levels for specific ecosystem functions, services, and/or aquatic life)?
8. Is it better to prioritize and target salt reductions during seasons (*e.g.*, early spring) where biology is more active and susceptible life stages such as eggs and larvae are present?
9. Is the growing use of stormwater infrastructure (that direct stormwater, salts, and contaminants into groundwater through infiltration) creating groundwater contamination problems that we will see as problems for years (decades) to come?
10. Under what hydrologic conditions and in which types of soils, minerals and media in stormwater BMPs are salt ions retained and contaminants released? Which cation exchange capacity, grain size, organic matter content, soil moisture, and redox gradients influence retention, release, and transformation of salts, nutrients, metals, and organics in response to FSS?

Conclusions

Previous work has seldom evaluated the holistic environmental impacts of FSS on contaminant mobilization across urban streams and floodplains. Freshwater salinization warrants recognition as a more complex process than increases in concentrations of salt ions alone and more research is needed on the effects of different salt ions and implications for all ecosystems. There are many lingering questions regarding the effects of different salt ions commonly used as road deicers, on mobilization of chemical cocktails of nutrients and metals across a broad range of urban streams. More work is necessary to also quantify changes in the magnitudes and durations of chemical cocktail loading in response to winter deicing events. Tracking magnitudes and duration of mobilization of chemical cocktails seasonally due to salinization is an ongoing challenge. More information is needed on how chemical cocktails of salts, metals, and nutrients vary in response to FSS across urban streams, which is critical for managing nonpoint source pollution in urban waters. Estimated rates of nutrient and metals mobilization can better inform protocols for enhancing the effectiveness of stormwater BMPs and stream restoration strategies. Future comparisons of the effects of different levels of salts and different deicer ions will also provide critical information regarding critical thresholds of salinity for contaminant mobilization. Analysis and synthesis of new empirical data showing effects of varying levels of different salt ions can provide critical information regarding critical thresholds of salinity for contaminant mobilization across stormwater management and stream restoration sites and can help identify which salt ions have the greatest impact on nutrients and metals. Our synthesis and analysis in this paper is among the first to quantify changes in the peaks and persistence of different chemical cocktails in response to winter deicing events and ecosystem impacts in urban stormwater management and stream restoration. Anticipating and addressing the effects of salt ions on mobilization of nutrients and metals can better inform plans for effective stream restoration and stormwater management strategies designed to improve urban water quality.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

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Relevance to SUSE5 Special Issue:

Our paper provides results that document the response of urban streams and stormwater management systems to Freshwater Salinization Syndrome. It will also provide future research needs on this topic related to water quality problems related to urban stream restoration.

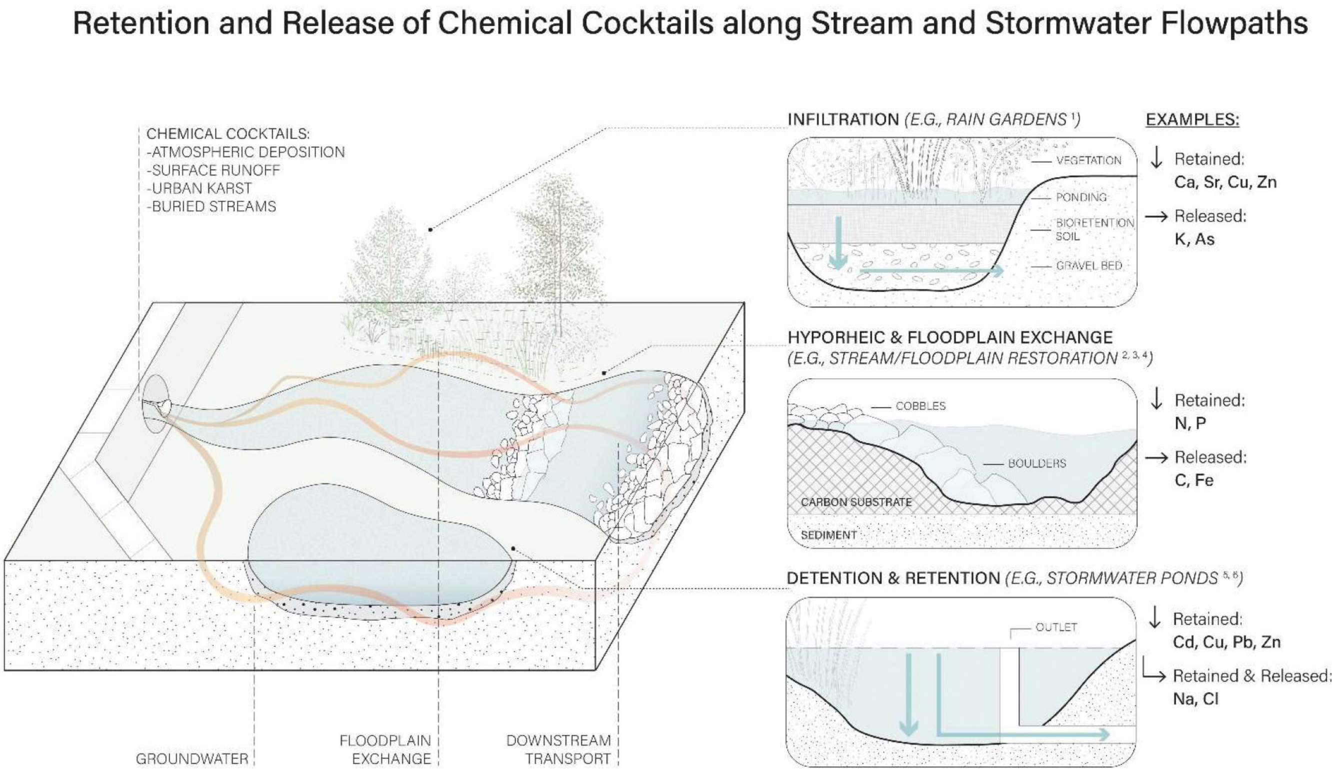

Figure 1.

There can be both retention and release of contaminant cocktails along hydrologic flowpaths through urban streams and various forms of stormwater management. Retention and release mechanisms can vary for different chemical cocktails. Examples of retention and release of different contaminants are shown in the illustration and referenced from the following studies: [1] Flanagan et al. 2019, [2] Duan et al. 2019, [3] Williams et al. 2016, [4] Cizek et al. 2018, [5] Barbier et al. 2018, [6] Semadeni-Davies 2006.

