Freshwater salinization syndrome alters retention and release of chemical cocktails along flowpaths: From stormwater management to urban streams

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Abstract: Freshwater salinization syndrome (FSS) refers to the suite of interactive effects of salt ions on degradation of physical, biological, and social systems. Best management practices (BMPs), which are methods to effectively reduce runoff and nonpoint source pollution (stormwater, nutrients, sediments), do not typically consider management of salt pollution. We investigate impacts of 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 USA 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 because of 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 because of lysing cells and changes in solubility; 4) substantial 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 substantial annual reduction (>50%) in Na^+ concentrations in an urban stream when road salt applications were dramatically reduced, which suggests potential for ecosystem recovery. We compare our original results with published metrics of contaminant retention and release across a broad range of stormwater BMPs from North America and

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Europe. Overall, urban streams and stormwater 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 BMPs. Reducing diverse chemical cocktails of contaminants mobilized by freshwater salinization is a priority for effectively and holistically restoring urban waters.

Key words: salinization, emerging contaminants, nonpoint source pollution, stormwater management, urban ecosystems, water quality

Freshwater salinization represents a growing risk to source water protection, infrastructure, and biodiversity and increasingly contributes 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 (chemical cocktails) and coinciding changes in pH and buffering capacity are called freshwater salinization syndrome (FSS) (Kaushal et al. 2018, 2019). FSS can negatively affect freshwater and 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, 2022).

Certain best management practices (BMPs) can enhance so-called hot spots or hot moments of both retention and release of nutrients, salts, metals, and organics along hydrologic flowpaths (Dietz and Clausen 2005, Groffman et al. 2005, Vidon et al. 2010, Natarajan and Davis 2015, Søberg et al. 2017, Burgis et al. 2020, Weitzman et al. 2021), which can complicate efforts to improve urban water quality. There is a growing need to better understand FSS impacts within the context of stormwater BMPs and stream–riparian restoration projects (Cooper et al. 2014, Szota et al. 2015, Kratky et al. 2017, Snodgrass et al. 2017, Burgis et al. 2020, Lam et al. 2020). Freshwater managers are presented with a dilemma because some types of stormwater management are effective at attenuating salt pulses that accompany stormwater runoff, but salinity remains a stressor in many urban restored streams (Cooper et al. 2014, Fanelli et al. 2019). Further, 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).

FSS may reduce the effectiveness of restoration efforts that aim to mitigate negative stormwater effects

In response to substantial 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 habitat-based designs, focusing on channel stability, flood prevention, and urban water-quality enhancement (sensu Bernhardt et al. 2005, Craig et al. 2008, Kaushal et al. 2008, Mayer et al. 2010). Project objectives include protecting infrastructure, preventing erosion that may damage adjacent property or degrade sewer systems, reducing stormwater flows, and enhancing biogeochemical functions that improve water quality. More recently, substantial financial resources have been committed to stream restoration projects that integrate stream–floodplain reconnection and innovative stormwater management (Hopkins et al. 2022, Mayer et al. 2022). These stream restoration and stormwater management strategies improve habitat quality and the provision of ecosystem services through approaches like 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), increasing hydrologic connectivity between streams and floodplains, and increasing hydrologic residence times (Bukaveckas 2007).

However, along with their benefits, these stream restoration and stormwater management approaches have the potential to affect C, N, and metal fluxes and to retain not only nutrients but also salt ions (e.g., Cooper et al. 2014, Snodgrass et al. 2017, Burgis et al. 2020). Unintended modification of stream salinity may magnify water-quality impacts of extant FSS based on location, size, and type of restoration (e.g., Newcomer Johnson et al. 2014, Maas et al. 2021). In addition, there may be both retention and release of chemical cocktails (sensu Kaushal et al. 2020), along hydrologic flowpaths through urban streams and various forms of stormwater management. For chemical cocktails involving ions, we provide charges only for those elements with 1 oxidation state throughout this paper, and we do not indicate charges on metals with multiple oxidation states. Retention and release mechanisms can vary for different chemical cocktails (see Fig. 1 for a conceptualization of such mechanisms based on Semadeni-Davies 2006, Williams et al. 2016, Barbier et al. 2018, Cizek et al. 2018 Duan et al. 2019, Flanagan et al. 2019). For example, in geographic regions where road salts are applied during winter months, urban streams can have corresponding pulses in salt ion concentrations. Also, streams may have pulses in elemental concentrations during the stream restoration process, often due to construction-related soil disturbances (Fig. 2A–H), although to date there has been little documentation of this phenomenon. However, there can also be rapid and significant year-round reductions in Na^+ concentrations (>50%) in urban restored streams during low road salt application years (Fig. 2H), which suggests the potential for recovery from FSS impacts.

Much previous research has focused on the effects of stormwater BMPs, which also retain road salt (Snodgrass et al. 2017), on reducing runoff and retention of nutrients. Also, infiltration-based BMPs, which are common in modern developments, may have high salt accumulation rates and high volumes of water directed through these landscape features (Kratky et al. 2017). Following stream–floodplain reconnection, restored floodplains can also accumulate salt ions in shallow groundwater (Cooper et al. 2014, Mayer et al. 2022). For instance, restored floodplains can retain Cl^- ions because of increased hydrologic connectivity designed to promote denitrification (Kaushal et al. 2008, Mayer et al. 2010; Fig. 3). Thus, stormwater BMPs and stream restoration features have the potential to accumulate different salt ions, which can lead to contaminant mobilization. The specific types of retained salt ions (e.g., Na^+, Ca^{2+}, Mg^{2+}) may preferentially mobilize certain contaminants (e.g., Cu), meaning that different types of BMPs and restoration strategies may interact with FSS to affect different ecosystem processes. However, relatively little is known about how the retention of FSS salt ions along urban flowpaths affects diverse biogeochemical processes. Interactions between FSS and retention and mobilization of contaminants in restoration features are poorly understood and represent a research frontier in urban watershed management.

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 analyzing original data from our long-term study sites and synthesizing information from published sources that show direct and indirect effects on multiple contaminants. These contaminants represent distinct combinations of elements formed from watershed biogeochemical processes (Kaushal et al. 2018, 2019, 2020, 2022). We provide new

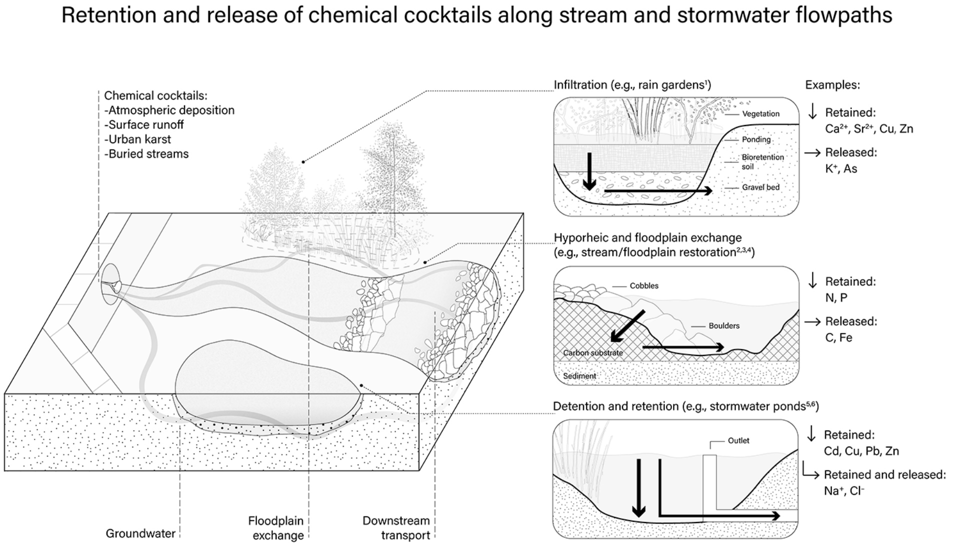

Figure 1. There can be both retention and release of contaminant cocktails along hydrologic flowpaths (shown by the darker ribbons) through urban streams and various forms of stormwater management. For chemical cocktails involving ions, we provide charges only for those elements with 1 oxidation state, and we do not indicate charges on metals with multiple oxidation states. In the detailed panels on the right side, down arrows represent retention, and the horizontal arrows represent release mechanisms, which 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.

