Biogeochemistry (2018) 141:463–486
https://doi.org/10.1007/s10533-018-0514-2

Episodic salinization and freshwater salinization syndrome mobilize base cations, carbon, and nutrients to streams across urban regions

Shahan Haq · Sujay S. Kaushal · Shuiwang Duan

Received: 26 January 2018 / Accepted: 11 October 2018 / Published online: 24 October 2018

Abstract Urbanized watersheds in colder climates experience episodic salinization due to anthropogenic salt inputs and runoff from impervious surfaces. Episodic salinization can be manifested as a 'pulse' in concentrations and fluxes of salt ions lasting from hours to days after snowstorms in response to road salting. Episodic salinization contributes to freshwater salinization syndrome, characterized by cascading mobilization of chemicals and shifting acid–base status. We conducted laboratory experiments and analyzed high-frequency sensor data to investigate the water quality impacts of freshwater salinization syndrome and episodic salinization across 12 watersheds draining two major metropolitan regions along the U.S. East Coast. Sediments from 12 watersheds spanning land use gradients across two metropolitan regions, Baltimore, Maryland and Washington DC, were incubated across a range of replicated salinity treatments (0–10 g/L sodium chloride). There were statistically significant linear increasing trends in calcium and potassium concentrations with experimental salinization across all 12 sites and in magnesium concentrations at 11 of 12 sites ($p < 0.05$), with mean rates of increase of 1.92 ± 0.31 mg-Ca per g-NaCl, 2.80 ± 0.67 mg–K per g-NaCl, and 1.11 ± 0.19 mg-Mg per g-NaCl, respectively. Similarly, there were statistically significant increasing linear trends in total dissolved nitrogen (TDN) concentrations with experimental salinization at 9 of the 12 sites, with a mean rate of increase of 0.07 ± 0.01 mg-N per g-NaCl. There were statistically significant increasing linear trends in soluble reactive phosphorus (SRP) concentrations with experimental salinization at 7 of the 12 sites ($p < 0.05$), with a mean rate of increase of 2.34 ± 0.66 µg-P per g-NaCl. The response of dissolved inorganic carbon (DIC) and organic carbon (DOC) concentrations to experimental salinization varied between sites, and dissolved silica did not show any significant response. High-frequency sensors near the experimental sites showed statistically significant positive linear relationships between nitrate concentrations, specific conductance, and chloride concentrations similar to relationships observed in laboratory incubations. Our results suggested that episodic salinization and freshwater salinization syndrome can mobilize base cations and nutrients to streams through accelerated ion exchange and stimulate different biogeochemical processes by shifting pH ranges and ionic strength.

Responsible Editor: Susana Bernal.

Electronic supplementary material The online version of this article (https://doi.org/10.1007/s10533-018-0514-2) contains supplementary material, which is available to authorized users.

S. Haq (✉) · S. S. Kaushal · S. Duan
Department of Geology & Earth System Science
Interdisciplinary Center, University of Maryland,
College Park, MD 20742, USA
e-mail: haq@umd.edu

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

Keywords Salt pollution · Emerging contaminants · Human-accelerated weathering

Introduction

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

Due to their ionic nature, most salts are retained in soils and groundwater (Cooper et al. 2014; Findlay and Kelly 2011). As such, salts accumulate in the watershed, and long-term salinization has been reported in rivers on most continents and biomes (Williams 2001; Kaushal et al. 2014a, b; Herbert et al. 2015). Urban areas are particularly vulnerable to salinization due to the combination of salt inputs (e.g., road salts, gypsum), impervious surfaces, and drainage infrastructure (Snodgrass et al. 2017; Kaushal et al. 2017; Marsalek 2003). In the Northeastern USA, for example, salinity has doubled from 1990 to 2011 and has exceeded the rate of urbanization (Corsi et al. 2015). Previous studies suggest that rural streams and rivers in the Eastern USA with as little as 5 percent impervious surface coverage within their watersheds can also be at significant risk for long-term salinization (Kelly et al. 2008; Conway 2007), while in the Midwestern USA, recent studies suggest that lakes with as little as one percent impervious surface coverage are at risk (Dugan et al. 2017).

Episodic and long-term salinization of fresh water can have ecosystem scale impacts such as the loss of native vegetation, disruptions in food webs, and the mobilization of contaminants (e.g., heavy metals) (Lofgren 2001; Norrstrom 2005; Backstrom et al. 2004; Amrhein et al. 1992). However, less is known regarding impacts of salinization on carbon and nutrient cycles in fresh water (Duan and Kaushal 2015). Episodic salinization can enhance the mobilization of carbon, nutrients, and cations due to coupled biotic and abiotic processes, such as ion exchange, rapid nitrification, pH, increased ionic strength, organic matter dispersion, and chloride complexation. While billions of dollars have been spent to reduce nitrogen and phosphorus loading by stream and riparian restoration (Bernhardt et al. 2005), salt pollution has been largely unmanaged and unregulated. Part of the reason why effects of salinization on carbon and nutrient dynamics in streams and rivers is not well understood may be the different temporal and spatial scales at which salinization can occur. For example, salinity (*e.g.*, chloride) concentrations in urban rivers may temporarily reach up to 33% the salinity of sea water in the hours to days following a snow storm, and then gradually accumulate in watershed sinks (e.g., groundwater, soil, lakes) (Kaushal et al. 2005; Kelly et al. 2008; Cooper et al. 2014). Acute and episodic salinization occurs over the course of hours to days following a snow event (e.g., road salt pulse) and chronic long-term salinization can occur over the course of seasons to decades (Kaushal et al. 2018). Some water quality effects of salinization, such as nutrient and cation mobilization, would likely occur over the course of several hours and would likely immediately follow increases in salinization (e.g., post-storm). However, these effects may not be captured by traditional water quality monitoring, which is conducted by sampling a fixed point in a stream or river on a weekly to monthly interval (as better explained in Rode et al. 2016; Pellerin et al. 2012). As such, these effects may be explored with a combination of lab experiments and high-frequency sensor data.

The goal of this study was to investigate the potential water quality effects of episodic salinization and freshwater salinization syndrome in urban watersheds induced by acutely elevated salinity across the sediment–water interface. We compared results of experimental salinization in the laboratory with patterns of episodic salinization (specific conductance and chloride) and nutrient loading (nitrate) from high-frequency field sensors. Sensor data were analyzed to provide additional insights on the timescales of salinity-nutrient interactions, underlying mechanisms, and potential controlling factors. An improved understanding of the interactions between salinization pulses and nutrient pollution is necessary to better manage streams and rivers and to identify unanticipated geochemical relationships that may impact stream restoration strategies and water quality goals.

Methods

We conducted laboratory experiments from sediments collected at 12 sites across two metropolitan regions and analyzed high-frequency sensor data from three sites to explore the potential relationships between episodic salinization and solute concentrations during snowstorms in streams. Laboratory experiments were used to characterize the potential release of base cations, carbon, and nutrients during episodic salinization from sediments to streams. Sediments, streamwater, and sodium chloride were incubated in a controlled lab environment to mimic post snowstorm conditions (i.e., high salinity runoff entering the stream). These methods for incubations were previously described in Duan and Kaushal (2015). We also explored high-frequency sensor data from the U.S. Geological Survey in the same vicinity as our laboratory experiments sites to investigate whether there were similar relationships between specific conductance (a proxy or surrogate for dissolved salts) and nitrate (a key pollutant in the Chesapeake Bay watershed leading to eutrophication).

Site description

Sediment and streamwater were incubated form 12 sites in the Baltimore-Washington Metropolitan Area in the Chesapeake Bay Watershed. Eight of the stream sites are within the U.S. National Science Foundation (NSF) supported Baltimore Ecosystem Study Long Term Ecological Research Project (BES-LTER), and are long-term, routinely monitored, and well characterized sites (e.g., Groffman et al. 2004; Shields et al. 2008; Duan et al. 2012; Majcher et al. 2018). These 8 stream sites are located in Baltimore, Maryland, where they exhibit a land use gradient (Fig. 1). These sites vary in drainage area (8–8350 ha), percent of watershed area covered in impervious surfaces (0–61%), population density (0 people/ha to 20 people/ha), and dominant land use (undisturbed forest in a state park, suburban, agricultural, urban residential, and heavily urban commercial) (Table 1). All eight of these sites are in close proximity and share the same hydrologic, geologic (piedmont), and biome (temperate deciduous/humid). Seven of these eight sites are collocated with US Geological Survey gaging stations (Table 1). Two of these eight sites (POBR, BARN) are nested in the relatively undisturbed 5500 ha Beaver Dam Watershed, which drains into the Gunpowder River watershed (then Chesapeake Bay) in Northern Baltimore County. The other 6 sites are nested in the heavily modified suburban and urban Gwynns Falls Watershed, which drains 17,500 ha (and empties into the Patapsco River and then Chesapeake Bay) in Southern Baltimore County and Baltimore City (Fig. 1).