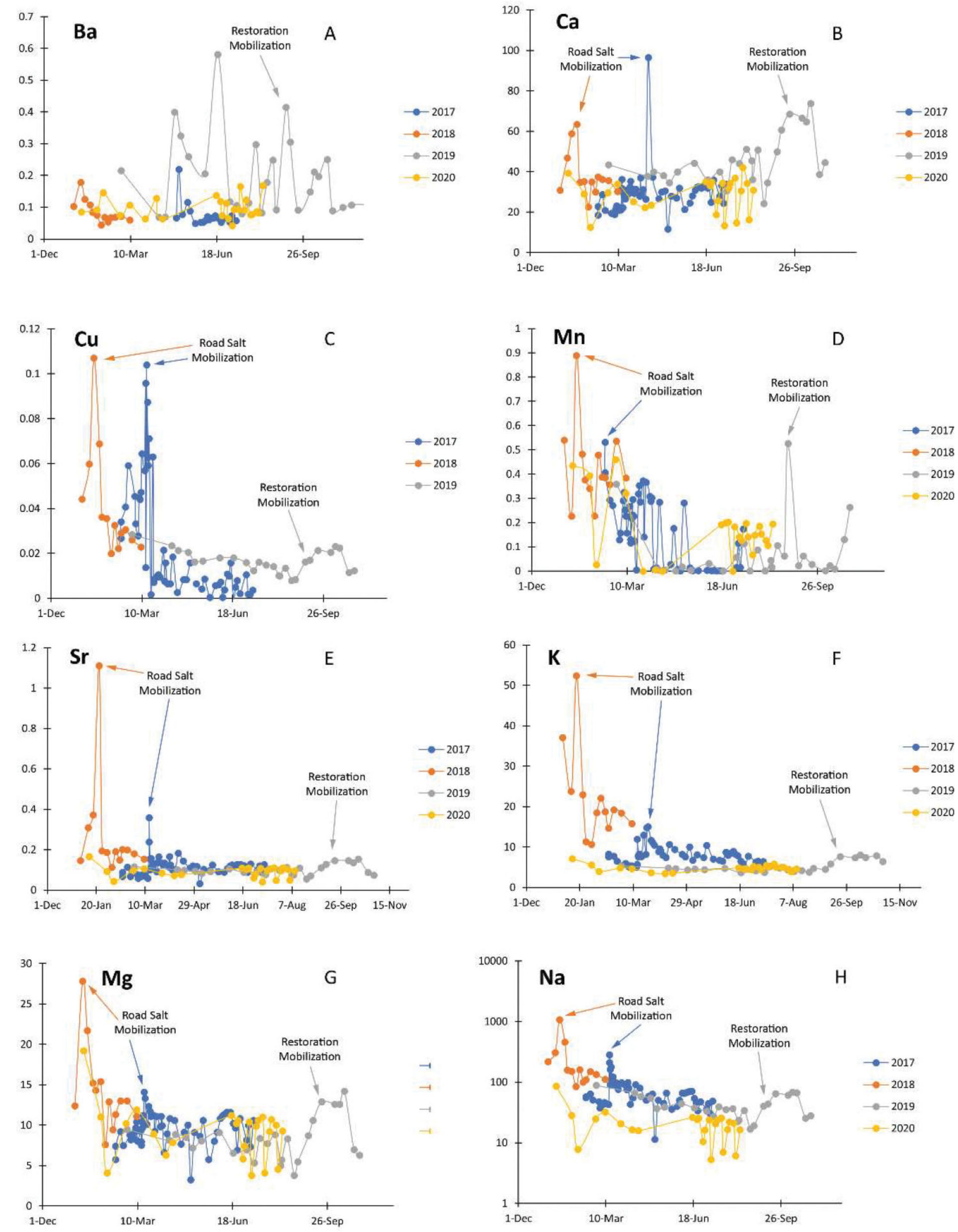

Figure 2.

Variations in elemental concentrations in Campus Creek, MD, USA, 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 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.

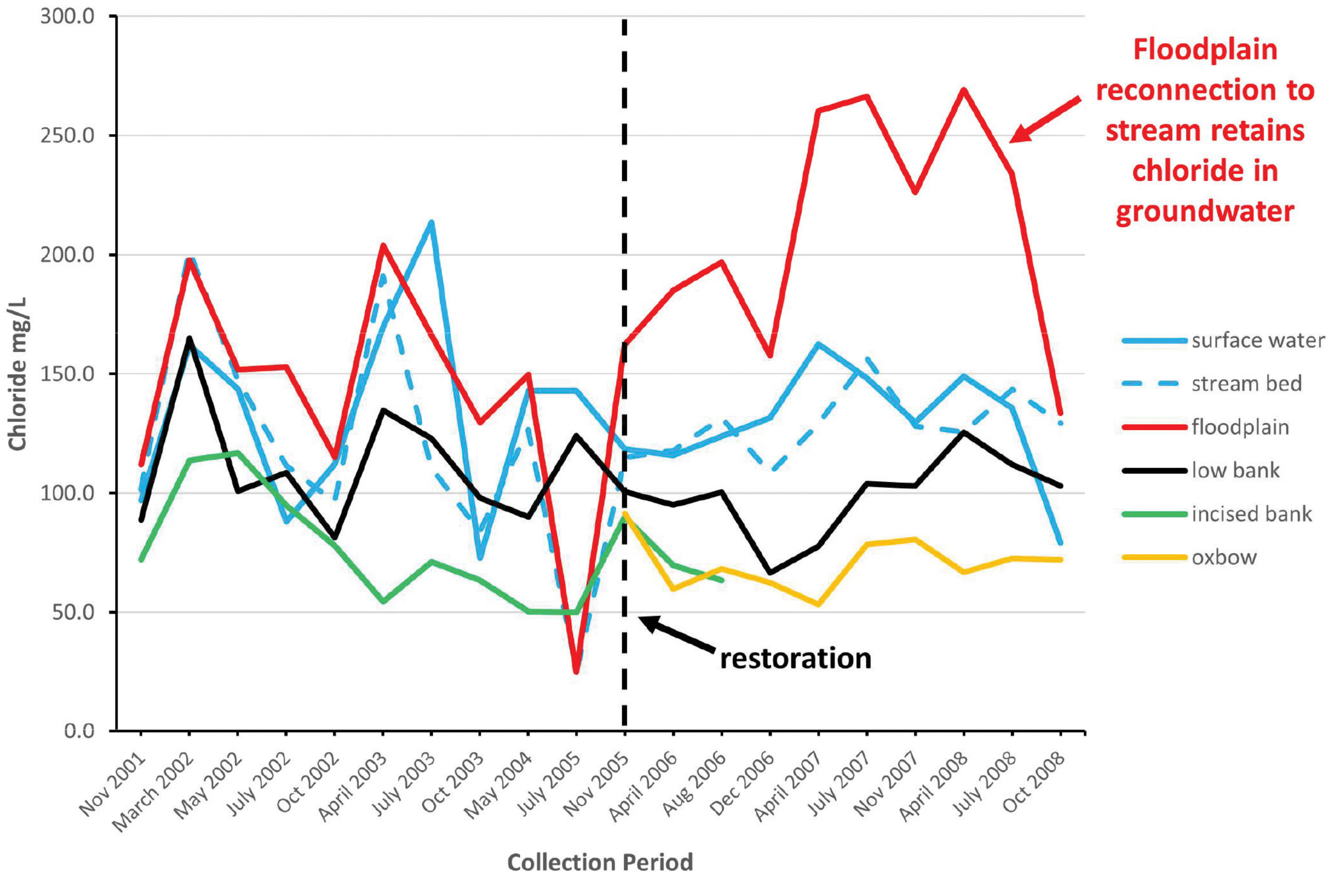

Figure 3.

Changes in Cl⁻ concentrations before and after stream restoration at Minebank Run, an urban stream in Baltimore, MD, USA. Cl⁻ concentrations increased in the restored floodplain following stream restoration likely due to the effects of floodplain reconnection on chemical retention processes (Kaushal et al. 2008, Mayer et al. 2010, Mayer et al. 2022).