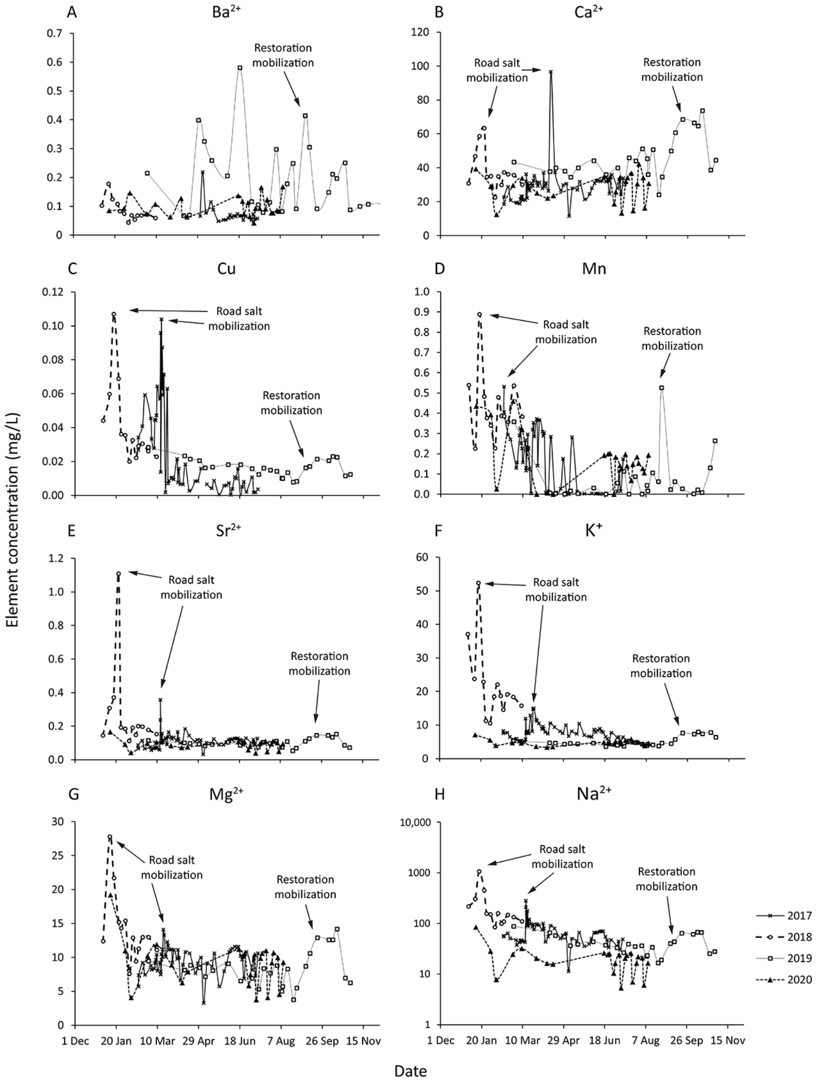

Figure 2. Variations in elemental concentrations (A–H) in Campus Creek, Maryland, USA, a stream undergoing restoration and conversion to regenerative stormwater conveyance. There were pulses (large changes in chemical concentrations over relatively short time scales) in elemental concentrations during road salt events and during construction disturbances associated with stream restoration in 2019. 2020 was a year with low or no road salt application, and Na^+ concentrations were lower throughout the whole year compared with previous years. Dec = December, Jan = January, Mar = March, Apr = April, Jun = June, Aug = August, Sep = September, Nov = November.

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 compared with other times of the year. Our original data is presented in case studies from 7 urban watersheds in the Baltimore, Maryland–Washington, DC, USA, metropolitan region, which have been intensively studied through long-term monitoring. However, because of limitations in inference given the small geographic area of the data we present, we compare our data with other studies of contaminant retention and release in stormwater BMPs in North America and Europe.

Much of the basic biogeochemistry and geochemistry of FSS and its impacts on urban stream and stormwater management flowpaths is either not clearly documented or poorly synthesized. Further, FSS is not explicitly and comprehensively considered in many watershed restoration strategies. Based on our growing understanding of FSS risks, we explore 2 questions: 1) How do flowpaths along urban streams and stormwater BMPs influence biogeochemical processes related to FSS? and 2) What are the current knowledge gaps and research frontiers regarding impacts of FSS and efficacy of stormwater BMPs in the context of FSS?

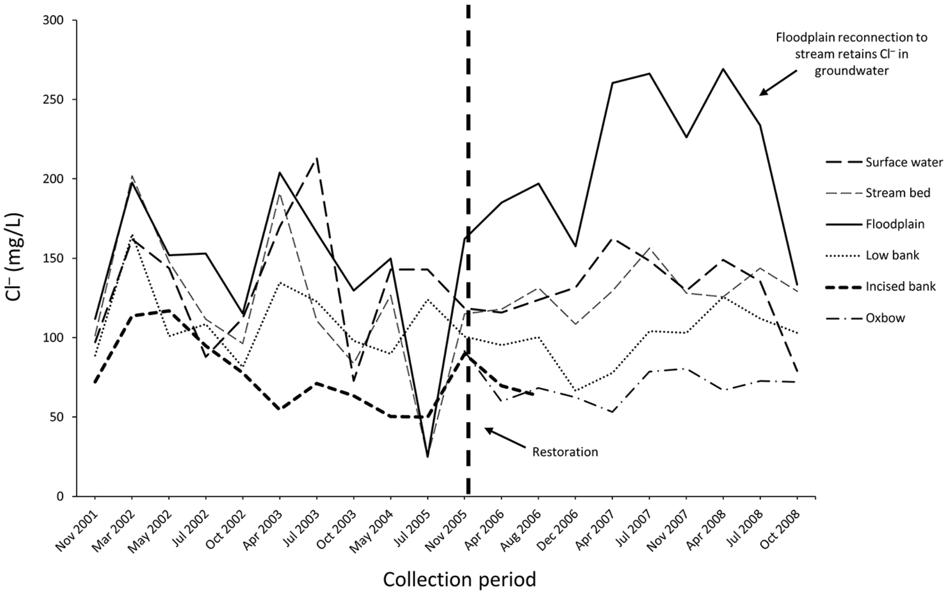

Figure 3. Changes in Cl^- concentrations before and after stream restoration (indicated by the vertical dashed black line) at Minebank Run, an urban stream in Baltimore, Maryland, USA. Data come from Mayer et al. (2022). The stream was restored in November 2005 to repair and reduce erosion and improve N uptake via reconnected banks. Cl^- concentrations increased in the restored floodplain following stream restoration, likely because of the effects of floodplain reconnection on chemical retention processes (Kaushal et al. 2008, Mayer et al. 2010, 2022). Mar = March, Apr = April, Jul = July, Aug = August, Oct = October, Nov = November, Dec = December.

The sections of our paper addressing these questions 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 (not recommendations) on the potential retention and release of salt ions and multiple contaminants across urban streams and stormwater BMPs. Our paper also points to priority research directions, which we derived 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 may also contribute to improved selection of deicers based on contaminant mobilization potential and may identify which types of urban streams and stormwater BMPs may be most affected by salt pollution.

HOW DO FLOWPATHS ALONG URBAN STREAMS AND STORMWATER BMPS INFLUENCE BIOGEOCHEMICAL PROCESSES RELATED TO FSS?

In this section, we investigate how flowpaths along urban streams and stormwater BMPs influence different biogeochemical processes related to FSS. We document different biogeochemical patterns and processes by both analyzing our own original data and synthesizing published literature. Through 4 case studies of different and distinct chemical cocktails, we provide examples of FSS impacts on stormwater BMPs and urban streams with original data from 7 long-term study sites in the Mid-Atlantic USA. Each of the 4 case studies represents a distinct chemical cocktail impacted by FSS, and examples are drawn from our multiple sites. These case studies include analyses of changes along urban streams and stormwater management flowpaths pertaining to the 1) mobilization of major ions and nutrients, 2) mobilization of metals, 3) alteration of alkalinization and acidification, and 4) alteration of quantity and quality of organic matter. We then place our data within the context of other studies of contaminant retention and release in stormwater BMPs in North America and Europe. Overall, the case studies and literature synthesis demonstrate how FSS triggers synergistic changes in the biogeochemical properties of freshwater ecosystems (e.g., changes in pH, increases in ionic strength, changes in chemical solubility, and changes in biological transformation rates and sorption potential of elements) as salt ions are retained and released along urban stormwater flowpaths (Fig. 1).