The remaining 4 of the 12 incubation stream sites are from the heavily urbanized Anacostia watershed

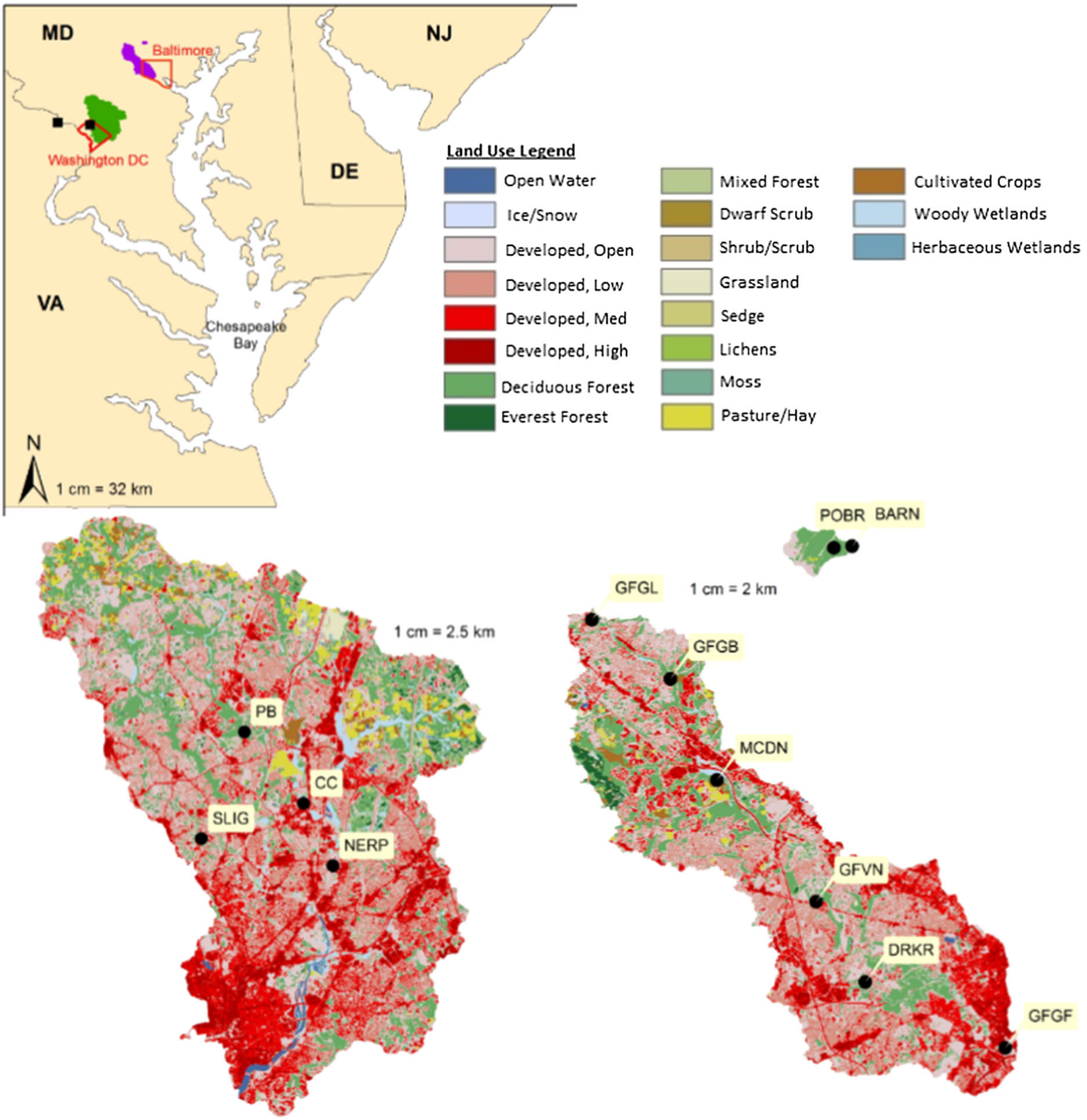

Fig. 1 Maps of the study area, with different spatial scales for each map. The high-frequency nitrate sensors are denoted as black squares in the Chesapeake Bay map (Rock Creek sensor is in Washington DC; Difficult Run sensor is in VA). Land use maps for Gwynns Falls and Baisman Run (Baltimore) watersheds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

(46,000 ha) in Southern Maryland, near Washington DC. The Anacostia is a major tributary of the tidal Potomac River and the Chesapeake Bay as described in Smith and Kaushal (2015), and Devereux et al. (2010). These four sites vary in both drainage area (200–18,800 ha) and impervious surface cover (27–41%) and offer a slightly different hydrology, geology (coastal plain), land use (Fig. 1), and drainage infrastructure (less leaky, less old, and more green/Best Management Practices stormwater features) than the Baltimore LTER sites. Three of these four

Table 1 Characteristics of the all sites for the sediment incubation experiments and the high-frequency sensor data analysis

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

Anacostia watershed sites are collocated with US Geological Survey gaging stations (Table 1).

Data from three sensors located in the Washington DC Area were used in this study; Difficult Run, Rock Creek, and Northeast Branch Anacostia. All three sensors are in close proximity to the Anacostia Watershed incubation sites (Fig. 1), and are maintained and operated by the US Geological Survey. The Northeast Branch Anacostia site was selected because the sensor is co-located with one of the experimental incubation sites (NERP), and it has a 14 year continuous record of high-frequency specific conductance (15 min intervals) and discrete (grab-sample) chloride data. The NERP sensor (Gaging Station 01649500) is a heavily urban site (Fig. 1) with short reaches of boulder embankment (previously channelized), and has a watershed size of 18,800 ha. The NERP sensor does not have high-frequency nitrate measuring capabilities.

The Difficult Run and Rock Creek sites were selected due to the availability of high-frequency nitrate measurements, and because of similarities in their discharge and watershed size to sites where experiment incubation were performed (described above). Although both sites have a predominately suburban and urban land cover, they also have a wide and undeveloped riparian zone consisting of hiking trails, recreational areas, and bands of intact forest with temperate deciduous trees (as described in Miller et al. 2013). The Difficult Run sensor (Gaging Station 01646000) is located near Great Falls, Virginia, approximately 24 km northwest of Washington DC, and the Rock Creek sensor (gaging station 01648010) is located in the northern corner of Washington DC (Fig. 1). Difficult Run has a watershed size of 15,000 ha, and Rock creek has a watershed size of 16,600 ha. Difficult Run has 5 years of continuous high-frequency 15 min interval measurements of specific conductance and nitrate, and Rock Creek has a 2 year length of record, also in 15 min intervals. Both Difficult Run and Rock Creek are tributaries of the Potomac River and the Chesapeake Bay. Previous studies have characterized the sediment and biogeochemical dynamics in Difficult Run (e.g., Hupp et al. 2013; Batson et al. 2015), and other work has characterized nutrient loading and emerging contaminants in the Rock Creek watershed (e.g., Miller et al. 2013; Battaglin et al. 2009).

Sediment incubation experiments across varying degrees of salinization

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

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

Streamwater chemistry analyses

Dissolved inorganic carbon (DIC), dissolved organic carbon (DOC, measured as non-purgeable organic carbon), and total dissolved nitrogen (TDN) concentrations in water were measured within 24 h after the incubation using a combustion-catalytic-oxidation-NDIR method on a Shimadzu Total Organic Carbon Analyzer (TOC-V CPH/CPN; Shimadzu, Columbia, Maryland, USA). Soluble reactive phosphorus concentrations (SRP) in the water were measured within 10 days after the incubation using an automated colorimetric-blue method on a Lachat QuickChem 8500 Series 2 FIA System (Hach, Loveland, Colorado, USA). Base cation (calcium, potassium, magnesium) and Si concentrations in the acidified water samples were measured within 12 months after the incubation via inductively coupled plasma optical emission spectrometry in an acidified analytical matrix on a Shimadzu Elemental Spectrometer (ICPE-9800; Shimadzu, Columbia, Maryland, USA).

High-frequency sensors: specific conductance as a predictor for chloride and nitrate concentrations in streams

High-frequency sensor data from US Geological Survey stations 01649500 (NERP), 01646000

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

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

Statistical analyses

For each site, the incubation experiments were conducted in duplicates (using the same sediments and streamwater grab samples), the resulting dissolved concentrations were averaged, and the averaged values were used for all statistical analyses. In order to isolate the effects of episodic salinization on the mobilization of base cations, carbon, and nutrients from the sediment to streamwater, the results from an untreated control flask for each site were subtracted from the results of each treatment (Duan and Kaushal 2015). The resulting dissolved water chemistry were statistically evaluated using ordinary linear regressions with sodium chloride treatment as the independent variable and base cation, carbon, or nutrient concentration as the dependent variable. Slopes with a p value < 0.05 were assumed statistically significant, and this p-value criteria was used to ascertain whether episodic salinization in laboratory experiments significantly affected the dissolved concentrations of different solutes. The r^2 coefficient of determination of the linear regression model was calculated for each experiment, and was used to characterize the variability in dose responses (i.e., a high r^2 value indicated alignment of the solute response with the linear model). For the experimental incubations, all data and statistical analyses was conducted using Microsoft Excel (Microsoft Corporation, Redmond, Washington, USA).