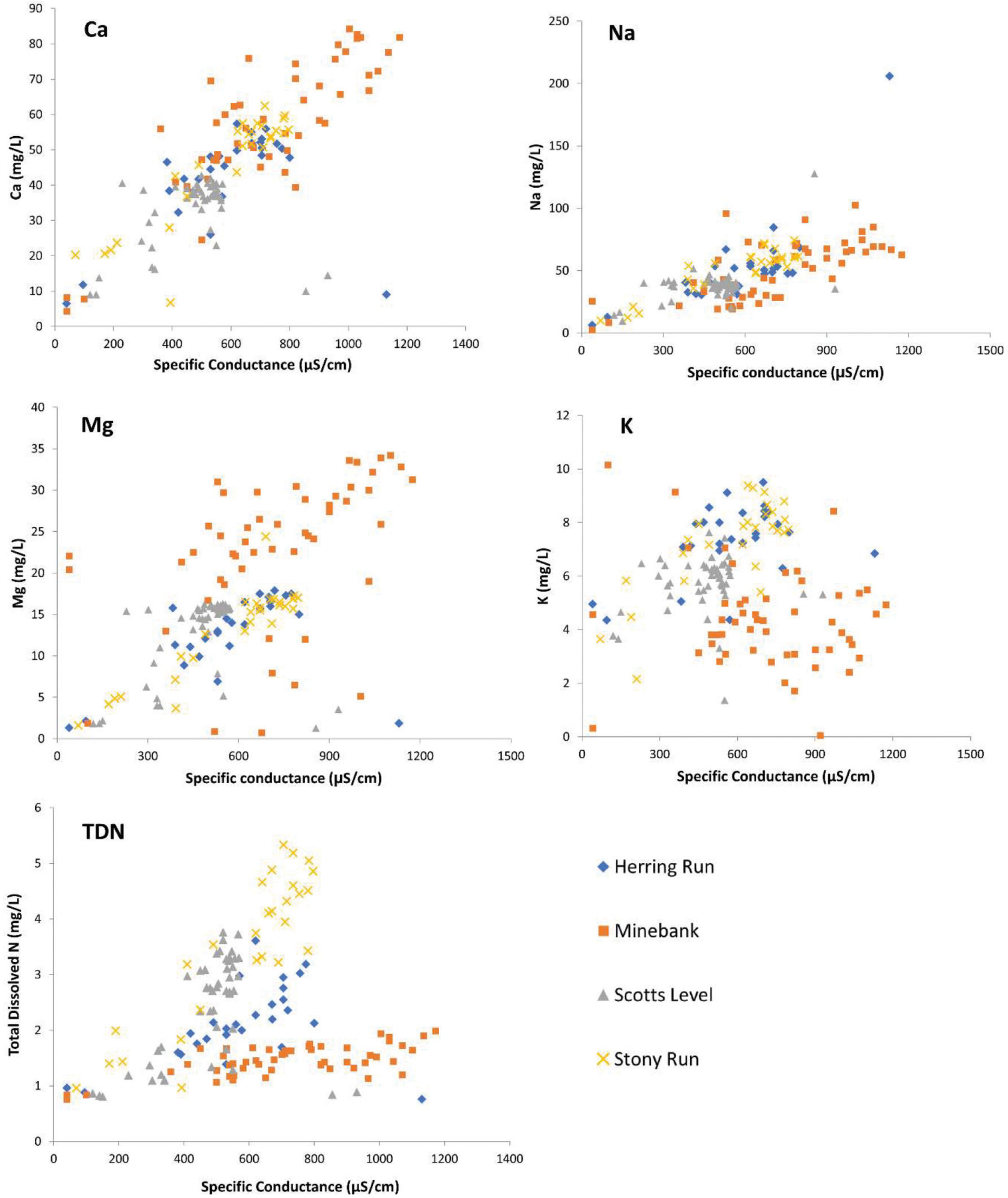

Figure 4.

Relationships between specific conductance and base cation concentrations in restored streams (Minebank Run, Stony Run, Scotts Level Branch) and an unrestored stream (Herring Run) in Baltimore, Maryland, USA (Top Panel). Relationships between specific conductance and nitrate-N concentrations in restored streams (Minebank Run, Stony Run, Scotts Level Branch) and an unrestored stream (Herring Run) in Baltimore, Maryland, USA.

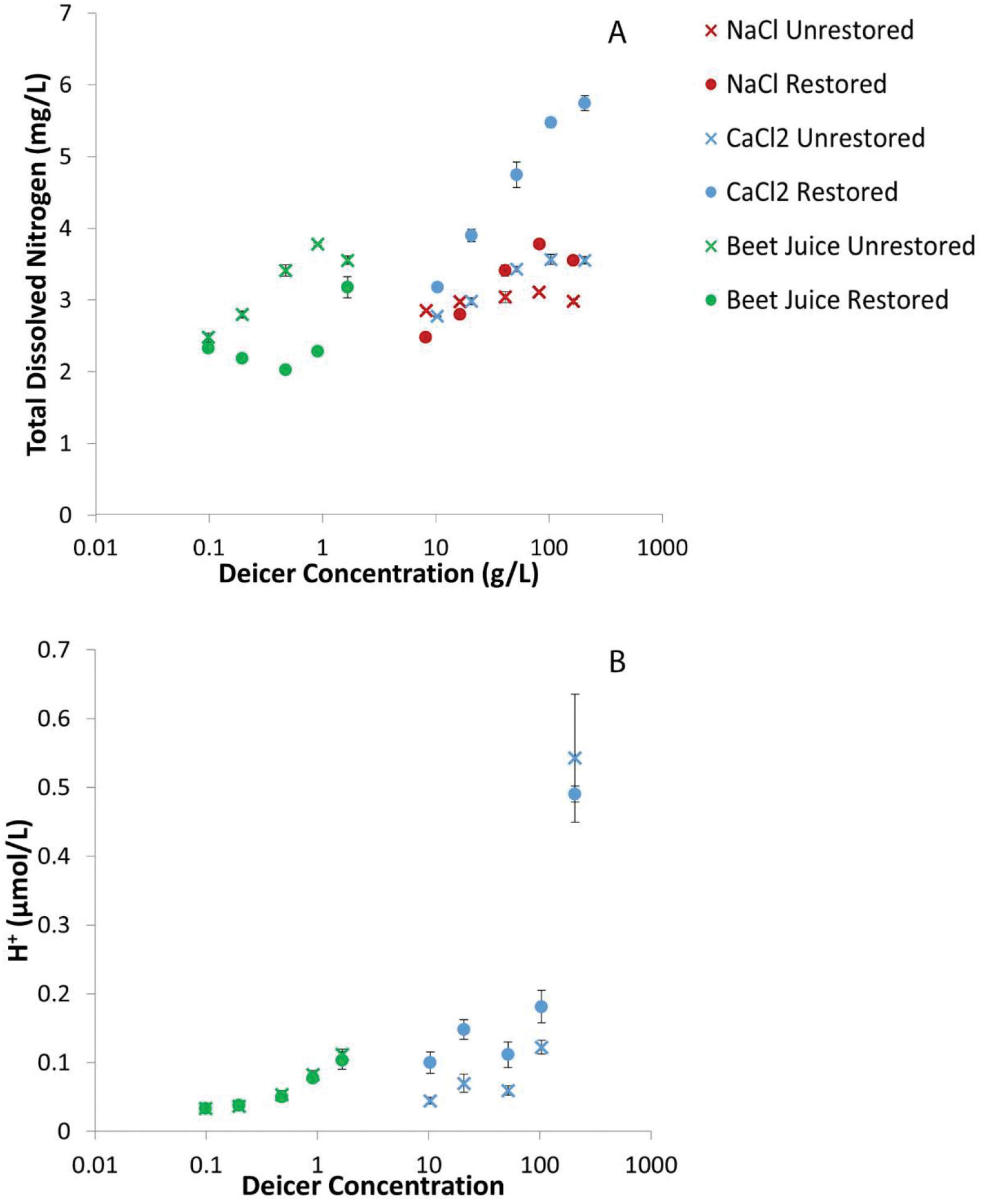

Figure 5.