Study design for case studies from the Mid-Atlantic USA

We present new, previously unpublished results from 7 urban watersheds in the Baltimore, Maryland –Washington, DC, metropolitan region in the Mid-Atlantic USA, which have been intensively studied through long-term monitoring

(Table S1). These watersheds are subject to road salt application, and 6 of these watersheds experienced some form of stream restoration and stormwater management. Original data from these sites consist 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 different levels and types of salt ions in incubations with sediments from urban streams and stormwater BMPs. 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, biweekly, seasonal, annual, and decadal. 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. 2018, Kaushal et al. 2019). Details on methods of chemical analyses can be found in our previous studies (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 USA

Here, we present site descriptions of the 7 study sites (Table S1) representing various stormwater BMPs and urban streams. Results from each of these study sites are reported throughout the 4 case studies of chemical cocktails in response to FSS impacts on different biogeochemical patterns and processes along flowpaths in stormwater BMPs and urban streams.

Campus Creek and Paint Branch Stream We collected streamwater samples for routine water quality monitoring and sediment samples for laboratory salinization experiments from Paint Branch Stream and 1 of its tributaries, Campus Creek. Both Paint Branch and Campus Creek are tributaries of the Anacostia River and the Chesapeake Bay. The sampling sites are located near the University of Maryland campus in College Park, Maryland, USA, ~8 km northeast of Washington, DC. Paint Branch Stream has a drainage area of 79 km^2 and contains 31.7% impervious cover, and Campus Creek has a drainage area of 1.76 km^2 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 We collected groundwater and surface streamwater samples from Minebank Run, an urban stream located in the Gunpowder Falls Watershed near Baltimore. We measured specific conductance at the same point where we collected surface water samples. 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, revegetation of riparian zones, and floodplain reconnection. Further details on site description can be found in Kaushal et al. (2008) and Mayer et al. (2010, 2022).

Herring Run Herring Run is an unrestored channelized stream located in Baltimore that discharges into the Back River. This waterway is 1 of the major urban streams draining Baltimore and was assessed for potential stream restoration in 2004. Water quality in Herring Run is of concern to local residents and organizations such as the Herring Run Watershed Association and Friends of Herring Run Park. As an unrestored stream lined with a concrete channel, we used Herring Run as a control, which allowed us to investigate biogeochemical patterns related to salinization across a broader gradient of site conditions compared with restored streams. We conducted routine monitoring of specific conductance and streamwater chemistry from grab samples of stream water. 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, has a drainage area of 1 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). We conducted routine monitoring of specific conductance and streamwater chemistry from grab samples of stream water in a restored section of the stream. We also collected sediments in a restored and directly adjacent unrestored section for salinization incubation experiments.

Stony Run Stony Run, located in north central Baltimore, has a drainage area of 2 km^2 and 28% impervious cover. We conducted routine monitoring of specific conductance and streamwater chemistry from grab samples of stream water. 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 with a drainage area of 19.1 km^2 and 29.2% impervious cover. We conducted routine monitoring of specific conductance and streamwater chemistry from grab samples of stream water. This stream contains extensive upland stormwater management systems with 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).

Case-study methods

Salinization experiments at Paint Branch and Campus Creek and in RSC systems We conducted salinization experiments to determine critical patterns and processes associated with different road salt ions that mobilize nutrients and metals as described in Duan and Kaushal (2015), Haq et al. (2018), and Galella et al. (2020) at each of 3 sampling locations along the Anacostia River watershed. We took samples at an RSC site on Campus Creek, a comparison site at Campus Creek without an RSC, and a reference site at Paint Branch. We collected ~6 kg of sediment along the flowpath of each of the 3 sites with a clean shovel and a new plastic bag for each site. We also collected ≥9 L of nearby surface water from each site into acid-washed high-density polyethylene bottles (Nalgene®, Rochester, New York), leaving no headspace. We transported sediments and surface water in a chilled cooler to the laboratory and kept samples cool and moist during the experimental setup (Duan and Kaushal 2015, Haq et al. 2018). To homogenize the samples for particle size, we sieved the sediments with a 4-mm sieve and retained the fine fraction (<4 mm) (Duan and Kaushal 2015, Haq et al. 2018). Each site's sediments were separated into ninety 60-g aliquots for use in experiments.

The common road salts we selected for this experiment were NaCl, $MgCl_2$, and $CaCl_2$. Using known Cl^- concentrations measured in the Baltimore, Maryland–Washington, DC, metropolitan area, we selected a range of 5 salinization levels (Table S2) for each salt, designed to represent the ambient range of salt concentrations present in urban stream water from the study region over an annual cycle. We salinized 100-mL aliquots of unfiltered stream water from each site to 1, 2, 4, and 8 g Cl^-/L concentrations of each salt, in addition to 1 control sample with stream water at 0 g Cl^-/L added salt. To simulate vertical water columns with a sediment–water interface, we added each aliquot of homogenized sediment to acid-washed glass Erlenmeyer flasks along with 100 mL of the prepared stream water added via pipette. To isolate the sediment–water interaction, we incubated a control flask containing only unfiltered stream water along with the treatment flasks. There were 4 to 6 replicates/treatment level depending on site (see Table S3 for replicates/treatment level including control for each site). The flasks were incubated on a shaking table (slow mode) in the dark for 24 h at room temperature (20°C). After incubation, we immediately and carefully removed the water from the flask using a pipette to avoid any disturbance to the sediment and then filtered the water through a pre-combusted 0.7-μm glass fiber filter (Whatman, Maidstone, United Kingdom). We immediately acidified an aliquot of the post-incubation filtered water in a small Nalgene bottle containing 0.5% high-purity nitric acid for base cation analysis. We stored the remaining post-incubation water in a refrigerator at 4°C or frozen for water-chemistry analysis (described below). We calculated Na^+ retention based on how much Na^+ was added during the experiment and how much was present in overlying stream water after the incubation. We estimated mobilization of elements from sediments in response to experimental salinization based on increases in elemental concentrations in overlying water following incubations with the different salt treatments.

Salinization experiments at Scotts Level Branch We conducted salinization experiments at Scotts Level Branch using similar methods as described above but with higher levels of salinity and the inclusion of beet juice as a deicer instead of $MgCl_2$ (Table S4). Relatively little work has investigated the effects of beet juice deicers on contaminant mobilization, particularly in comparison with other road salt ions. We chose 2 adjacent study sites in the Scotts Level Branch watershed to be representative of restored and unrestored reaches. We collected ~3 L of stream water from each site into 1-L Nalgene bottles, leaving no headspace. We collected ~2 L of sediment from each site with a clean shovel, which we stored in 1-gal resealable plastic bags. We then sieved sediment with a 2-mm sieve and retained particles <2 mm in diameter for analysis. We transported samples in a cooler on ice and kept them refrigerated or frozen until analysis.

In addition to lab-grade NaCl and $CaCl_2$ dihydrate (≥99% pure), we also used Beet 55™ salt (Smith Fertilizer & Grain, Knoxville, Iowa), a beet-juice-derived deicer we prepared as a 100-g/L brine for use in the incubation experiments. We prepared Beet 55, NaCl, and $CaCl_2$ dihydrate at 6 different concentrations, from 0 g/L (the stream water without any additional deicer), an initial concentration, and 2, 5, 10, and 20× the initial concentration (Table S4), plus 1 blank of deionized water. We pipetted aliquots of 60 g of sediment and 100 mL of water into flasks and shook them on a shaker table for 24 h. After incubation, we immediately used a pipette to remove the water from the flask to avoid any disturbance to the sediment and then filtered the water through a pre-combusted 0.7-μm glass-fiber filter (Whatman). We kept the filtered sample water refrigerated until later analysis (described below). Triplicates were run for each concentration and the deionized-water blank, creating a sum of 21 incubations for each of the site and deicer combinations.

Water-chemistry analyses In the lab, we analyzed streamwater samples from all experimental sites for water-chemistry characteristics. We measured specific conductance of streamwater samples with a Cole-Parmer™ Oakton™ PCTSTestr 50 Waterproof Pocket Tester, (Premium 50 Series; Thermo Fisher Scientific, Waltham, Massachusetts) after multipoint calibration. We measured base cation (Ca^{2+} K^{+}, Mg^{2+}) and trace metal (Mn, Zn, Sr^{2+}, Ba $^{2+}$, Cu) concentrations in the acidified water samples 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; Kyoto, Japan). For base cation measurements, we nebulized the acidified samples in radial mode across a plasma flame. For trace metal measurements, we nebulized the acidified samples 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 United States Environmental Protection Agency (e.g., USEPA 1983, APHA 1998).