Gaps in the high-frequency nitrate and specific conductance sensor measurements were not estimated by interpolation as they were normally distributed about their means, with the exception of some specific conductance outliers (e.g., the episodically high specific conductance). At each site, a high-frequency chloride record was estimated based on a linear relationship between the continuous high-frequency specific conductance measurements and discrete chloride grab sample measurements, as mentioned above. The magnitude of the relationship between estimated continuous chloride and sensor-measured continuous nitrate was also assessed by ordinary linear regression with estimated chloride as the independent variable and sensor-measured nitrate as the response variable. In order to assess the impact of extreme outliers, a least squares linear regression with iterative bi-square weighting was also performed, and the resulting slope was compared to the ordinary linear regression slope for agreement. A p-value < 0.01 was used to demarcate statistical significance of the slope, and whether an in situ empirical relationship exists between chloride and nitrate concentrations. The r^2 coefficient of determination of the linear regression model was used to assess the strength of the relationship. For the high-frequency sensors component of this study, all data and statistical analyses were conducted using MATLAB (MathWorks Inc., Natick, Massachusetts, USA).

Results

Sediment incubation experiments across varying degrees of salinization

Base cations, nitrogen, silica, phosphorus and carbon

As expected, the ambient streamwater chemistry varied across sites (Table 2). Chloride varied from a minimum of 2.72 mg/L at a headwater forested site (POBR, Baltimore) to a maximum of 135 mg/L at a headwater suburban site (GFGL, Baltimore). TDN varied from a minimum of 0.33 mg/L N at a headwater forested site (POBR, Baltimore) to a maximum of 5.96 mg/L N at a small agricultural stream (MCDN, Baltimore). SRP varied from a minimum of 2.05 μg/L P at POBR to a maximum of 97.15 μg/L P at GFGL. DIC varied from a minimum of 2.61 mg/L at POBR to a maximum of 38.70 mg/L at GFGL, while DOC varied from a minimum of 1.45 mg/L at MCDN to a maximum of 4.52 mg/L at a small suburban creek (CC, Anacostia). Silica concentrations varied from a minimum of 0.87 mg/L Si at a second order urban stream (NERP, Anacostia) to a maximum of 6.75 mg/L Si at GFGL. Although elemental silicon was measured in this study, we are reporting the results as silica as it is the dominant form of silicon in streamwater (e.g., Treguer et al. 1995; Conley 2002). The sum of the base cations (calcium, magnesium, potassium, and sodium) varied from a minimum of 9.19 mg/L at POBR to a maximum of 192.45 mg/L at a suburban mid-size stream with sanitary infrastructure leak issues (DRKR, Baltimore). The sediment composition also varied between sites, with sediment organic matter ranging from a minimum of 0.17% at two mid-size streams (SLIG, Anacostia, suburban with old growth trees) and (GRGF, Baltimore, urban and heavily polluted) to a maximum of 0.99% at MCDN.

Table 2 Ambient site chemistry at the time of the sample collection (i.e., starting in-stream conditions for the sediment incubation experiments)

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

Broadly, the ambient chemistry was not a good predictor of the effects of episodic salinization. However, there were significant linear correlations between ambient SRP concentrations and the magnitude of SRP mobilization (i.e., incubation slopes), between ambient DIC concentrations and DIC response, and between ambient chloride concentrations and the magnitude of potassium mobilization

There were consistent increases in base cation concentrations with increasing salinity across sites (Figs. 2, 3, 4). There were statistically significant linear increases in calcium and potassium concentrations with increasing sodium chloride treatments at all 12 sites, with rates of increase ranging from 0.20 ± 0.02 to 3.96 ± 0.37 mg Ca^{2+} per g NaCl and 0.38 ± 0.12 to 7.60 ± 0.53 mg K^{+} per g NaCl, respectively. There were statistically significant linear increases in magnesium concentrations at 11 of the 12 sites with rates of increase ranging from 0.38 ± 0.12 to 2.35 ± 0.51 mg Mg^{2+} per g NaCl. Salinization did not have a significant effect on magnesium at the remaining site (GFGB, Baltimore, suburban). Ambient stream chemistry was not a good predictor of the response of calcium or magnesium to salinization. However, there was a statistically significant linear correlation between ambient in-stream chloride concentrations during the sample grab, and the mobilization of potassium from the experiments (i.e., incubation rates of increase).

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

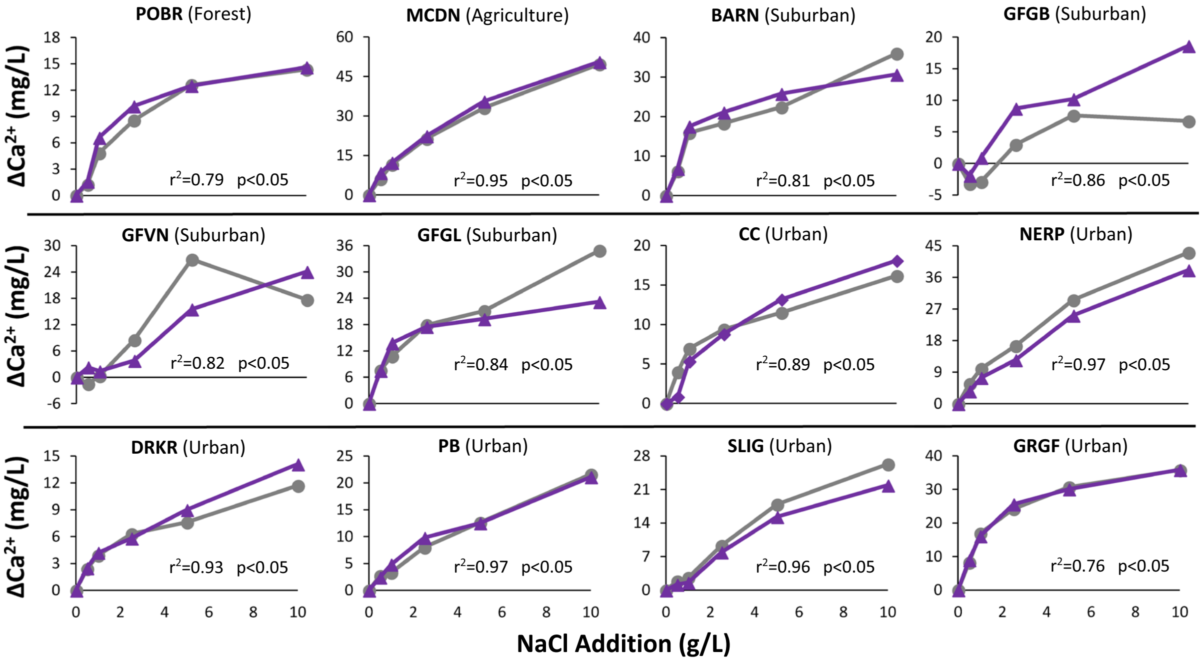

Fig. 2 Responses of dissolved calcium to experimental salinization (relative to an untreated control incubation). There was a significant linear mobilization of calcium at all 12 sites. The results from trial 1 are displayed as gray lines with circular data points, while the results from trial 2 are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

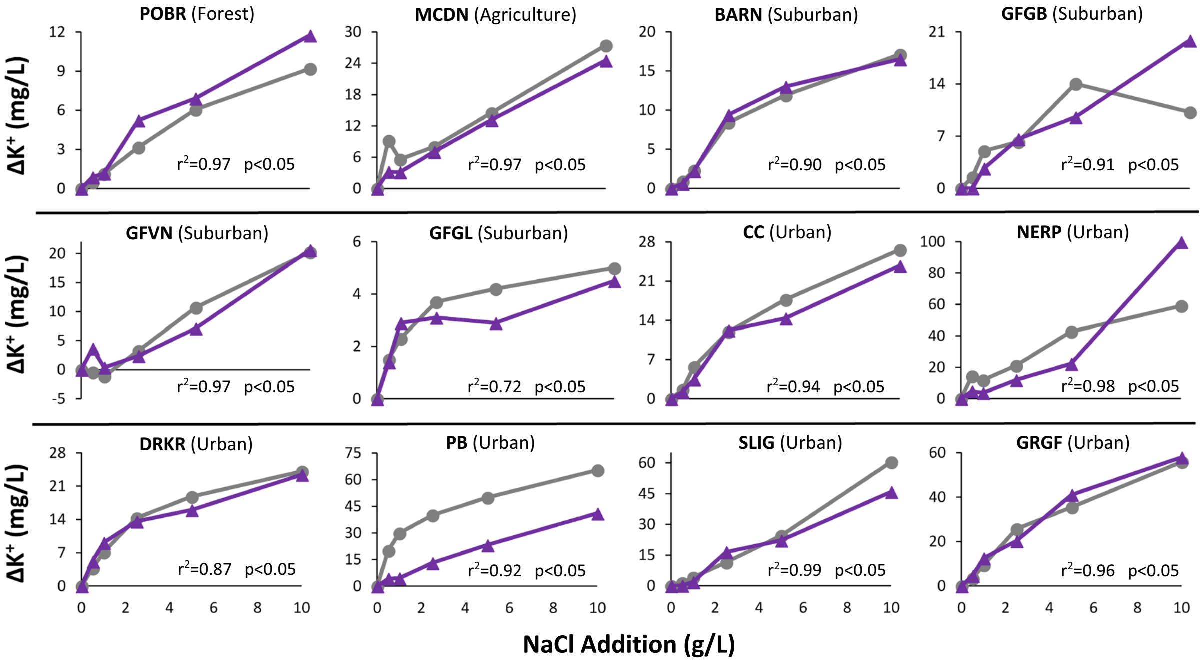

Fig. 3 Responses of dissolved potassium to experimental salinization (relative to an untreated control incubation). There was a significant linear mobilization of potassium at all 12 sites. The results from trial 1 are displayed as gray lines with circular data points, while the results from trial 2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