Experimental salinization can cause a release of N from sediments to overlying streamwater in Scotts Level Branch, a restored stream in Baltimore, Maryland, USA (top panel). Effects of experimental salinization on increasing H$^+$ ion concentrations (acidification) in incubations of stream sediments with streamwater from Scotts Level Branch (bottom panel). Experimental methods are based on Duan and Kaushal (2015), Haq et al. (2018), and Kaushal et al. (2019).

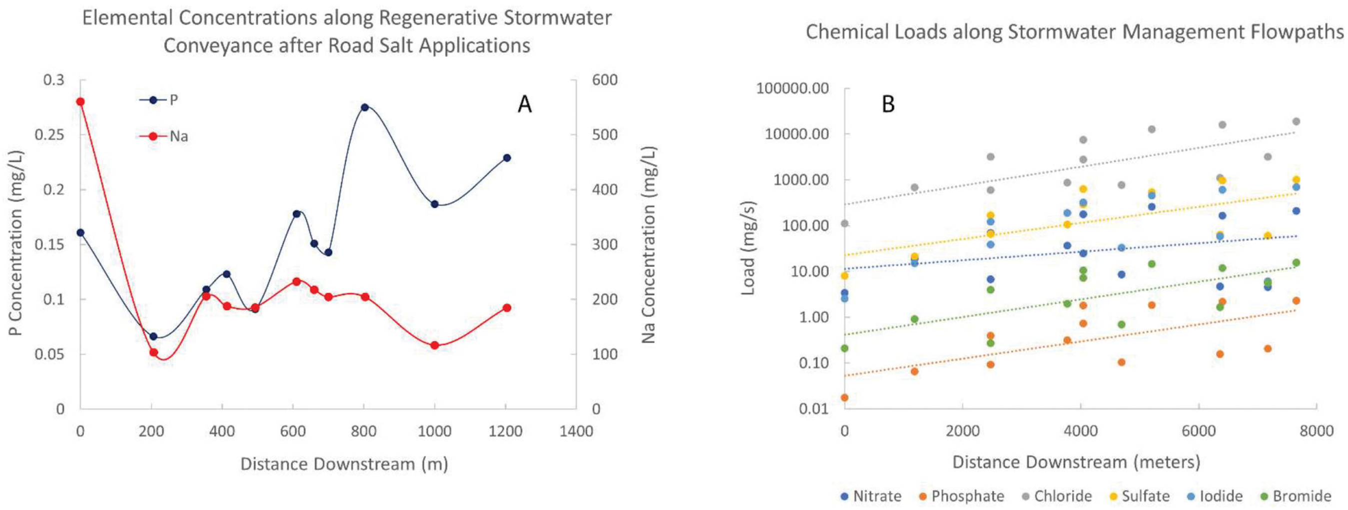

Figure 6.

Downstream changes in elemental concentrations in Campus Creek, an urban stream in College Park, MD, USA, which was restored using regenerative stormwater conveyance (Kaushal et al. 2019, 2020, 2021). Na^+ concentrations decrease along the hydrologic flowpath whereas P concentrations increase potentially due to ion exchange and other geochemical changes (Top Panel). Red Run is an urban stream in the Gwynns Falls watershed in Baltimore County, MD, USA, draining stormwater management structures. There were downstream changes in loads (mass transport per unit time) of anions in Red Run (Bottom Panel); further details on the Red Run study site can be found in our methods section and elsewhere (Pennino et al. 2016).

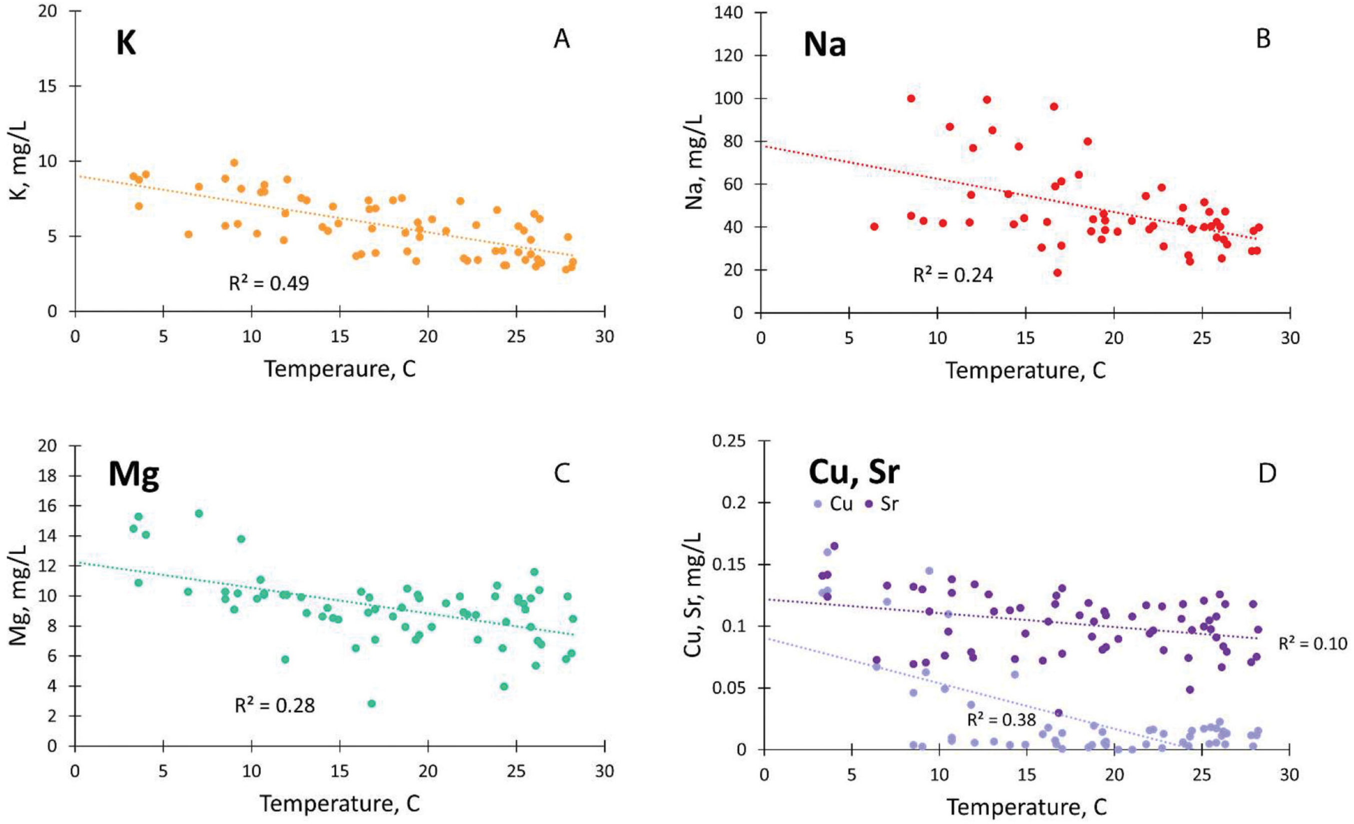

Figure 7.

Relationships between stream water temperature and base cation and trace elemental concentrations in Paint Branch, a stream that was restored with floodplain reconnection, located at the University of Maryland campus in College Park, MD, USA.