We analyzed streamwater samples for C and N. We measured dissolved organic C (measured as non-purgeable organic C), dissolved inorganic C, and total dissolved N with a total organic C analyzer (TOC-V CPH/CPN; Shimadzu) total N module, which uses chemiluminescence to derive total dissolved N (Haq et al. 2018). Dissolved organic C and dissolved inorganic C were derived from a high-temperature catalytic oxidation method (Duan and Kaushal 2013). Samples were diluted with deionized water before analysis so that their Cl^{-} concentration did not exceed 0.5 g/L. We also analyzed samples from stream monitoring during snow events by fluorescence spectroscopy to characterize dissolved organic matter (DOM) sources and quality. This included analyses for the biological autochthonous inputs index (defined as the ratio of fluorescence intensity at the emission wavelength of 380 nm to the intensity emitted at 430 nm at the excitation wavelength of 310 nm; Huguet et al. 2009) and the fluorescence index (defined as the ratio of emission intensities at wavelengths of 470 and 520 nm with an excitation wavelength of 370 nm; McKnight et al. 2001).

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 quality assurance/quality control protocols were documented in quality assurance project plans archived at the United States Environmental Protection Agency's Office of Research and Development (Galella et al. 2020).

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 BMPs in North America and Europe (Table S5). We used Google™ Scholar (Mountain View, California) to complete a systematic search to identify and compile relevant studies. These studies included literature reviews and case-study articles, and most of the studies focused on stormwater management features in urban areas. 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; and 3) salt ion types associated with stormwater BMPs, including base cations, trace metals, and nutrients. We grouped key words together based on the stormwater BMP type and the salt ion of interest. Information from each study, such as study location, sampling sites, and period of study, are reported in Table S5. Some arid climates were not represented.

To address the hydrological and biogeochemical mechanisms of contaminant retention and release, we classified mechanisms based on the authors' conclusions and those mechanisms highlighted in Fig. 1 (e.g., atmospheric deposition, surface runoff, etc.), and we obtained retention and release metrics from each article. We used author-generated estimates of changes in concentrations when provided, but where raw data were provided, we calculated retention and release metrics for loads from the inflow and outflow 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 the following equation:

$$1 - (\text{outflow}/\text{inflow}) \times 100. \qquad \text{(Eq. 1)}$$

We excluded papers that did not provide enough information on inflow and outflow metrics for each stormwater BMP type.

RESULTS AND DISCUSSION

Case study 1: FSS can mobilize major ions and nutrients along urban streams and stormwater management flowpaths in the Mid-Atlantic USA

Road salts are linked to the mobilization of major ions and nutrients. For example, our monitoring work at the Campus Creek study site shows large pulses in Ca^{2+}, Cu, Mn, Sr^{2+}, K^{+}, Mg^{2+}, and Na^{+} during winter months concurrent with road salt application events (Fig. 2B–H). Specific conductance, which is a measure of the ability to conduct electrical current, is often related to concentrations of major ions such as Na^+ and Cl^- (Kaushal et al. 2018, 2021). In the study streams, we observed likely relationships between specific conductance and a variety of base cations and total dissolved N, suggesting comobilization of chemical cocktails at our Herring Run, Minebank Run, Scotts Level Branch, and Stony Run study sites (Fig. 4A–E). Only K^+ did not show these likely relationships at the study sites, probably because of strong biotic demand in terrestrial watersheds as a limiting nutrient (i.e., K^+ was limiting) (Tripler et al. 2006). These results agree with other salinization experiments in soil and stream sediments from this region (Duan and Kaushal 2015, Haq et al. 2018), which also found comobilization and formation of chemical cocktails. Experimental data from the Scotts Level Branch study site appears to show preliminary evidence that salinization, with a variety of salt ions and deicers, can mobilize N from sediments to stream water (Fig. 5A, B). Na^+ can displace $NH_4{}^+$ and 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. 2018).

Changes in retention and release are often related to cation exchange capacity, the capacity of soil particles to hold on to positively charged ions. Specific surface area, which is linked to the amount of clay and organic matter in the sediment, is the soil property accounting for the most variability in cation exchange capacity (Yukselen and Kaya 2006). 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, $NO_3{}^-$, and $NH_4{}^+$ 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, elevated Na^+ and Cl^- concentrations due to road salt inputs enhance ion exchange and displace

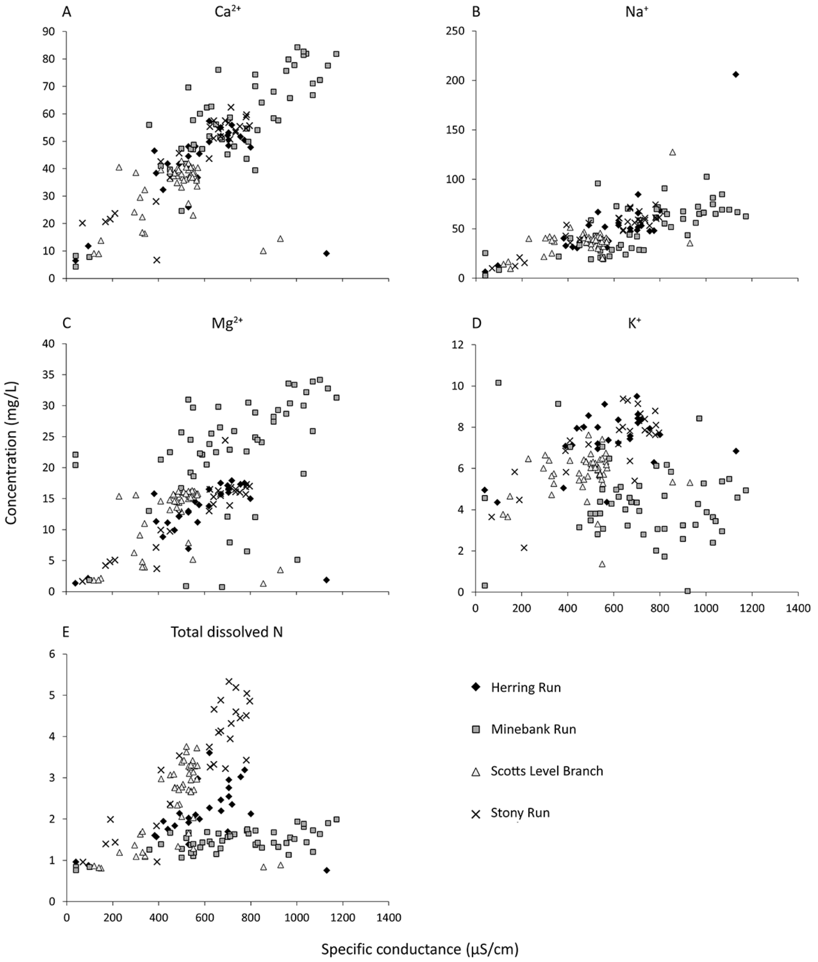

Figure 4. Relationships between specific conductance and base cation concentrations (A–D) and total dissolved N (TDN) concentrations (E) in restored streams (Minebank Run, Stony Run, Scotts Level Branch) and an unrestored stream (Herring Run) in Baltimore, Maryland, USA.

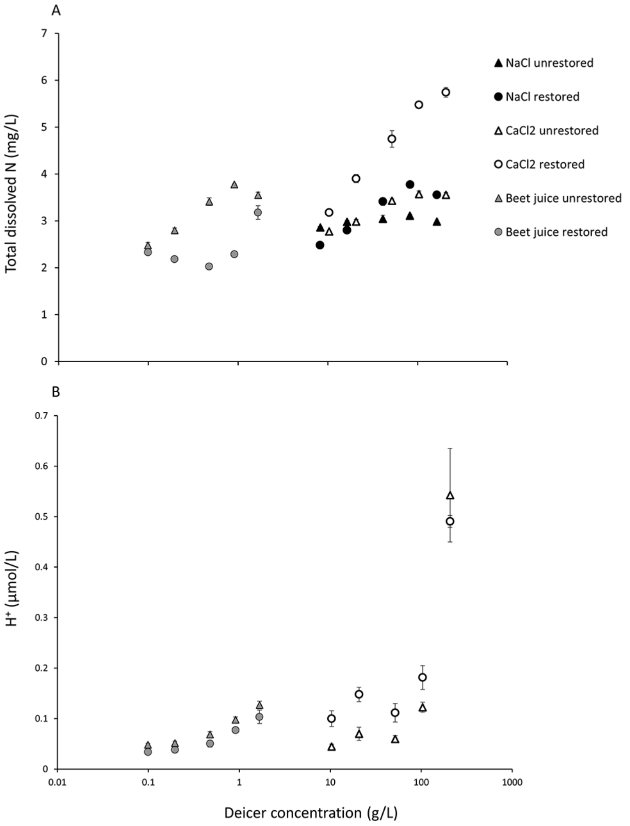

Figure 5. Experimental salinization appears to have caused a release of N from sediments to overlying stream water (A) and increased H^+ ion concentrations (acidification) (B) from samples taken from restored and unrestored study sites in Scotts Level Branch in Baltimore, Maryland, USA. Error bars represent ±1 SD of the mean.