to episodic salinization was more variable than the response of TDN, the magnitude of the response was stronger (as indicated by the greater slopes in Table 4).

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

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

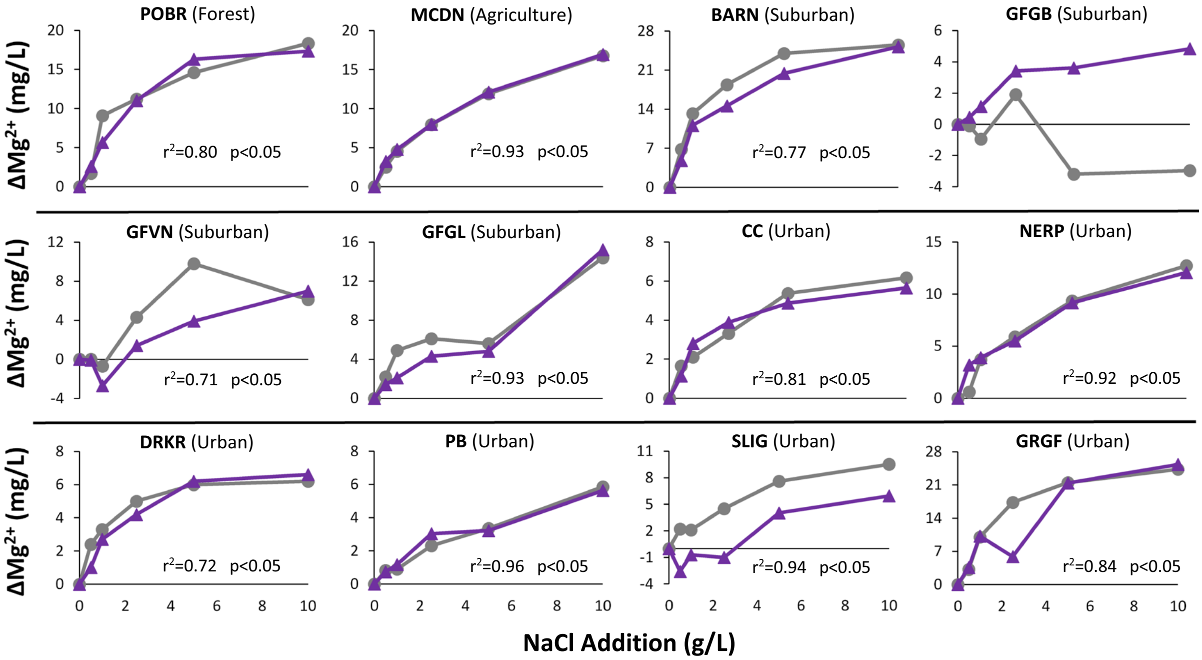

Fig. 4 Responses of dissolved magnesium to experimental salinization (relative to an untreated control incubation). There was a significant linear mobilization of magnesium at 11 of the 12 sites. The results from trial 1 are displayed as gray lines with circular data points, while the results from trial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

have a detectable effect on sediment organic matter at any site (Supporting Fig. S4).

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

Relationships between high-frequency specific conductance and nitrate concentrations in streams

Episodic salinization is shown in Fig. 8 as a pulse of elevated specific conductance in the winter months directly ensuing a snow storm (e.g., road salt application). At each site, the episodically high specific conductance is at least an order of magnitude above both the baseflow measurements and the long-term average, and the magnitude and duration of the pulse varied between sites. There was a large variation in the chloride and nitrate data at both sensor sites. As expected, there was a strong positive correlation between specific conductance and chloride concentration at these sites (Fig. 8). There were weak but still statistically significant increases in nitrate concentrations with increasing chloride concentrations at both high-frequency sensor sites (Fig. 9). At the Difficult Run sensor (near Great Falls, Virginia), the rate of increase was 1.46 ± 0.12 mg N per g Cl (ANOVA, $r^2 = 0.08$, df = 1583, $p < 0.01$), and at the Rock Creek sensor (northern Washington DC), the rate of increase was 0.46 ± 0.06 mg N per g Cl (ANOVA, $r^2 = 0.10$, df = 484, $p < 0.01$).

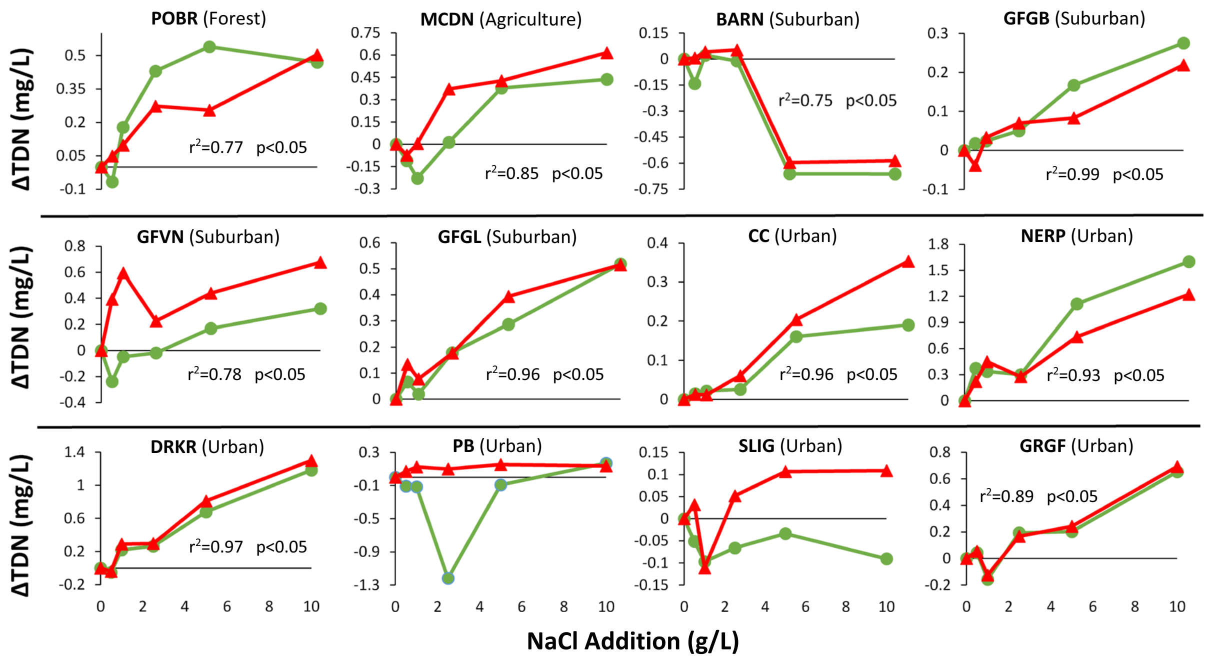

Fig. 5 Responses of dissolved nitrogen to experimental salinization for (relative to an untreated control incubation. There was a significant linear mobilization of TDN at 9 of the 12 sites. The results from trial 1 are displayed as green lines with circular data points, while the results from trial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

Discussion

Evidence for the water quality effects of episodic salinization and freshwater salinization syndrome

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

In our experiments, we attempted to simulate episodic salinization as it is a realistic exposure scenario that is faced by streams and rivers experiencing freshwater salinization syndrome (Fig. 8). When it comes to the response of organisms to salinization, recent research suggests that the extent of deviation from the norm (i.e., dosage and recovery time) is more important that the duration of exposure, and may largely determine the adversity of its impact (Woo and Salice 2017). The same principal may be extended to the geochemical and biogeochemical behavior of a stream ecosystem upon salinization. Episodic salinization can rapidly alter the pH and ionic strength of streamwater, which can change the sediment dispersal and coagulation dynamics, chemical complexation reactions, and the microbial processing of nutrients (Kaushal et al. 2017; Kaushal et al. 2018). Unlike at lower salinity levels, during episodically high salinity, cation exchange sites may become saturated, biotic mechanisms might be inhibited, and there may be corresponding changes to nutrient and carbon cycles, which can impact ecosystems (Duan and Kaushal 2015).