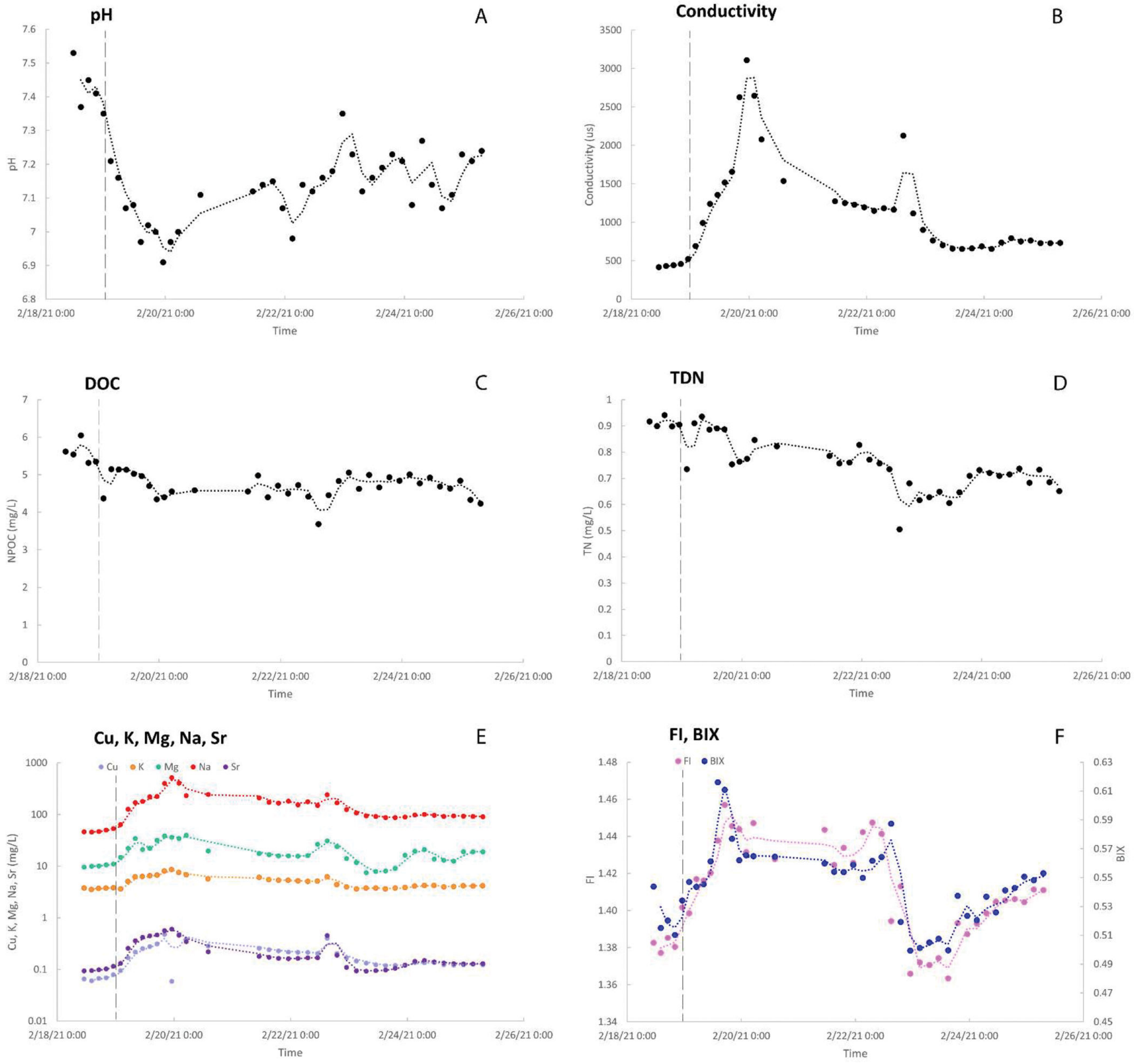

Figure 8.

Pulses in water quality impacts during a winter road salt event in Campus Creek, an urban stream in College Park, MD, 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.

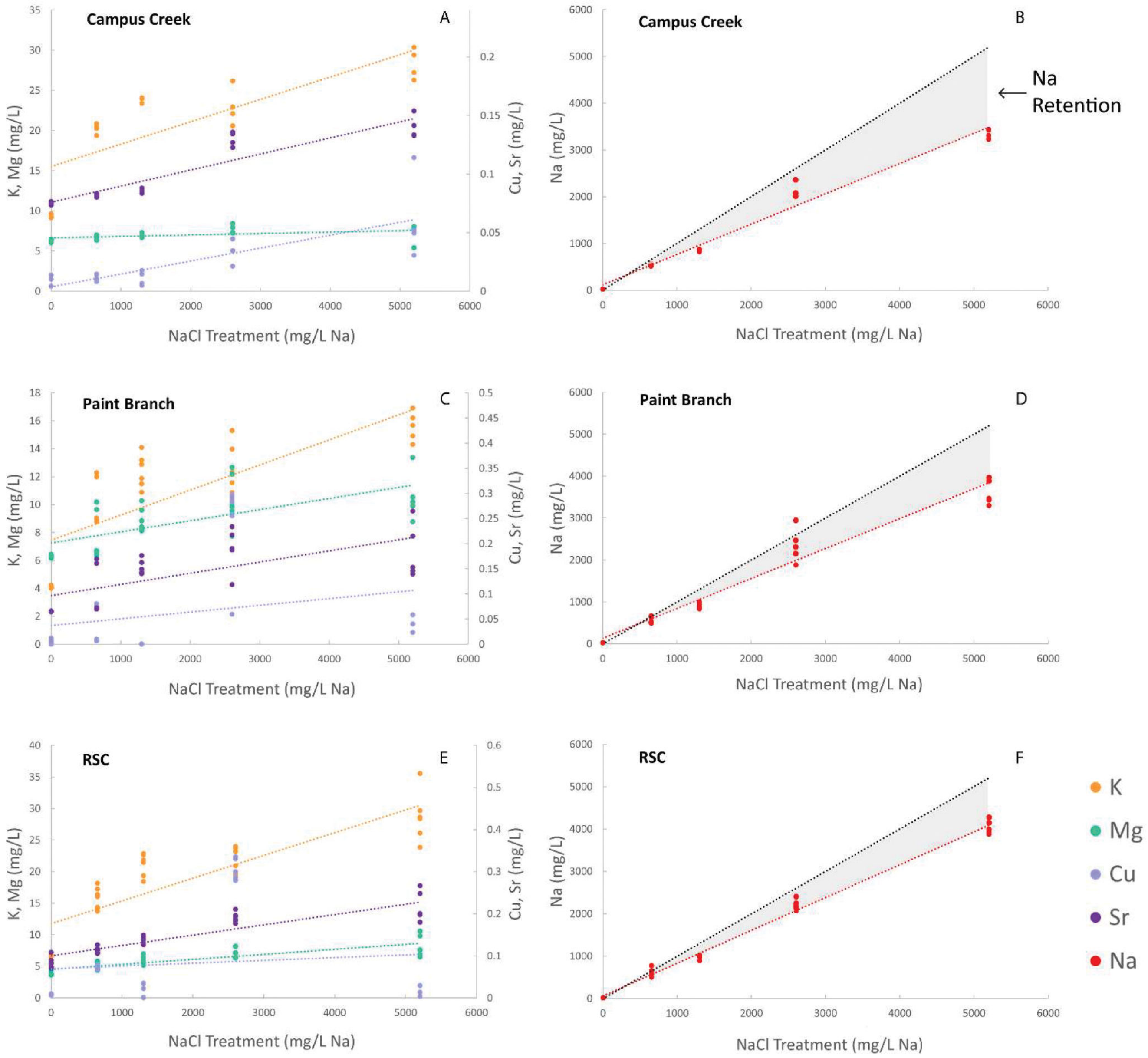

Figure 9.