Mg^{2+}, Ca^{2+}, NO_3^-, and NH_4^+ from exchange sites on sediments and soils.

Stormwater BMPs can potentially retain and reduce concentrations of nutrients, such as N, P, and K, as well as metals and organic matter along flowpaths (Table S6). However, FSS may cause retention of unwanted chemicals and the release of dissolved ions, organics, and metals along hydrologic flowpaths, which could affect water quality (Table S6). This FSS effect is shown by our experimental salt additions, in which increasing deicer concentrations appear to have enhanced N mobilization from soils and stream sediments to stream water at the Scotts Level Branch study site (Fig. 5A). Likewise, other studies have shown release of other nutrients and ions with increasing salinization (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 the Campus Creek study site (Fig. 6A). 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 (Fig. 4A–E). These relationships can be due to similarities in hydrologic flowpaths (groundwater), anthropogenic sources and inputs (e.g., road salts, sewage), and 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 N in urban streams because most research has focused on biological controls on N in restored streams (Newcomer Johnson et al. 2016). In addition, more work is needed to understand the influence of ion exchange processes along hydrologic flowpaths.

Case study 2: FSS can mobilize metals along urban streams and stormwater management flowpaths in the Mid-Atlantic USA

Our long-term monitoring study indicates that FSS can mobilize metals along stormwater BMPs. Over annual periods, concentrations of metals and base cations at the Paint Branch study site appeared to increase as water temperatures declined and road salt was applied during winter months (Fig. 7A–C). Likewise, there were pulses in metal concentrations at the Campus Creek study site during winter road salt events (Fig. 8E). Our experimental salinization data from the Paint Branch and Campus Creek study sites also appear to show that ~30 to 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 (Fig. 9A–F). In addition, experimental work at Paint Branch appears to show that the types of salt ions involved in FSS can play a substantial role in the specific types of metals mobilized (Figs 10A–C, 11A–D). 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 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 USA, 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 because of automobile traffic (Schuler and Relyea 2018) but can be readily released into solution because of increased salinization. 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

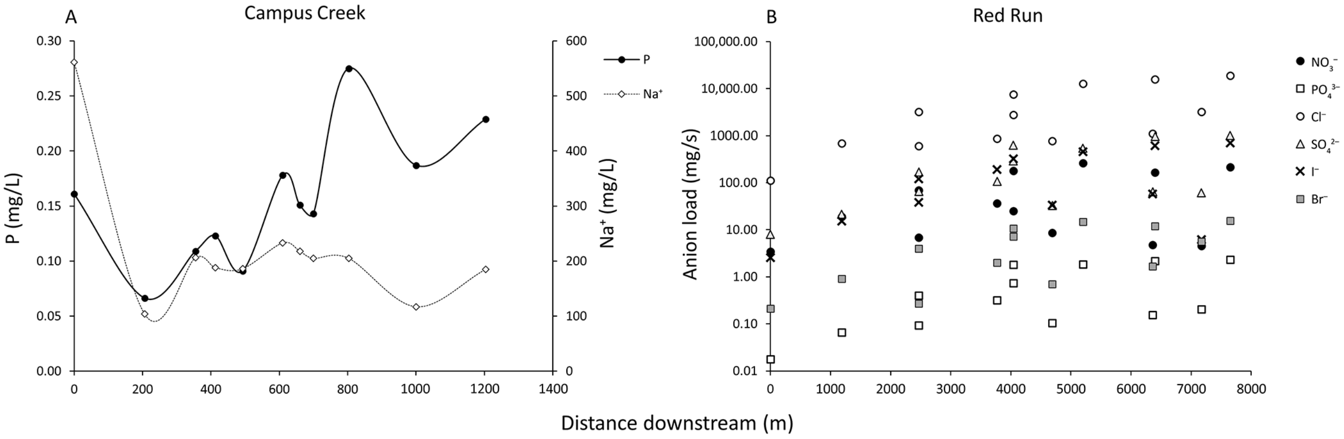

Figure 6. Downstream changes in elemental concentrations in Campus Creek (A), an urban stream in College Park, Maryland, USA, which was restored using regenerative stormwater conveyance (Kaushal et al. 2019, 2020, 2021). Na^+ concentrations decrease along the hydrologic flow path, whereas P concentrations increase potentially because of ion exchange and other geochemical changes. Downstream changes in loads (mass transport/unit time) of anions in Red Run (B), an urban stream in the Gwynns Falls watershed in Baltimore County, Maryland, USA, draining stormwater management structures. Note that the *y*-axis is scaled by $\log_{10}$. Data analysis from this figure is modified from Pennino et al. (2016), and data were used with permission by the author.

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, DOM 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. Overall, FSS mobilizes a diversity of metals from sediments to water through a variety of biogeochemical processes.

Case study 3: FSS can alter alkalinization and acidification in urban streams and stormwater management flowpaths in the Mid-Atlantic USA

Our long-term monitoring study indicates that FSS can contribute to acidification and alkalinization along urban stream and stormwater management flowpaths. During winter road salt events, the monitoring data at the Campus Creek study site demonstrate sharp declines in pH (acidification) in response to road salt applications, likely because of mobilization of H^+ from soil exchange sites by Na^+ (Fig. 8A). Similarly, complementary results from experimental salt additions at the Scotts Level Branch study site appear to show acidification and rapid increases in H^+ ion concentrations due to H^+ mobilization from sediments (Fig. 5B). Short-term responses to salinization events can yield episodic acidification events due to mobilization of H^+ and strong acid anions like Cl^- (e.g., Fig. 5B), 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 because of increased complexation with dissolved Cl^-, SO_4^{2-}, OH^-, and CO_3^{2-}.

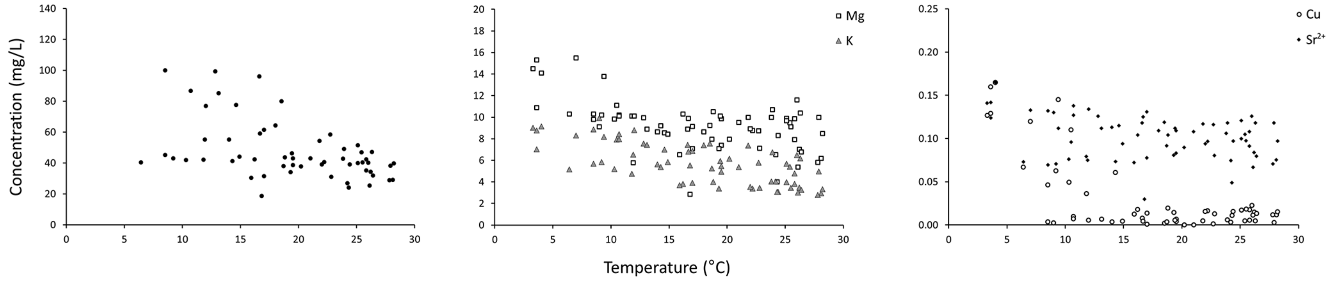

Figure 7. Patterns between streamwater temperature and base cation and trace elemental concentrations (A–C) in Paint Branch, a stream that was restored with floodplain reconnection, located at the University of Maryland campus in College Park, Maryland, USA.