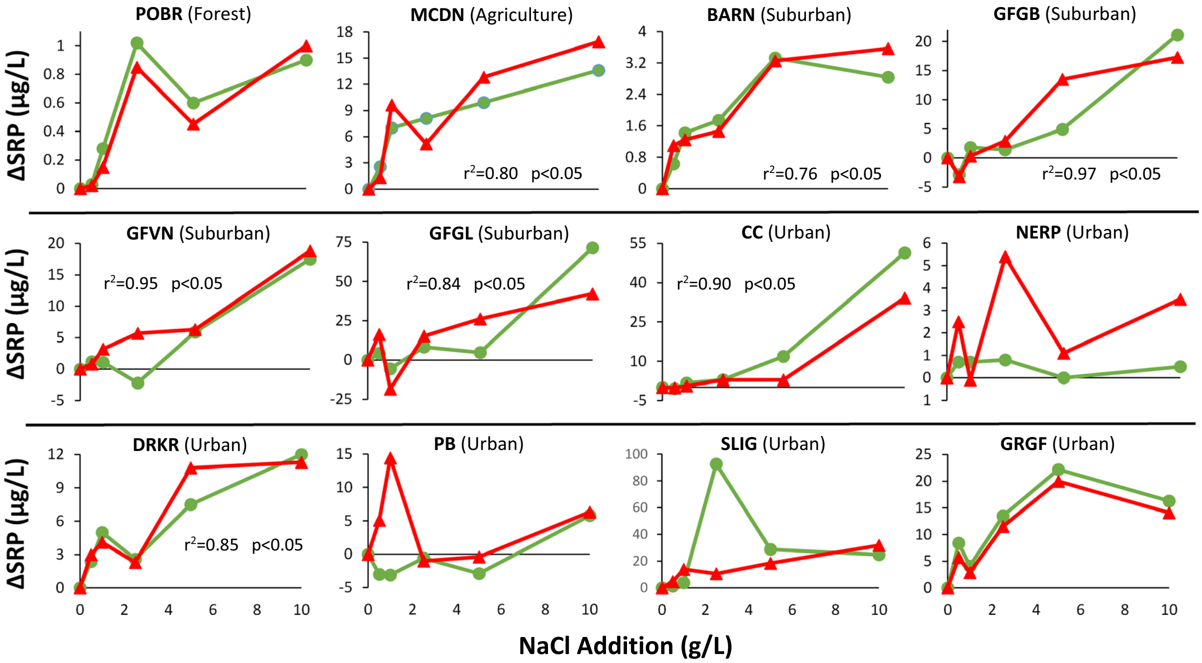

Fig. 6 Responses of dissolved phosphorus to experimental salinization for (relative to an untreated control incubation). There was a significant linear mobilization of SRP at 7 of the 12 sites. The results from trial 1 are displayed as green lines with circular data points, while the results from trial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

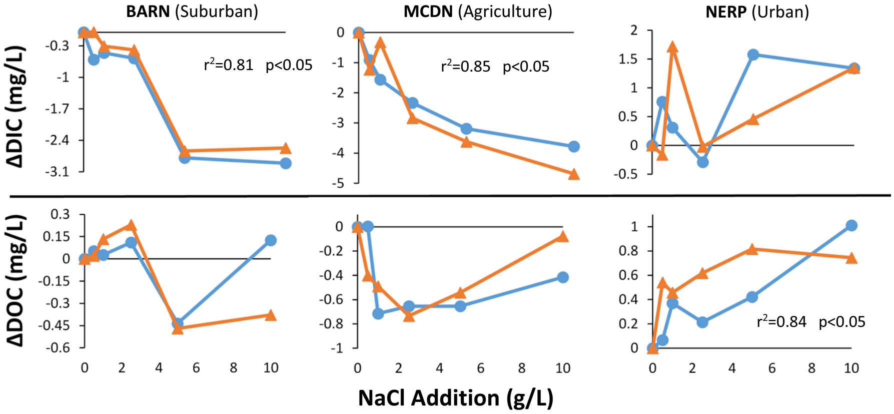

Fig. 7 Responses of DIC and DOC to experimental salinization for 3 of the 12 sites. The effects of salinization on carbon was variable, and this subset of sites was selected to demonstrate the variability. For each treatment level, a positive value indicates carbon was released from the sediment into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

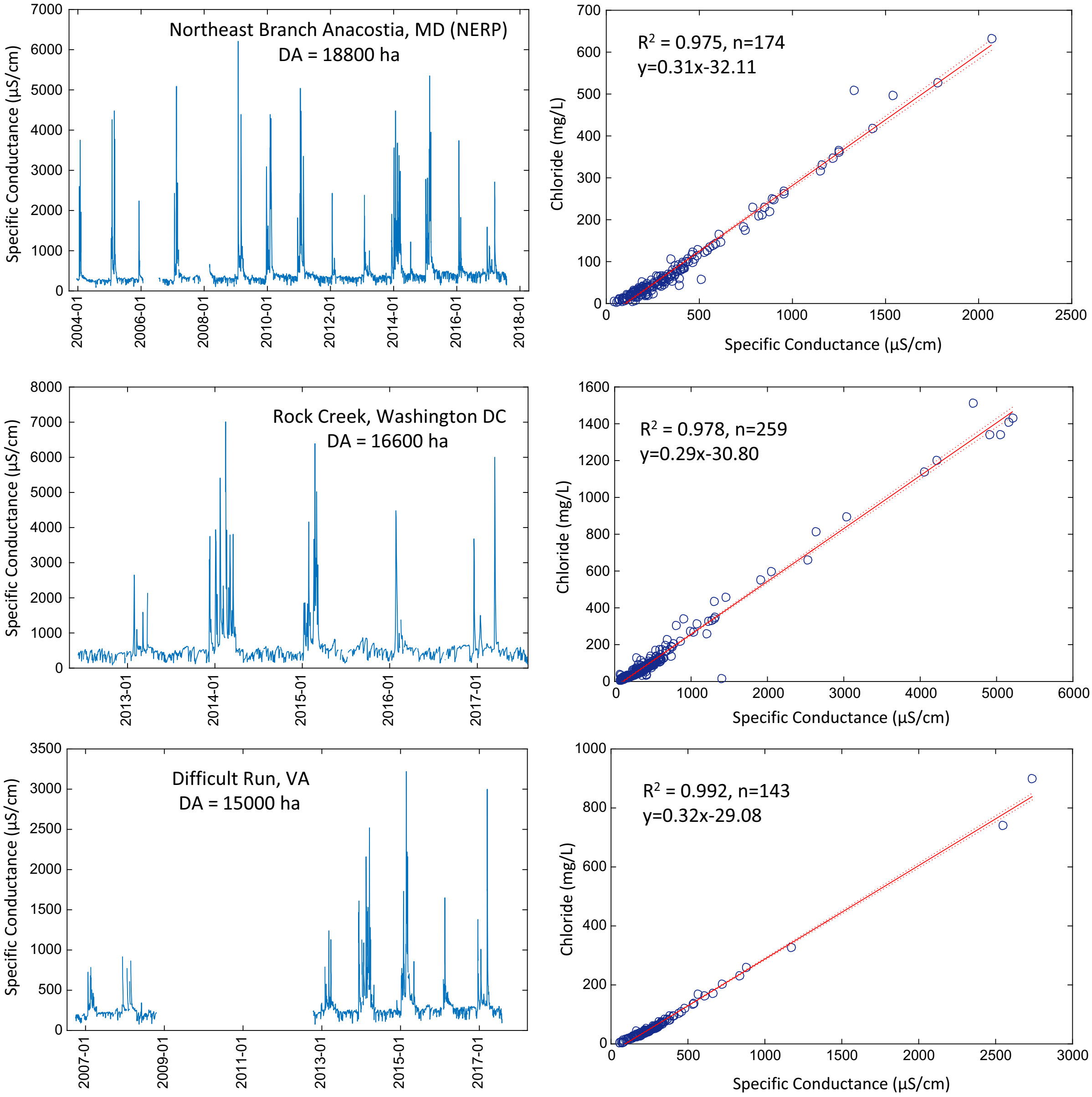

Fig. 8 (Left panel) Timeseries of daily average values of specific conductance. Episodic salinization manifests in the high-frequency sensor record as a pulse in specific conductance in the hours to days following a snowstorm. Experiments were conducted to determine potential effects of the salinization pulse on sediment biogeochemistry. (Right panel) Relationship between dissolved chloride from grab samples and the nearest instantaneous specific conductance measurement. There was a strong, positive, linear relationship between specific conductance and chloride concentrations. Dotted red line is the 95% confidence bounds for the regression. NERP is also an incubation experiment site. Difficult Run and Rock Creek are nearby to the incubation experiment sites, and the in situ relationships between salinity and nitrate were assessed at these sites