Retention and release of base cations are shown during experimental salinization experiments from one site along Paint Branch with a reconnected floodplain and two sites along Campus Creek, one with regenerative stormwater conveyance (RSC) and one without. Campus Creek and Paint Branch are two restored streams flowing through the University of Maryland campus in College Park, MD, USA. Experimental incubations consisted of stream sediments incubated with streamwater. Experimental additions of NaCl at varying levels resulted in significant retention of Na^+ and release of other base cations and metals. Na^+ retention was calculated based on how much Na^+ was added during the experiment and how much was present in overlying streamwater after the incubation (gray shading represents Na^+ retention or the difference between how much Na^+ was added and how much was measured after the incubation). Details on methods can be found in Duan and Kaushal (2015), Haq et al. (2018), and Kaushal et al. (2019).

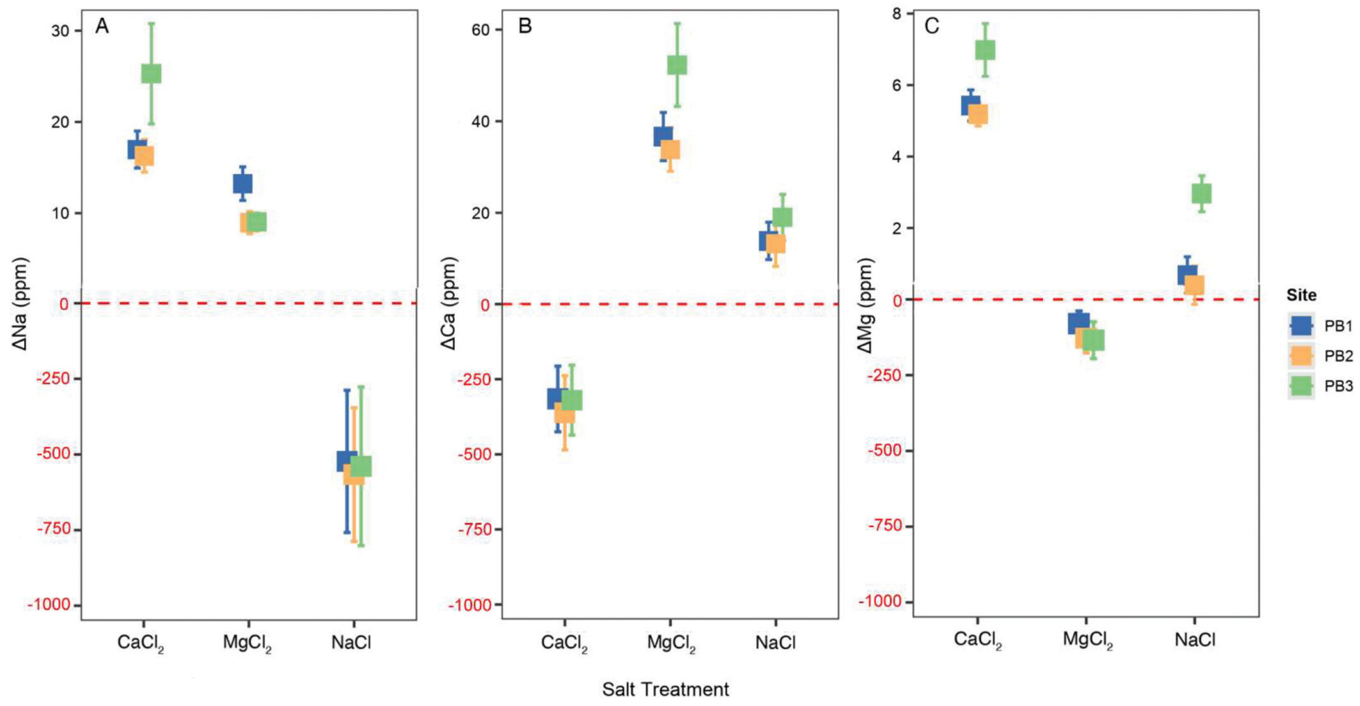

Figure 10.

Paint Branch is a stream restoration with floodplain reconnection flowing through the University of Maryland campus in College Park, MD, USA. Positive values above 0 (the red dashed line) indicate ‘release’ whereas negative values indicate ‘retention.’ We observed a release in base cations due to cation exchange from stream sediments in response to experimental salinization of streamwater in Paint Branch. Conversely, cations that were added experimentally showed retention in stream sediments in Paint Branch (indicated in red). Data are from integrating triplicate incubation experiments at salinization levels of 2, 4, 6, and 8 g/L of chloride. Details on methods can be found in Haq et al. (2018) and Kaushal et al. (2019).

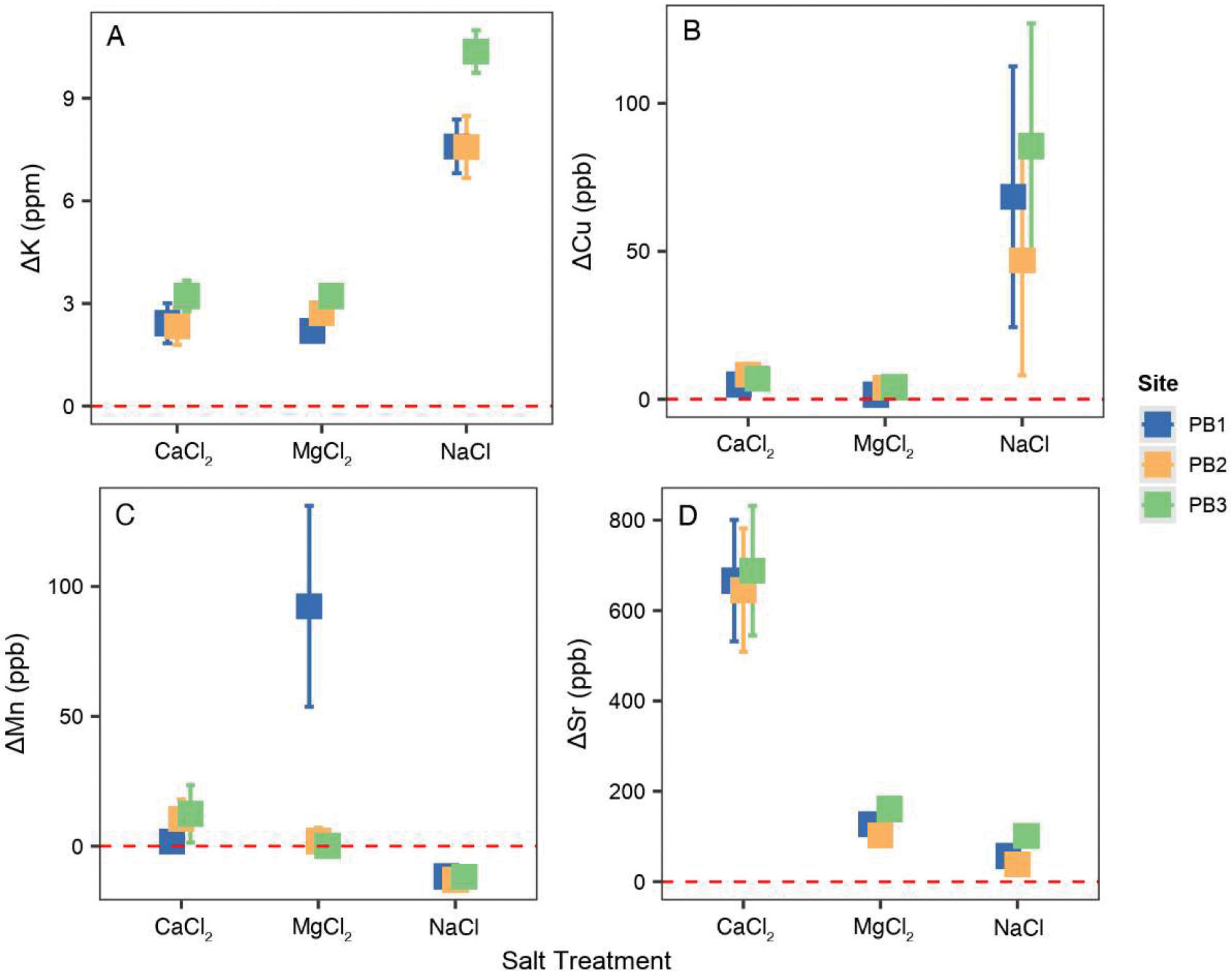

Figure 11.