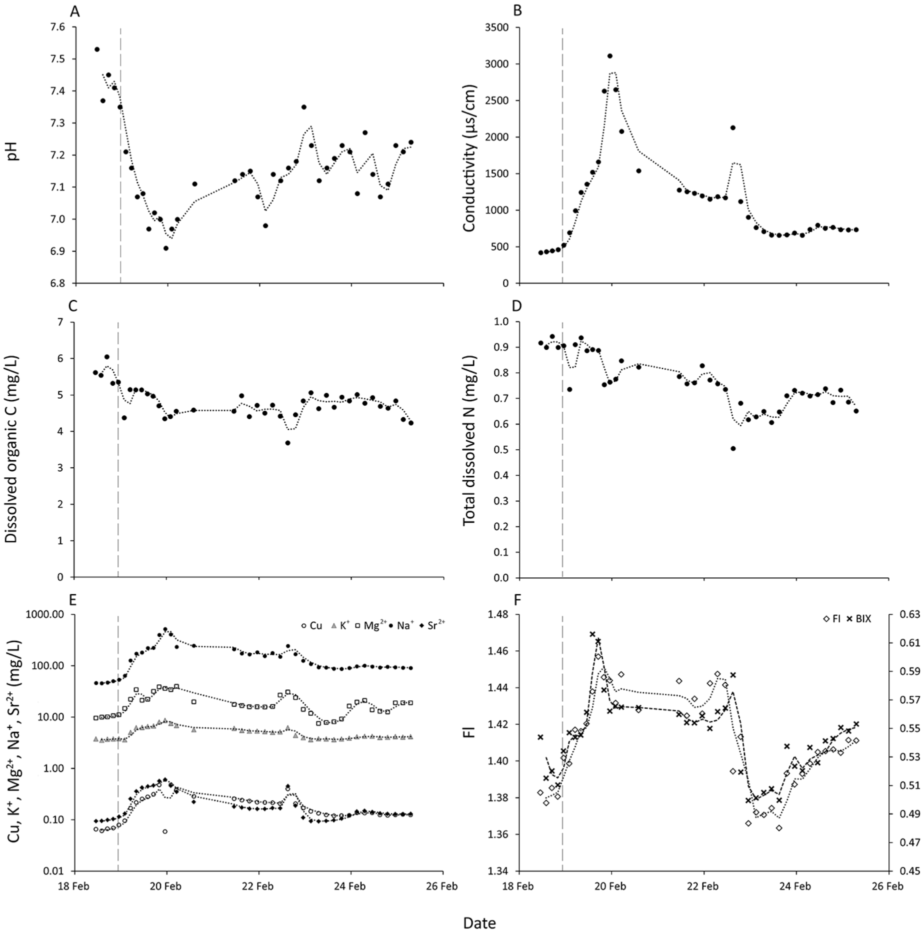

Figure 8. Pulses in water-quality impacts during a winter road salt event (during the year 2021) in Campus Creek, an urban stream in College Park, Maryland, USA, restored using regenerative stormwater conveyance. Water-quality measures shown are pH (A), conductivity (B), dissolved organic C (C), total dissolved N (D), trace metals (E), and organic matter (F). Vertical dashed 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 increase was based on fluorescence spectroscopy and the fluorescence index (FI) and biological autochthonous inputs index (BIX) in response to road salt applications likely because of lysing cells or changes in solubility.

Salinization can also contribute to alkalinization of urban waters over longer time scales (sensu Kaushal et al. 2018), particularly as Na^+ and other base cations displace H^+ from ion exchange sites in soils. Previous work in urban watersheds suggests that chemical weathering of impervious surfaces can enhance urban stream alkalinization by increasing concentrations of base cations, bicarbonate, and acid-neutralizing capacity (Kaushal et al. 2017). Relationships between impervious surfaces in urban areas and alkalinization are influenced by road salts, mobilization of base cations such as Ca^{2+} and Mg^{2+} from cation exchange sites in soils (Cooper et al. 2014), and elevated concentrations of Ca^{2+} and Mg^{2+} from weathering of impervious surfaces (Sivirichi et al. 2011). Alkaline conditions caused by long-term salinization with base cations and weathering of impervious surfaces favor the release of P from oxyhydroxides in sediments and soils, which contributes to freshwater eutrophication (Duan and Kaushal 2015, Haq et al. 2018). In addition, 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. Overall, FSS can contribute to acidification or alkalinization depending on time scales and the influence of different salt ions.

Case study 4: FSS can alter quantity and quality of organic matter in urban streams and stormwater management flowpaths in the Mid-Atlantic USA

Our long-term monitoring study indicates that FSS can alter organic matter quality in urban streams and stormwater management flowpaths. Monitoring results from the Campus

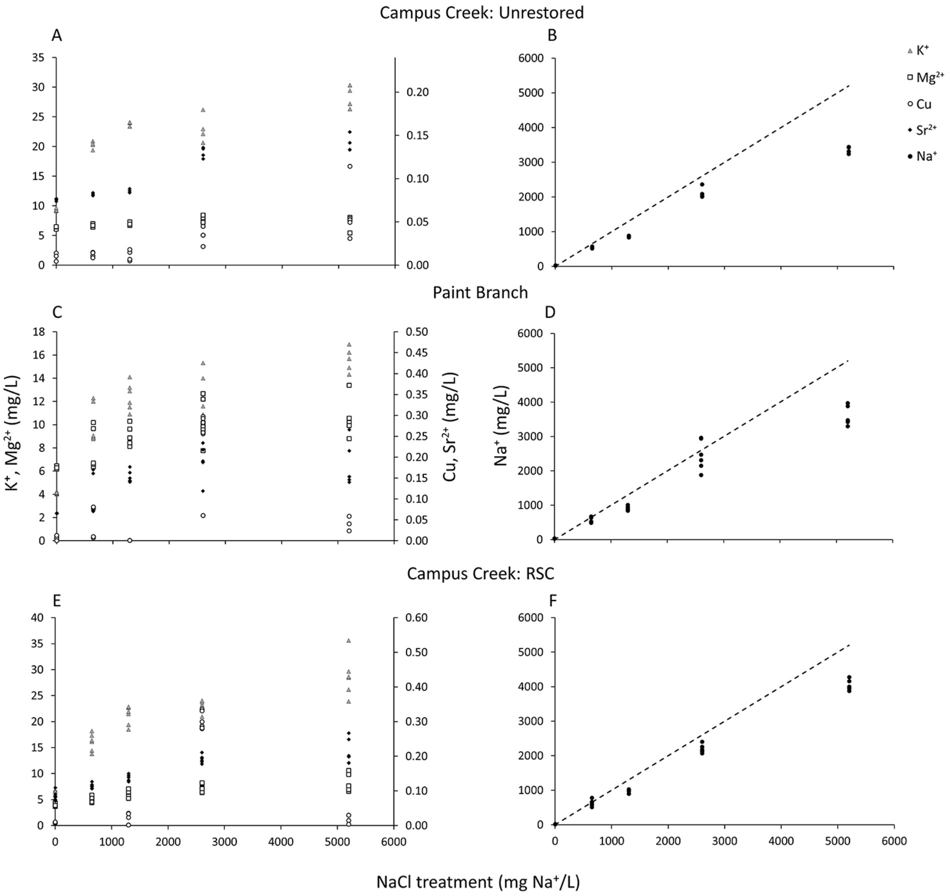

Figure 9. Retention and release of base cations during experimental salinization experiments from 1 unrestored site along Campus Creek (A, B), 1 site along Paint Branch that was restored with floodplain reconnection (C, D), and 1 site along Campus Creek that was restored with regenerative stormwater conveyance (RSC) (E, F). Campus Creek and Paint Branch both flow through the University of Maryland campus in College Park, Maryland, USA. Experimental incubations consisted of stream sediments incubated with stream water. Experimental additions of NaCl at varying levels resulted in release of base cations and metals (A, C, E) but retention of Na^+ (B, D, F). Na^+ retention was calculated based on how much Na^+ was added during the experiment and how much was present in overlying stream water after the incubation (values below the dashed line represent Na^+ retention or the difference between how much Na^+ was added and how much was measured after the incubation; B, D, F). The x-axis mentions NaCl treatment (mg Na^+/L) because we are explicitly comparing the Na^+ concentration added at the beginning of the incubation with the Na^+ concentration in the overlying water at the end of the incubation.