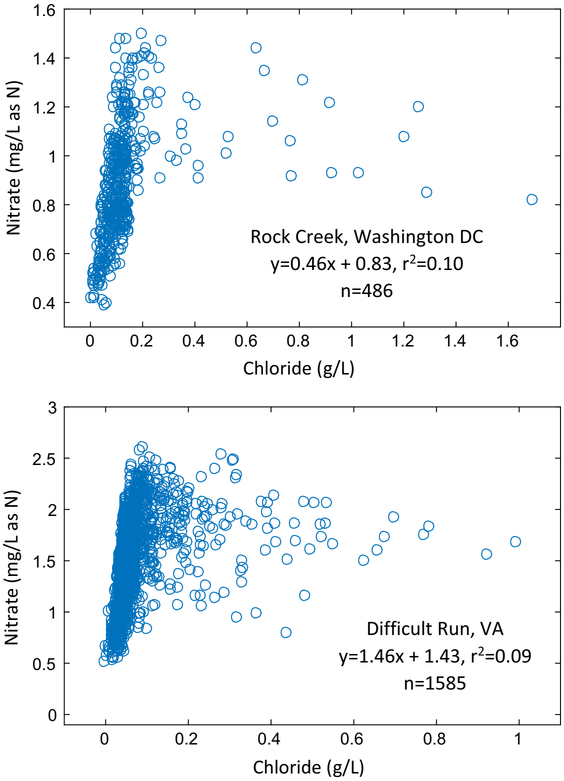

Fig. 9 Linear relationships between chloride (as estimated from daily average values of specific conductance) and nitrate in the high-frequency sensor record. The slope from the Rock Creek sensor (top panel) is within the same order of magnitude as the mean slope from the experiments, while the slope from the Difficult Run sensor (bottom panel) is an order of magnitude larger (contrasted in units of mg N per g Cl). The NERP sensor lacks nitrate measuring capabilities

Potential effects of episodic salinization and freshwater salinization syndrome on base cations

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

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

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

The mobilization of base cations from soils and sediments to streamwater due to episodic salinization and freshwater salinization syndrome could further

Table 3 Results of a linear regression analysis of the base cation response at each incubation site to sodium chloride additions

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

Units for calcium slopes are mg-Ca per g-NaCl, potassium slopes are mg–K per g-NaCl, and magnesium slopes are mg-Mg per g-NaCl. Bold slopes are significant at the $p < 0.05$ level

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

Potential effects of episodic salinization and freshwater salinization syndrome on dissolved carbon

The response of carbon to episodic salinization varied largely across sites and across salinity treatment levels (Fig. 7). Our results agree with a recent sediment salinization study, which indicated that salinization can increase sediment releases of DOC at some sites but not others potentially based on organic matter quality (Duan and Kaushal 2015). Although our study did not characterize the quality of DOC, Duan and Kaushal (2015) found that salinization consistently and considerably increased net releases of the protein-like fluorophore, but the effects of salinization on humic-like fluorophore releases were not consistent. This difference was attributed to variations in the effect of salinization on humic versus protein fractions of organic carbon. Increasing ionic strength caused by salinization can enhance the solubility of the proteinaceous materials via sodium dispersion processes (Green et al. 2008, 2009) or through nonspecific electrostatic interactions at low salinities (e.g., a "salting-in" effect) (Tanford 1961; Chen et al. 1989).

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

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

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

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

Table 4 Results of a linear regression analysis of the nutrient response at each incubation site to sodium chloride additions

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

Units for TDN slopes are mg-N per g-NaCl, SRP slopes are µg-P per g-NaCl, DIC and DOC slopes are mg-C per g-NaCl, and silica slopes are mg-Si per g-NaCl. Bold slopes are significant at the $p < 0.05$ level may suppress microbial transformations of carbon in the sediment and pore-water, which could alter in-stream DIC concentrations (Oren 2001). Similar to DOC, our study showed that the effect of salinization on DIC dynamics is more complicated, if we extend salinity to a wider and more realistic range of salinization for urban sites.

Potential effects of episodic salinization and freshwater salinization syndrome on dissolved nitrogen, phosphorus, and silica

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

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

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

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

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

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

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

Our results of increasing SRP with salinization are more consistent with investigations of stream, wetland, and marine sediments. Although Duan and Kaushal (2015) determined SRP release from stream sediments to decrease with salinization at five of the same sites in this study, they also reported that releases of SRP from sediments increased at two urban sites. They suggested that these SRP increases were coupled with the release of large amounts of labile DOC, which could result in redox conditions that are favorable for SRP release. However, in our study, there was no observable relationship between the responses of SRP and DOC. Furthermore, increased salinity has been associated with increases in streamwater phosphate concentrations and net watershed phosphorus export in a recent study (Merrikhpour and Jalali 2012). Experimental studies of wetland sediments indicated both releases of phosphate with salinization, attributed to enhanced anaerobic organic matter (and phosphorus) mineralization (Kim and Koretsky 2013), or the retention of phosphorus on sediments with salinization, attributed to the formation and precipitation of insoluble iron-phosphate complexes (Baldwin et al. 2006). In marine and estuarine sediments, phosphate was mobilized (i.e., decreased sorption) linearly with increasing salinity, and the magnitude of release depended heavily upon the sediment's exchangeable phosphorus content (Zhang and Huang 2011; Clavero et al. 1990; Spiteri et al. 2008). These releases of phosphorus in coastal environments were attributed to a combination of desorption from iron and aluminum oxides with increasing salinity, increased aqueous complexation of phosphate with cations, and enhancements in anoxic microbial sulfate reduction (Spiteri et al. 2008). Changes in SRP dynamics between sediments and streamwater with salinization are complex and warrant further evaluation, especially within the context of redox changes.

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

Implications for managing episodic salinization and freshwater salinization syndrome

Increases in the frequency and magnitude of episodic salinization of rivers and streams is expected to occur with future urbanization, given the strong relationship between impervious surface cover and salinization of fresh water (Kaushal et al. 2005; Dugan et al. 2017; Gutchess et al. 2018). The mobilization of nutrients caused by episodic salinization, as evidenced in this study, could undermine costly efforts to curtail watershed nutrient pollution. Perturbations in the watershed carbon cycle, could cause long-term changes in organic matter lability, aquatic food webs, and microbial and plant communities. Changes in ionic strength represented by increases in multiple ions from sediments and soils as symptoms of freshwater salinization syndrome could also impact contaminant toxicity. Therefore, watershed management plans should now consider targeted strategies for reducing salt pollution and episodic salinization. The current US Environmental Protection Agency water quality criteria for chloride, 4 day (chronic) average concentration exceeding 230 mg/L or 1 h (acute) average concentration exceeding 860 mg/L, has not been updated since 1988 (Corsi et al. 2015). Dissolved salts in freshwater are currently not regulated at any broad regional scale (i.e., federal or state) for drinking water in the U.S. (Kaushal 2016), possibly because there has been little information on the long-term effects of salinization on water quality, environmental health, or human well-being (Canedo-Arguelles et al. 2016). Given growing evidence demonstrating mobilization of nutrients and other ions, managing the effects of freshwater salinization syndrome and episodic salinization represents a serious emerging issue for improving the efficacy of water quality management and stream and river restoration projects.

Acknowledgements Steven Hohman, Jonathan Coplin, Benjamin Smith, and Rose Smith assisted with experimental set up and laboratory analyses. Nathan Bailey, Kelsey Wood, and Tom Doody provided logistical support. We also thank the USGS Richmond Field Office and USGS MD-DE-DC Water Science Center for the maintenance of stream sensors and providing access to data. Funding was provided by NSF EAR 1521224, NSF SEES 1426844 and NSF DEB 1027188.