Paint Branch is a stream restoration with floodplain reconnection flowing through the University of Maryland campus in College Park, MD, USA. Positive values above 0 (the red dashed line) indicate 'release' and negative values indicate 'retention.' There was a release of K^+ and trace elements due to cation exchange in sediments from Paint Branch in response to experimental salinization of streamwater. Data are from integrating triplicate incubation experiments at salinization levels of 2, 4, 6, and 8 g/L of Cl^-. Details on methods can be found in Haq et al. (2018) and Kaushal et al. (2019).

Table 1.

Descriptions of study sites where we conducted monitoring of water chemistry and/or collected sediments and streamwater for laboratory salinization experiments.

Site	Metro Area	Latitude	Longitude	NLCD 2016 % Impervious	Drainage Area (km^2)	Year Restored	Restoration Techniques
Campus Creek	DC.	38°59’34.7” N	76°56’9.10” W	26.5	1.76	2019	-Regenerative stormwater conveyance (RSC)
Paint Branch	DC.	38°59’28.8” N	76°56’7.50” W	31.7	79	2015	-Bank stabilization -Floodplain reconnection -Habitat improvements
Minebank Run (Downstream)	Baltimore	39°24’41.4” N	76°33’15.8” W	21	5.3	2005	-Channel stabilization -Re-vegetation -Floodplain reconnection
Herring Run	Baltimore	39°19’4.7” N	76°33’18.5” W	25	5.5	n/a	n/a
Scotts Level Branch	Baltimore	39°21’41.7” N	76°45’42.3” W	29	1.0	2014	-Bank stabilization -Flow control -Habitat improvements
Stony Run	Baltimore	39°20’22.2” N	76°37’32.5” W	28	2.0	2009	-Bank stabilization -Floodplain reconnection
Red Run	Baltimore	39°24’16.6” N	76°46’46.6” W	29.2	19.1	n/a	-Extensive upstream stormwater management systems (e.g., detention, bioretention, sand filters)

Table 2.

Synthesis of elemental retention and release in stormwater management Best Management Practices (BMPs). In some cases, we simply reported increases or decreases in concentrations and loads of contaminants in stormwater BMPs. In other cases, we reported changes in load removal efficiencies. Positive load removal efficiencies indicate net retention of a contaminant within a stormwater BMP. Negative load removal efficiencies indicate net contaminant release from a stormwater BMP. If calculations of reduction percentages for loads were not given in a citation, they were estimated using: [1-(Outflow/Inflow)] ×100.

Green Infrastructure and definition	Ions, Organic Matter, nutrients, metals associated with F SS	Inflow Pollution Source	Outflow Retention Metrics	Mechanism	Substrate	Citations
Stormwater management ponds (SWMPs)/Retention Ponds Permeable pool of water that stores stormwater until it is displace by the next inflow event. (Semadeni-Davies 2006)	Base cations (Na^+, Mg^{2+}, Ca^{2+}, K^+)	Road salt	Conc. decrease: Na^+: 10%; Ca: 6%; K: 11%; Mg: 63%	Infiltration: salt percolates into the ditch with permeable soil. Salt stored in the surficial layers of soil	Concrete slab at the bottom with soil on top; Soil	Semadeni-Davies 2006, Barbier et al. 2018
	Cl^-	Road salt and Meltwater Events	Load removal: −130 to 77%	Retention: high density inflow sinks below the pond water; can act as a source during rainfall event	Concrete slab at the bottom with soil on top; Soil	Semadeni-Davies 2006, Barbier et al. 2018
	Heavy metals (As, Cd, Cr, Cu, Hg, Ni, Pb, Zn)	Road salt and Meltwater Events	Average removal efficiencies: As: 50%, Cd: 75%, Cr: 39%, Cu: 49%, Hg: 56%, Ni: 41%, Pb:42%, Zn: 48%	Retention: contaminants sink into salty water	Pond sediments	Semadeni-Davies 2006
	TSS	Road salt and Meltwater Events	TSS load decrease: 34–74%	Sand as a friction material and lengthy dry periods	Pond sediments	Semadeni-Davies 2006
Regenerative Stormwater Conveyance (RSC) Open channel, sandfiltering system with a series of pools and riffle weirs with native vegetation. (Cizek et al. 2017)	Fe^{2+}	Precipitation and post construction runoff	Increased Fe concentrations in baseflow: 1220%; in stormflow: 250%	Iron flocculation from iron-oxidizing bacteria; depends on source of reducing Fe, availability of DOC, low flow, warm temperatures	Sand, wood chips, riparian soils	Williams et al. 2016
	Dissolved Organic Carbon (DOC)	Urban stormwater runoff	Conc. increase: 18–54%	Released from OM; bacteria use humics and quinones as electron acceptors and abiotically reduce Fe	Wood chips and leaf litter	Duan et al. 2019
	Total Dissolved Nitrogen (TDN)	Urban Stormwater Runoff	Conc. decrease: 16–37%	Assimilation and/or denitrification; residence time, flow rate, area of water-sediment interface, uptake of aquatic plants	Organic matter on streambed substrate	Williams et al. 2017, Cizek et al. 2018, Duan et al. 2019
	Soluble Reactive Phosphorus (SRP)/ Total Phosphorus (TP)	Urban stormwater runoff	TP conc. decrease by 28%	Fe/Mn hydroxides (where P sorbs) are unstable under anoxic conditions. Also removed by physical removal	Organic matter on streambed substrate; more released on leaf litter than wood; highest	Cizek et al. 2018, Duan et al. 2019