Creek study site showed sharp increases in organic matter from microbial and algal sources in response to road salt applications, likely because of lysing cells and changes in solubility, which was reflected as peaks in the fluorescence index and biological autochthonous inputs index (Fig. 8F). Interestingly, concentrations of dissolved organic C and total dissolved N didn't appear to show strong responses during or after the road salt event at the Campus Creek study site (Fig. 8C, D). Salinization can substantially affect organic matter sources, but its impacts on total quantity can sometimes be more complex. 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 have been correlated with changes in quantity and quality of DOM (Duan and Kaushal 2015, Gabor et al. 2015, Gao et al. 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 a primary form of retention 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+} because the introduction of these cations into solution increases the transformation of dissolved DOM into particulate form through

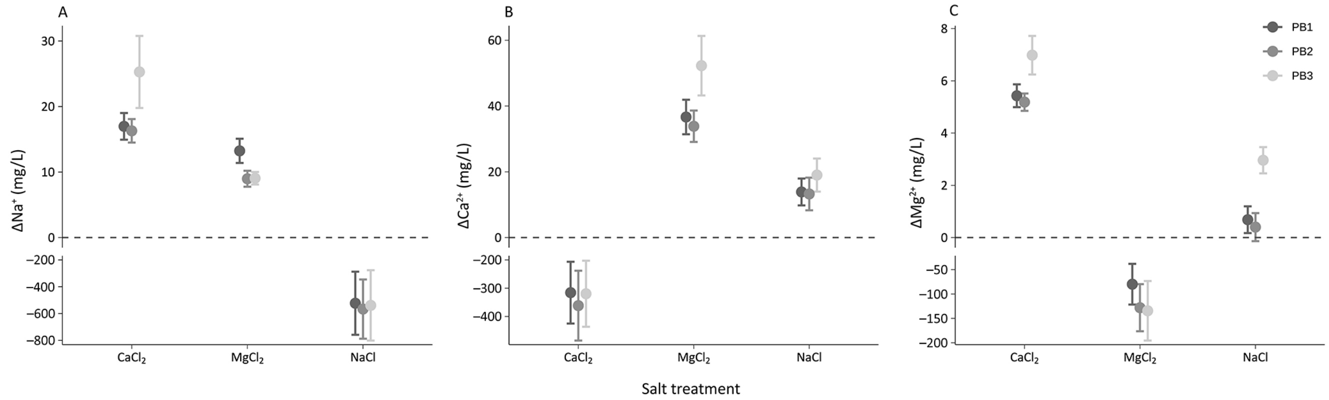

Figure 10. Base cations were released from stream sediments because of cation exchange in response to experimental salinization of stream water from 3 sites at Paint Branch (PB), a stream restored with floodplain reconnection flowing through the University of Maryland campus in College Park, Maryland, USA. Positive values >0 (dashed line) indicate release, whereas negative values indicate retention. Conversely, cations that were added experimentally showed retention in stream sediments in Paint Branch. Error bars represent ±1 SD of the mean.

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 substantially (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 potentially 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 BMPs. Salting in refers to the positive correlation between ionic strength and the solubility of organic matter, such as 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. The threshold between salting in and salting out is controlled both by the ionic strength of the solution and the concentration of various salt ions. Salting in occurs at lower ionic strength, when the addition of salt ions can increase the solubility of proteins. Further, at low salt concentrations, proteins will dissolve more easily with increases in ionic strength. Salting out occurs at higher ionic strengths, where proteins can form protein-to-protein bonds that become hydrophobic and then precipitate out of the water column. Therefore, at higher ionic strengths, salting out can decrease the concentrations of DOM in solution. Also, at high salt concentrations, protein will precipitate out with increases in ionic strength. The ability of anions relevant in this study to salt in proteins (from highest to lowest; see the Hofmeister series in Hyde et al. 2017) is: $CO_3^{2-} > SO_4^{2-} > Cl^-$, and for cations relevant to this study the order is: $NH_4^+ > K^+ > Na^+ > Mg^{2+} > Ca^{2+}$. We surmise that because FSS from different sources increases the concentrations of these anions and cations in urban waters, FSS can affect the solubility and quality of different forms of organic matter.

Case studies from the literature: Evidence for retention and release of multiple contaminants along stormwater flowpaths

Our synthesis of 29 case studies of changes in distinct chemical cocktails along urban stormwater BMP flowpaths from North America and Europe showed similar findings to our original data and other results from the Mid-Atlantic USA (Table S5). 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 (Table S6). For example, Cl^- ranged from –130% export to a 94% decline along flowpaths from inflow to outflow, with 38.25% average retention. The primary mechanisms for the declines in Cl^- concentrations, across studies, were infiltration and storage. Na^+ showed substantial retention along flowpaths compared with the rest of the base cations (Mg^{2+}, Ca^{2+}, and K^+), which was similar to our results from the Mid-Atlantic USA (Fig. S1). Na^+ retention measured in multiple BMPs (a stormwater management pond, a bioretention cell, and a bioswale) showed consistent decreases in concentrations from 10 to 47% along flowpaths, also related to storage and infiltration. In contrast, Mg^{2+}, Ca^{2+}, and K^+ all showed patterns of increasing concentrations along stormwater management flowpaths because of cation exchange processes. Instead of retention, these elements typically showed patterns of release with values of –63 to 1230% for Mg^{2+}, –6 to 152% for Ca^{2+}, and –22 to 211% for K^+, with the highest values of release in bioswales. However, in the stormwater management pond, these elements showed patterns

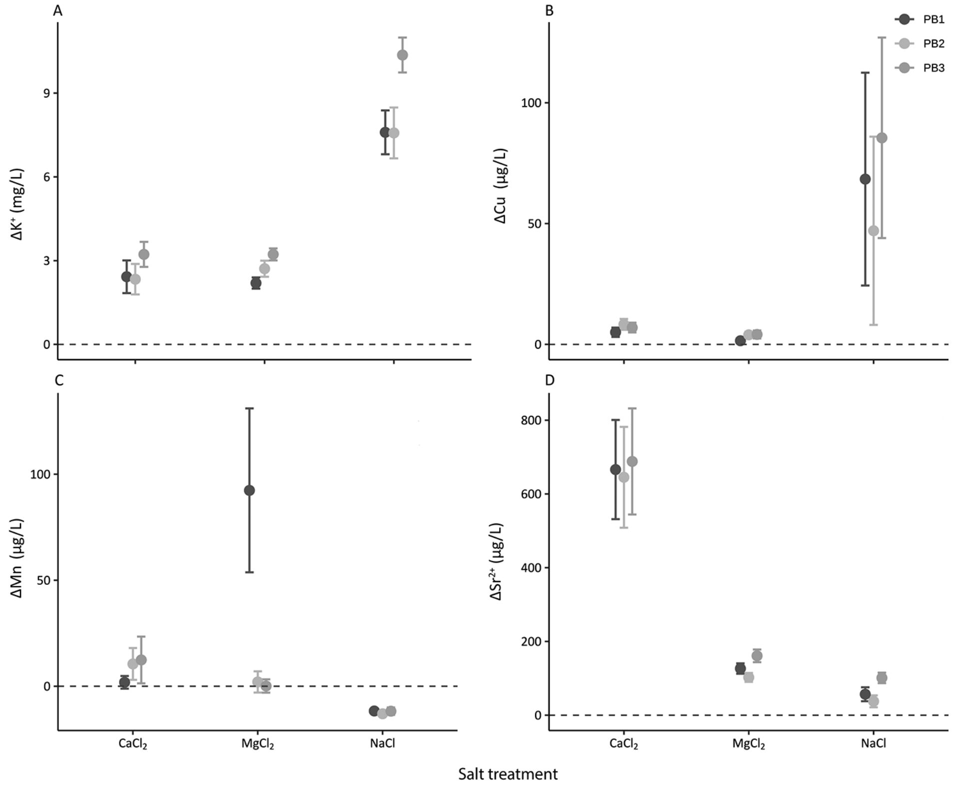

Figure 11. K^+ and trace elements were released from stream sediments because of cation exchange in response to experimental salinization of stream water from 3 sites at Paint Branch (PB), a stream restored with floodplain reconnection flowing through the University of Maryland campus in College Park, Maryland, USA. Positive values >0 (dashed line) indicate release and negative values indicate retention. Error bars represent ±1 SD of the mean.

of retention because of increased hydrologic residence times and trapping of sediment. Across studies and BMPs, nutrients, including N and P, primarily showed retention, with denitrification and microbial uptake as the primary retention mechanisms, respectively. N concentrations ranged from 16 to 100% retention, with an average retention of 33.5%. On the other hand, P showed variable retention and release in the constructed wetland and bioretention (Table S6). Overall, our case studies and literature analysis show that flowpaths along urban streams and stormwater BMPs influence biogeochemical processes related to FSS. FSS was linked with trends in mobilizing metals, base cations, and nutrients, contributing to acidification and alkalinization of waters and influencing the quality of organic matter.