References

Aiken GR, McKnight DM, Wershaw RL et al (1985) Human substances in soil, sediment, and water: geochemistry, isolation, and characterization. Wiley, New York

Akin GW, Lagerwerff JV (1965) Calcium carbonate equilibria in aqueous solutions open to the air. I. The solubility of calcite in relation to ionic strength. Geochim Cosmochim Acta 29(4):343–352

Amrhein C, Strong JE, Mosher PA (1992) Effect of deicing salts on metal and organic matter mobilization in roadside soils. Environ Sci Technol 26(4):703–709

Backstrom M, Karlsson S, Backman L et al (2004) Mobilisation of heavy metals by deicing salts in a roadside environment. Water Res 38(3):720–732

Baldwin DS, Rees GN, Mitchell AM et al (2006) The short-term effects of salinization on anaerobic nutrient cycling and microbial community structure in sediment from a freshwater wetland. Wetlands 26(2):455–464

Barnes RT, Raymond PA (2009) The contribution of agricultural and urban activities to inorganic carbon fluxes within temperate watersheds. Chem Geol 266(3–4):318–327

Batson J, Noe GB, Hupp CR et al (2015) Soil greenhouse gas emissions and carbon budgeting in a short-hydroperiod floodplain wetland. J Geophys Res Biogeosci 120(1):77–95

Battaglin WA, Rice KC, Focazio MJ et al (2009) The occurrence of glyphosate, atrazine, and other pesticides in vernal pools and adjacent streams in Washington, DC, Maryland, Iowa, and Wyoming, 2005–2006. Environ Monit Assess 155(1–4):281–307

Bernhardt ES, Palmer MA, Allan JD et al (2005) Synthesizing U.S. River restoration efforts. Science 308(5722):636–637

Bunn RA, Magelky RD, Ryan JN et al (2002) Mobilization of natural colloids from an iron oxide-coated sand aquifer: effect of pH and ionic strength. Environ Sci Technol 36(3):314–322

Canedo-Arguelles M, Kefford BJ, Piscart C et al (2013) Salinisation of rivers: an urgent ecological issue. Environ Pollut 173:157–167

Canedo-Arguelles M, Hawkins CP, Kefford BJ et al (2016) Saving freshwater from salts. Science 351(6276):914–916

Chen CC, Zhu Y, Evans LB (1989) Phase Partitioning of Biomolecules: Solubilities of Amino Acids. Biotechnol Prog 5(3):111–118

Clavero V, Fernandez JA, Niell FX (1990) Influence of salinity on the concentration and rate of interchange of dissolved phosphate between water and sediment in Fuente Piedra lagoon (S. Spain). Hydrobiologia 197(1):91–97

Compton JE, Church MR (2011) Salt additions alter short-term nitrogen and carbon mobilization in a coastal oregon andisol. J Environ Qual 40(5):1601–1606

Conley DJ (2002) Terrestrial ecosystems and the global biogeochemical silica cycle. Global Biogeochem Cycles 16(4):68-1–68-8

Conway TM (2007) Impervious surface as an indicator of pH and specific conductance in the urbanizing coastal zone of New Jersey, USA. J Environ Manag 85:308–316

Cooper CA, Mayer PM, Faulkner BR (2014) Effects of road salts on groundwater and surface water dynamics of sodium and chloride in an urban restored stream. Biogeochemistry 121(1):149–166

Corsi SR, Graczyk DJ, Geis SW et al (2010) A fresh look at road salt: aquatic toxicity and water-quality impacts on local, regional, and national scales. Environ Sci Technol 44(19):7376–7382

Corsi SR, De Cicco LA, Lutz MA et al (2015) River chloride trends in snow-affected urban watersheds: increasing concentrations outpace urban growth rate and are common among all seasons. Sci Total Environ 508:488–497

Cunningham MA, Snyder E, Yonkin D et al (2008) Accumulation of deicing salts in soils in an urban environment. Urban Ecosyst 11(1):17–31

Daniel MHB, Montebelo AA, Bernardes MC et al (2002) Effects of urban sewage on dissolved oxygen, dissolved inorganic and organic carbon, and electrical conductivity of small streams along a gradient of urbanization in the Piracicaba River Basin. Water Air Soil Pollut 136(1–4):189–206

Devereux OH, Prestegaard KL, Needelman BA et al (2010) Suspended-sediment sources in an urban watershed, Northeast Branch Anacostia River, Maryland. Hydrol Process 24(11):1391–1403

Dove PM, Elston SF (1992) Dissolution kinetics of quartz in sodium chloride solutions: analysis of existing data and a rate model for 25 C. Geochim Cosmochim Acta 56(12):4147–4156

Duan S, Kaushal SS (2015) Salinization alters fluxes of bioreactive elements from stream ecosystems across land use. Biogeosciences 12:7331–7347

Duan Z, Sun R (2003) An improved model calculating CO_2 solubility in pure water and aqueous NaCl solutions from 273 to 533 K and from 0 to 2000 bar. Chem Geol 193(3–4):257–271

Duan S, Kaushal SS, Groffman PM et al (2012) Phosphorus export across an urban to rural gradient in the Chesapeake Bay watershed. J Geophys Res Biogeosci 117(G1):G01025. https://doi.org/10.1029/2011JG001782

Duckworth CMS, Cresser MS (1991) Factors influencing nitrogen retention in forest soils. Environ Pollut 72(1):1–21

Dugan HA, Bartlett SL, Burke SM et al (2017) Salting our freshwater lakes. Proc Natl Acad Sci USA 114(17):4453–4458

Evans A, Zelazny LW, Zipper CE (1998) Solution parameters influencing dissolved organic carbon levels in three forest soils. Soil Sci Soc Am J 52(6):1789–1792

Findlay SEG, Kelly VR (2011) Emerging indirect and long-term road salt effects on ecosystems. Ann N Y Acad Sci 1223:58–68

Fox LE (1991) The transport and composition of humic substances in estuaries. In: Baker RA (ed) Human and Soils, vol 1. Lewis Publishers, Chelsea MI, pp 129–162

Green SM, Machin R, Cresser MS (2008) Effect of long-term changes in soil chemistry induced by road salt applications on N-transformations in roadside soils. Environ Pollut 152(1):20–31

Green SM, Machin R, Cresser MS (2009) Does road slating induce or ameliorate DOC mobilisation from roadside soils to surface waters in the long term? Environ Monit Assess 153:435–448

Groffman PM, Law NL, Belt KT et al (2004) Nitrogen fluxes and retention in urban watershed Ecosystems. Ecosystems 7(4):393–403

Gutchess K, Jin L, Ledesma JLJ et al (2018) Long-term climatic and anthropogenic impacts on streamwater salinity in New York State: INCA simulations offer cautious optimism. Environ Sci Technol 52(3):1339–1347

Hale RL, Groffman PM (2006) Chloride effects on nitrogen dynamics in forested and suburban stream debris dams. J Environ Qual 35(6):2425–2432

Hedges JI, Keil RG (1999) Organic geochemical perspectives on estuarine processes: sorption reactions and consequences. Mar Chem 65(1–2):55–65

Herbert ER, Boon P, Burgin AJ et al (2015) A global perspective on wetland salinization: ecological consequences of a growing threat to freshwater wetlands. Ecosphere 6(10):1–43

Homer CG, Dewitz JA, Yang L et al (2015) Completion of the 2011 National Land Cover Database for the conterminous United States—representing a decade of land cover change information. Photogramm Eng Remote Sens 81(5):345–354

Hupp CR, Noe GB, Schenk ER et al (2013) Recent and historic sediment dynamics along difficult run, a suburban Virginia Piedmont stream. Geomorphology 180–181:156–169

Jun M, Altor AE, Craft CB (2013) Effects on increased salinity and inundation on inorganic nitrogen exchange and phosphorus sorption by tidal freshwater floodplain forest soils, Georgia (USA). Estuaries Coasts 36:508–518

Kaushal SS (2016) Increases salinization decreases safe drinking water. Environ Sci Technol 50:2765–2766

Kaushal SS, Belt KT (2012) The urban watershed continuum: evolving spatial and temporal dimensions. Urban Ecosystems 15(2):409–435

Kaushal SS, Groffman PM, Likens GE et al (2005) Increased salinization of fresh water in the northeastern United States. Proc Natl Acad Sci USA 102(38):13517–13520

Kaushal SS, Groffman PM, Band LE et al (2011) Tracking nonpoint source nitrogen pollution in human-impacted watersheds. Environ Sci Technol 45(19):8225–8232

Kaushal SS, Likens GE, Utz RM et al (2013) Increased River Alkalinization in the Eastern U.S. Environ Sci Technol 47(18):10302–10311

Kaushal SS, Mayer PM, Vidon PG et al (2014a) Land use and climate variability amplify carbon, nutrient, and contaminant pulses: a review with management implications. J Am Water Resour Assoc 50(3):585–614

Kaushal SS, McDowell WH, Wollheim WM (2014b) Tracking evolution of urban biogeochemical cycles: past, present, and future. Biogeochemistry 121(1):1–21. https://doi.org/10.1007/s10533-014-0014-y

Kaushal SS, Duan S, Doody TR et al (2017) Human-accelerated weathering increases salinization, major ions, and alkalinization in fresh water across land use. Appl Geochem 83:121–135

Kaushal SS, Likens GE, Pace ML et al (2018) Freshwater salinization syndrome on a continental scale. Proc Natl Acad Sci USA 115(4):E574–E583

Kelly VR, Lovett GM, Weathers KC et al (2008) Long-term sodium chloride retention in a rural watershed: legacy effects of road salt on streamwater concentration. Environ Sci Technol 42(2):410–415

Kim S, Koretsky C (2011) Influence of NaCl and $CaCl_2$ on lake sediment biogeochemistry. Appl Geochem 26:S198–S201

Kim S, Koretsky C (2013) Effects of road salt deicers on sediment biogeochemistry. Biogeochemistry 112(1–3):343–358