Green Infrastructure and definition	**Ions, Organic Matter, nutrients, metals associated with F SS**	**Inflow Pollution Source**	**Outflow Retention Metrics**	**Mechanism**	**Substrate**	**Citations**
				mechanisms such as sedimentation and filtration.	P release on Fe-containing sands	
Bioretention/Rain Garden/Biofilters Vegetated filter media placed in a trench or basin with detention storage. (Søberg et al. 2014)	Base Cations (Na^+, Mg^{2+}, Ca^{2+}, K^+)	Stormwater from rain and snowmelt events with road salt	Average conc. decrease: Na^+: 47%; Average conc. increase: Mg^{2+}: 383%, Ca^{2+}: 152%, K^+: 22%	Temporarily stores or infiltrates the Na^+ and Cl^- in plants, soil, and groundwater. Cation exchange of Na^+ with K^+, Mg^{2+}, Ca^{2+}	Engineered soil material (ESM) on top of gravel	Burgis et al. 2020
	Cl^-	Stormwater from rain and snowmelt events with road salt	Average conc. decrease: 40%; Average load Reduction: 80%	Temporarily stores or infiltrates the Na^+ and Cl^- in plants, soil, and groundwater	Engineered soil material (ESM) on top of gravel	Burgis et al. 2020
	Heavy Metals (Cd, Pb, Zn, Cu)	Synthetic salt contaminated runoff	Average Conc. decrease: Cd: 96%–99%; Cu: 82% – 98%; Pb: 89% – 99%; Zn: 97.5% – 99.3%	Removed *via* mechanical filtration, cation exchange, adsorption, precipitation, complexation, and fixation to clay minerals	Dried sands	Søberg et al. 2017, Kratky et al. 2017
	Phosphorus (TP)	Glasshouse experiments, numerical modeling	TP Load Reduction: −240% to 79%; Removal Efficiency: >93%	Enhance P removal by adding a saturated zone (for vegetative uptake) or aluminum or iron oxide amendment; Removal depends mainly on adsorption to media.	Mulch layer, thick soil media, vegetation, underdrain	Roy-Poirier et al. 2010, Zhang et al. 2011, Kratky et al. 2017
	Nitrogen (TN, NO_3^-)	Roof runoff	NO_3^- conc. decrease by 35.4%; NH_3 conc. decrease by 84.6%; TKN conc. decrease by 31.2%	Organic nitrogen mineralization, ammonium adsorption, microbial and plant uptake, nitrification and denitrification. Dissolved N primarily removed through assimilation via biomass growth.	Mulch layer, thick soil media, vegetation, underdrain; Penwood Loamy sands	Dietz and Clausen 2005, Kratky et al. 2017
	TSS	Synthetic salt contaminated runoff	Over 80% Removal Efficiency	Mechanical filtration and sedimentation of suspended material	Dried sands	Søberg et al. 2017, Kratky et al. 2017
Bioswales/Vegetated Swales Shallow vegetated open channels in narrow areas along trails or roadways. (Sharma and Malaviya 2021)	Na^+	Road salt	Average conc. decrease: 19%; Average load decrease: 78%	Temporarily stores or infiltrates the Na^+ and Cl^- in plants, soil, and groundwater; Small % of Na^+ stored long-term attached to soil particles by ion exchange	Engineered soil material (ESM) on top of gravel	Burgis et al. 2020
	K^+, Mg^{2+}, Ca^{2+}	Road salt	Average conc. increase: Mg^{2+}: 1,230%, Ca^{2+}: 573%, K^+: 211%;	Export due to soil cation exchange. High due to lower	Engineered soil material (ESM) on top of gravel	Burgis et al. 2020

Green Infrastructure and definition	Ions, Organic Matter, nutrients, metals associated with F SS	Inflow Pollution Source	Outflow Retention Metrics	Mechanism	Substrate	Citations
			Average load increase: Mg^{2+}: 385%; Ca^{2+}: 108%, K^+: 39%	stormwater runoff reduction		
	Cl^-	Road salt	Average conc. decrease: 4%; Average load decrease: 76%	Export due to soil cation Exchange; export of cations occurred during and after storms with high Na+ conc.	Engineered soil material (ESM) on top of gravel	Burgis et al. 2020
Accidental wetlands Form naturally by a byproduct of human activities, but not designed or managed. (Maas et al. 2021)	Cl^-	Road salt	Conc. decrease: up to 94%	Residence time of salt ions	Sediment from the surrounding area	Maas et al. 2021
	N	Inflow from the Salt River, AZ	N load decrease: 51–86%	Reduce nitrate *via* microbial denitrification	Riparian Soil	Palta et al. 2017, Suchy et al. 2020
	P	Fluvial sources (Salt River, AZ; Minebank Run, MD)	PO_3- load increase: 0.23 – 24.84 P/m2/day	Processed by sediment microbes, water column algae or macrophytes; Exported P from release of Fe-bound P from anoxic sediments	Mix of sand, silt, clay and vegetation	Harrison et al. 2014, Palta et al. 2017
Sand Filters Stratified sand bed supported by gravel layer that water is drained through to remove nutrients and ions. (Healy et al. 2007)	Nutrients (N, P)	Dairy wastewater	NH_4-N load decrease: 85–100%; PO_4-P load decrease: 26–94%	Denitrification due to anoxic zone	Sand of various grain size	Healy et al. 2007
	Fe, Mn	Simulated groundwater	Removal efficiency Fe^{2+}: 100%; removal efficiency of Mn^{2+}: 90%	Increased redox potential	Sand coated in Mn	Cheng et al. 2020
Permeable Pavements Paving material that allows water infiltration and conveyed through the material matrix, open joints, or voids. (Drake et al. 2013)	Base Cations (Ca^{2+}, Mg^{2+})	Road salt stormwater runoff	Load removal efficiency: Ca^{2+}: −41 to −50%; Mg^{2+}: −63 to −68%	Ca^{2+} and Mg^{2+} could have been mobilized by cation replacement in soil	Permeable asphalt, permeable concrete, permeable pavers	Selbig et al. 2019
	Cl^-	Road salt stormwater runoff	Load removal efficiency: −10 to −33%	Provides temporary storage and allows for dilution. Poorly attenuated, migrates easily, cation exchange leads to leaching or mobilization of heavy metals; Causes change in soil structure	Permeable asphalt, permeable concrete, permeable pavers	Drake et al. 2013, Selbig et al. 2019
	Heavy Metals (Pb, Cu, Cd, Zn)	Urban runoff, artificial traffic runoff	Conc. decrease: Cd: 67% – 99%, Pb: 79% – 99%, Cu: 98% – 99%, Zn: 72 – 96%	Accumulation on the surface of previous asphalt; related to suspended solid retention and adsorption of dissolved metals on	Laboratory rigs with different joint fillers	Legret et al. 1996, Dierkes et al. 2005, Scholz 2013

Green Infrastructure and definition	**Ions, Organic Matter, nutrients, metals associated with F SS**	**Inflow Pollution Source**	**Outflow Retention Metrics**	**Mechanism**	**Substrate**	**Citations**
				structure-constituting materials		
	Suspended solids	Urban runoff	Conc. decrease: 64%	Reservoir structure filters runoff	Woven geotextiles, a 35 cm layer of crushed material, 2 10 cm thick layer of aggregates, and one 6 cm thick layer of asphalt	Legret et al. 1996, Scholz 2013
	TP	Winter storm urban runoff	TP load removal efficiency: 19 to 43%	Traps or filters particulate forms of P; Transformed via biologically-mediated processes	Pavement cells underlain with geotextiles, soils, and native soils	Drake et al. 2014, Selbig et al. 2019
Constructed Wetlands Biological and physiochemical processes using vegetation, media and microbes to remediate inflow water (Sharma and Malaviya 2021)	Cl^-	Winter storm urban runoff	Cl^- conc. decrease: 36–55%; Cl mass reduction: 45%	Reduction due to dilution. Accumulates in soil and flushed out	50% sand and 50% existing evacuated soils	Natarajan and Davis 2015, Forgione n.d.
	Heavy Metals (Cd, Cu, Pb, Zn)	Runoff from motorway (Gill et al)	Conc. decrease: Cd: 5%; Cu: 60% – 83%; Pb: 31%–74%; Zn: 52–86%	Adsorption to sediment particles, complexation with organic and inorganic substances	20 cm of soil below soil with organic matter (wood chips), fertilizer, inorganic sulfur, gypsum, and then another 20 cm layer of soil	Gill et al. 2017, Knox et al. 2021
	Nutrients (N, P)	Dairy wastewater	NH_4-N conc. decrease 39–70%; P decrease up to 90%	N: Physical settlement, denitrification, plant/microbial uptake P: Uptake by bacteria/algae/duckweed/macrophytes for short term. Long term storage *via* peat accumulation and substrate fixation	Substrates rich in Fe, Ca^{2+}, Al underlain with soil and gravel	Healy et al. 2007