KNOWLEDGE GAPS AND EMERGING RESEARCH FRONTIERS

Currently, it is known that FSS is increasing in freshwaters globally, there are multiple ions associated with FSS, and FSS has the potential to mobilize contaminants. Stream restoration and urban stormwater BMPs have also increased over time, and there is some potential for these strategies to reduce urban runoff and improve water quality. In this paper, we have shown that FSS can reduce the effectiveness of stream restoration and urban stormwater BMPs by causing changes in water chemistry. Additionally, the amounts and types of salt ions influence the level of mobilization of contaminants. The potential for reducing applications of road salts to prevent mobilization of contaminants and to maximize the beneficial effects of stream restoration and BMPs on overall stream health, therefore, is a research avenue that needs pursuing. 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 (Fig. 2A–H). More work is also needed to elucidate the impacts of FSS on restored ecosystems and stormwater management features and to determine whether stormwater management is either impaired by FSS or can be implemented as a BMP to ameliorate the effects of FSS.

One mechanism by which FSS may diminish the positive effects of stream restoration is through the unintended accumulation of salts in floodplains where stream restoration or stormwater management BMPs have been implemented. For instance, salt accumulation in restored floodplains (Fig. 3) can affect the efficacy of stream restoration on enhancing water quality, as shown by the sustained levels of elevated salinity from road salt runoff at Minebank Run following restoration to repair and reduce erosion and improve N uptake via reconnected banks (Kaushal et al. 2008, Cooper et al. 2014). Other stormwater management approaches designed to reduce flashy runoff, increase groundwater infiltration, and improve N uptake, like RSC (Duan et al. 2019), can also contribute to unintended Cl^- storage in groundwater or shallow surface pools, thereby leading 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 baseflow conditions, suggesting that stormwater management can contribute to groundwater plumes of Cl^- and, therefore, potentially also 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 BMPs, suggesting the interplay of retention and release of salt ions along hydrologic flowpaths (Fig. 6A, B). Furthermore, there may be associated effects of increased salt ion concentrations and loads on contaminant mobilization of elements like P along hydrologic flowpaths (Fig. 6A, B), which warrants further study.

Salinity may be chronically elevated in urban streams because of groundwater retention, but stormwater features may attenuate severe peaks of salts by shifting salt pulses to press regimes (Fanelli et al. 2019). For example, wetlands that formed naturally in stormwater features reduced the timing and peaks of salinity pulses from road salts in an urban ecosystem in North Carolina, USA (Maas et al. 2021). In fact, peak salinities were reduced by 94% and pulses were delayed by 45 d because of storage of salt-laden water in the ground and subsequent slow release over a longer period of time (Maas et al. 2021; Table S6). In addition, these wetlands also reduced peak temperatures, and temperature, in addition to conductivity, can serve as a proxy for salinity in some cases. There can be relationships between lower streamwater temperatures during winter, which coincide with road salt applications, and concentrations of ions and metals (Fig. 7A–C). It is important to note that pulses in salt ions associated with road salting events also are characterized by elevated levels of other mobilized contaminants (Fig. 8A–F). It is unknown whether stress to aquatic organisms in urban streams is attributable to seasonal salt ion pulses, chemical cocktails of other contaminants, or a combination of both (Mount et al. 1997, Cormier et al. 2013), nor how shifting peaks in salts to press regimes exacerbates or relieves this stress, which presents another pressing question to be investigated.

Hydrologic disconnection between streams and floodplains exacerbates Cl^- pulses and is another area that would benefit from further research. Daley et al. (2009) recommended reducing 1st-flush Cl^- pulses often seen in flashy urban systems by engineering stormwater management that increases hydrologic residence and reconnects surface water and groundwater. Slosson et al. (2021) showed downstream delivery of Cl^- from road salts by channelized streams with armored banks and limited groundwater connection, whereas streams with higher surface water–groundwater connection delivered 50% less Cl^- than the channelized streams. Extreme disconnection, such as occurs when streams are placed in pipes and conduits (i.e., buried streams), 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 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 affected by road salt runoff, whereas downstream, connected stream reaches were buffered by groundwater discharge, which was 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, such as increased alkalinity, on aquatic life (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 of 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 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, reducing water-holding capacity, root penetration, seedling emergence, increasing runoff and erosion, and, ultimately, causing imbalances in plant nutrient availability (Qadir and Oster 2004). Restoration of sodic and saline-sodic soil systems is promoted by providing Ca^{2+} to replace excess Na^+ from the cation exchange sites, often through costly gypsum amendments, which can reduce sodicity by up to ~60% (Qadir and Oster 2004). Vegetative bioremediation can be effective (up to ~50% 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 sodicity where crop growth is variable and patchy (Qadir and Oster 2004). However, long-term (50-y) implementation of forest management practices have been found to improve soil sodicity and increase soil organic C content and Ca^{2+} while decreasing soil pH (Pandey et al. 2011).

Soil amendment is a key strategy for effective management of sodic and saline soils and is another critical area for research. Organic mulching provides organic matter that can be a source of Ca^{2+} and Mg^{2+} that enhance exchange of Na^+ from soils and improve soil porosity, thereby allowing for better leaching of Na^+ (Saifullah et al. 2018). Applying manure and FeS_2 increases soil methanotrophs in saline rice fields, thereby reducing CH_4 production (Pandey et al. 2011). In some cases, biochar soil amendments may help remediate salt-contaminated soil, but amendment effectiveness is dependent upon tailoring biochar to the contaminants of concern (Saifullah et al. 2018). Biochar use is also limited by feedstock sourcing and cost-effective production. Applying various cyanobacteria, salt tolerant bacteria, and methanotrophs to remediate salty and sodic soils is another area where research is needed, and understanding soil bacterial communities and rhizosphere ecology will be critical to their use in restoring ecosystem function, especially in agricultural systems (Pandey et al. 2011).

Ultimately, preventing and remediating salt damage is dependent upon water managers, stakeholders, and scientists collaborating to identify cost benefits of BMPs (Canedo-Arguelles et al. 2016). Critical questions remain about which stormwater features, including detention and retention ponds, rain gardens, natural and 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 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 processes, such as surface water–groundwater interactions, bank storage, precipitation, and discharge and 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. In addition, stormwater management in predominantly lake systems may be at particular risk of salt contamination because accumulation is likely to far exceed flushing rates (Dugan et al. 2017, McGuire and Judd 2020). Ancillary or unexpected consequences of stormwater management, such as accumulation of salts in soils and groundwater, mobilization of various ions and metals (Galella et al. 2021), longevity of projects, and trade-offs in outcomes (Wood et al. 2022) must also be considered. It is possible that stormwater BMPs 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

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 synthesized questions from a wide range of stakeholders, practitioners, environmental managers, and researchers. Recently, we communicated with these broader groups in a United States Environmental Protection Agency webinar on freshwater salinization and chemical cocktails (see https://www.epa.gov/water-research/water-research-webinar-series; Mayer et al. 2021). We received ~130 questions covering a wide range of science and management issues from among 1600 attendees representing all 50 United States (plus 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, as well as about how to better manage FSS to avoid contaminant risks.

Question 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 are there substantial impacts year-round?

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

Question 3 How does FSS affect groundwater concentrations of contaminants over time? What are long-term trends in salts, hardness, and metals in groundwater flowpaths associated with stormwater BMPs (particularly more infiltration-based approaches)?

Question 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?

Question 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, services, and potential toxicity to certain forms of aquatic life?

Question 6 Are there any risks to public health owing to salt impairment of groundwater, and do stormwater BMPs contribute to or ameliorate this risk?

Question 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, or aquatic life)?

Question 8 Is it better to prioritize and target salt reductions during seasons when biology is more active and susceptible life stages, such as eggs and larvae, are present (e.g., early spring)?

Question 9 Is the growing use of stormwater infrastructure that directs stormwater, salts, and contaminants into groundwater through infiltration creating groundwater contamination problems that we will see as problems for years (decades) to come?

Question 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 and on the mobilization of chemical cocktails of nutrients and metals across a broad range of urban streams. More work is necessary to quantify changes in the magnitudes and durations of chemical-cocktail loading in response to winter deicing events. Tracking magnitudes, seasonality, and duration of the mobilization of chemical cocktails that results from 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 vital information regarding critical thresholds of salinity for contaminant mobilization. Analysis and synthesis of empirical data showing effects of varying levels of different salt ions across sites will also help identify which salt ions have the greatest impact on nutrients and metals. Our synthesis and analysis in this paper is among the 1st to quantify changes in the peaks and persistence of different chemical cocktails in response to winter deicing events and to infer ecosystem impacts in urban stormwater BMPs and restored streams. Anticipating and addressing the effects of salt ions on the mobilization of nutrients and metals will better inform plans for effective stream restoration and stormwater management strategies designed to improve urban water quality.

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