Kipton H, Powell J, Town RM (1992) Solubility and fractionation of humic acid—effect of pH and ionic medium. Anal Chim Acta 267(1):47–54

Li X, Rengel Z, Mapfumo E et al (2007) Increase in pH stimulates mineralization of 'native' organic carbon and nitrogen in naturally salt-affected sandy soils. Plant Soil 290(1–2):269–282

Li M, Zhao L, Zhang J (2013) Effect of temperature, pH, and salt on fluorescent quality of water extractable organic matter in black soil. J Integr Agric 12(7):1251–1257

Lofgren S (2001) The chemical effects of deicing salt on soil and stream water of five catchments in Southeast Sweden. Water Air Soil Pollut 130(1–4):863–868

Majcher EH, Woytowitz EL, Reisinger AJ et al (2018) Factors affecting long-term trends in surface-water quality in the Gwynns Falls watershed, Baltimore City and County, Maryland, 1998-2016. Open-File Report 2018-1038. U.S. Geological Survey, Reston

Marsalek J (2003) Road salts in urban stormwater: an emerging issue in stormwater management in cold climates. Water Sci Technol 48(9):61–70

Mayer PM, Groffman PM, Striz EA et al (2010) Nitrogen dynamics at the groundwater-surface water interface of a degraded urban stream. J Environ Qual 39(3):810–823

McClain ME, Boyer EW, Dent CL et al (2003) Biogeochemical hot spots and hot moments at the interface of terrestrial and aquatic ecosystems. Ecosystems 6(4):301–312

Merrikhpour H, Jalali M (2012) The effects of road salt application on the accumulation and speciation of cations and anions in an urban environment. Water Environ J 27(4):524–534

Meybeck M (2003) Global occurrence of major elements in rivers. In: Holland HD, Turekian KK (eds) Surface and ground water, weathering, and soils. Treatise on geochemistry, vol 5, 1st edn. Elsevier, Amsterdam, pp 207–223

Miller CV, Chanat JG, Bell JM (2013) Water quality in the Anacostia River, Maryland and Rock Creek, Washington, D.C.: Continuous and discrete monitoring with simulations to estimate concentrations and yields of nutrients, suspended sediment, and bacteria. Open-File Report 2013-1034. U.S. Geological Survey, Reston

Newcomer-Johnson TA, Kaushal SS, Mayer PM et al (2014) Effects of stormwater management and stream restoration on watershed nitrogen retention. Biogeochemistry 121(1):81–106

Nieder R, Benbi DK, Scherer HW (2011) Fixation and defixation of ammonium in soils: a review. Biol Fertil Soils 47(1):1–14

Norrstrom AC (2005) Metal mobility by de-icing salt from an infiltration trench for highway runoff. Appl Geochem 20(10):1907–1919

Norrstrom AC, Bergstedt E (2001) The impact of road de-icing salts (NaCl) on colloid dispersion and base cation pools in roadside soils. Water Air Soil Pollut 127(1–4):281–299

Novotny V, Muehring D, Zitomer DH et al (1998) Cyanide and metal pollution by urban snowmelt: Impact of deicing compounds. Water Sci Technol 38(10):223–230

Ondrasek G, Rengel Z, Domic R et al (2012) Salinity decreased dissolved organic carbon in the rhizosphere and increases trace element phyto-accumulation. Eur J Soil Sci 63(5):685–693

Oren A (2001) The bioenergetic basis for the decrease in metabolic diversity at increasing salt concentrations: implications for the functioning of salt lake ecosystems. Hydrobiologia 466(1–3):61–72

Pellerin BA, Saraceno JF, Shanley JB et al (2012) Taking the pulse of snowmelt: in situ sensors reveal seasonal, event and diurnal patterns of nitrate and dissolved organic matter variability in an upland forest stream. Biogeochemistry 108(1–3):183–198

Pellerin BA, Bergamaschi BA, Downing BD et al (2013) Optical techniques for the determination of nitrate in environmental waters: guidelines for instrument selection, operation, deployment, maintenance, quality assurance, and data reporting. U.S. Geological Survey Techniques and Methods 1-D5

Pennino MJ, Kaushal SS, Mayer PM et al (2016) Stream restoration and sewers impact sources and fluxes of water, carbon, and nutrients in urban watersheds. Hydrol Earth Syst Sci 20:3419–3439

Price JR, Szymanski DW (2014) The effects of road salt on stream water chemistry in two small forested watersheds, Catoctin mountain, Maryland, USA. Aquat Geochem 20(2–3):243–265

Radtke DB, Davis JV, Widle FD (2005) 6.3 Specific electrical conductance. US Geological Survey National Field Manual for the Collection of Water-quality Data, TWRI book 9

Ramakrishna DM, Viraraghavan T (2005) Environmental impact of chemical deicers—a review. Water Air Soil Pollut 166(1–4):49–63

Robinson HK, Hasenmueller EA, Chambers LG (2017) Soil as a reservoir for road salt retention leading to its gradual release to groundwater. Appl Geochem 83:72–85

Rode M, Wade AJ, Cohen MJ et al (2016) Sensors in the stream: the high-frequency wave of the present. Environ Sci Technol 50(19):10297–10307

Romero-Aranda MR, Jurado O, Cuartero J (2006) Silicon alleviates the deleterious salt effect on tomato plant growth by improving plant water status. J Plant Physiol 163(8):847–855

Saiers JE, Lenhart JJ (2003) Ionic-strength effects on colloid transport and interfacial reactions in partially saturated porous media. Water Resour Res 39(9):1256

Shanley JB (1994) Effects of ion exchange on stream solute fluxes in a basin receiving highway deicing salts. J Environ Qual 23(5):977–986

Shi Y, Wang Y, Flowers TJ (2013) Silicon decreases chloride transport in rice (*Oryza sativa* L.) in saline conditions. J Plant Physiol 170(9):847–853

Shields CA, Band LE, Law N et al (2008) Streamflow distribution of non-point source nitrogen export from urban-rural catchments in the Chesapeake Bay watershed. Water Resour Res 44(9):W09416. https://doi.org/10.1029/2007WR006360

Sholkovitz ER (1976) Flocculation of dissolved organic and inorganic matter during the mixing of river water and seawater. Geochim Cosmochim Acta 40(7):831–845

Smith RM, Kaushal SS (2015) Carbon cycle of an urban watershed: exports, sources, and metabolism. Biogeochemistry 126(1–2):173–195

Snodgrass JW, Moore J, Lev SM et al (2017) Influence of modern stormwater management practices on transport of road salt to surface waters. Environ Sci Technol 51(8):4165–4172

Spiteri C, Van Cappellen P, Regnier P (2008) Surface complexation effects on phosphate adsorption to ferric iron oxyhydroxides along pH and salinity gradients in estuaries and coastal aquifers. Geochim Cosmochim Acta 72(14):3431–3445

Srividya S, Soumya S, Pooja K (2009) Influence of environmental factors and salinity on phosphate solubilization by a newly isolated *Aspergillus niger* F7 from agricultural soil. Afr J Biotech 8(9):1864–1870

Steele MK, Aitkenhead-Peterson JA (2011) Long-term sodium and chloride surface water exports from the Dallas/Fort Worth region. Sci Total Environ 409(16):3021–3032

Steele MK, Aitkenhead-Peterson JA (2012) Urban soils of texas: relating irrigation sodicity to water-extractable carbon and nutrients. Soil Sci Soc Am J 76(3):972–982

Steele MK, Aitkenhead-Peterson JA (2013) Salt impacts on organic carbon and nitrogen leaching from senesced vegetation. Biogeochemistry 112(1–3):245–259

Stets EG, Lee CJ, Lytle DA et al (2018) Increasing chloride in rivers of the conterminous U.S. and linkages to potential corrosivity and lead action level exceedances in drinking water. Sci Total Environ 613–614:1498–1509

Tanford C (1961) Physical chemistry of macromolecules. Wiley, New York

Treguer P, Nelson DM, Van Bennekom AJ et al (1995) The silica balance in the world ocean: a reestimate. Science 268(5209):375–379

Weiss RF (1974) Carbon dioxide in water and seawater: the solubility of a non-ideal gas. Mar Chem 2(3):203–215

Weston NB, Dixon RE, Joye SB (2006) Ramifications of increased salinity in tidal freshwater sediments: geochemistry and microbial pathways of organic matter mineralization. J Geophys Res Biogeosci 111(G1):G01009. https://doi.org/10.1029/2005JG000071

Williams WD (2001) Anthropogenic salinisation of inland waters. Hydrobiologia 466:329–337

Woo TJ, Salice CJ (2017) Timing is everything: pulsed versus constant exposures in assessing effects of road salt on aquatic organisms. Integr Environ Assess Manag 13(4):792–794

Zhang J, Huang X (2011) Effects of temperature and salinity on phosphate sorption on marine sediments. Environ Sci Technol 45(16):6831–6837