Sensors track mobilization of ‘chemical cocktails’ in streams impacted by road salts in the Chesapeake Bay watershed

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Keywords: freshwater salinization syndrome, chemical cocktails, metals, salt, road salt, base cations, cation exchange

Abstract

Increasing trends in base cations, pH, and salinity of freshwaters have been documented in US streams over 50 years. These patterns, collectively known as freshwater salinization syndrome (FSS), are driven by multiple processes, including applications of road salt and human-accelerated weathering of impervious surfaces, reductions in acid rain, and other anthropogenic legacies of change. FSS mobilizes chemical cocktails of distinct elemental mixtures via ion exchange, and other biogeochemical processes. We analyzed impacts of FSS on streamwater chemistry across five urban watersheds in the Baltimore-Washington, USA metropolitan region. Through combined grab-sampling and high-frequency monitoring by USGS sensors, regression relationships were developed among specific conductance (SC) and major ion and trace metal concentrations. These linear relationships were statistically significant in most of the urban streams (e.g. \( R^2 = 0.62 \) and 0.43 for Mn and Cu, respectively), and showed that specific conductance could be used as a proxy to predict concentrations of major ions and trace metals. Major ions and trace metals analyzed via linear regression and principal component analysis showed co-mobilization (i.e. correlations among combinations of specific conductance (SC), Mn, Cu, Sr\(^{2+}\), and all base cations during certain times of year and hydrologic conditions). Co-mobilization of metals and base cations was strongest during peak snow events but could continue over 24 h after SC peaked, suggesting ongoing cation exchange in soils and stream sediments. Mn and Cu concentrations predicted from SC as a proxy indicated acceptable goodness of fit for predicted vs. observed values (Nash–Sutcliffe efficiency > 0.28). Metals concentrations remained elevated for days after SC decreased following snowstorms, suggesting lag times and continued mobilization after road salt use. High-frequency sensor monitoring and proxies associated with FSS may help better predict contaminant pulses and contaminant exceedances in response to salinization and impacts on aquatic life, infrastructure, and drinking water.

1. Introduction

Freshwater salinization is an emerging environmental problem around the world, degrading the quality of ground and surface waters (Kaushal et al 2005, 2018b, 2019, Cañedo-Argüelles et al 2016). For example, freshwater salinization has impacted streams, rivers, reservoirs, and lakes in North America, with concurrent positive trends in major ions such as Cl\(^-\), Na\(^+\), Ca\(^{2+}\), Mg\(^{2+}\) over half a century (Kaushal et al 2005, 2018b, Corsi et al 2010, Anning and Flynn 2014, Dugan et al 2017b, Stets et al 2020). Similar increasing trends in concentrations of base cations (Na\(^+\), Ca\(^{2+}\), Mg\(^{2+}\), and K\(^+\)) have been observed in Europe, China, Russia and Iran over the past century (Kaushal et al 2019). Coinciding increases in major ions, changes in specific conductance (SC) and pH, and the increased direct and indirect impacts of salt ions on water quality, ecosystems, and infrastructure have been called the freshwater salinization syndrome.
(FSS) (Davies et al 2010, Kaushal et al 2013, 2018a, 2019). FSS is an emerging environmental issue caused by multiple salt ions originating from diverse sources such as road deicers, irrigation, agricultural liming and potash, sewage, mining, and weathering of concrete in the built environment and surficial geology due to erosion and acidic precipitation (Davies et al 2010, Kunz et al 2013, Dugan et al 2017a, Haq et al 2018, Kaushal et al 2018b, 2020, Schulz and Cañedo-Argüelles 2019). FSS is expected to increase due to increased use of roadway deicers, construction materials, fertilizers, and other anthropogenic substances. For example due to the legacy of human construction, annual road salt sales in the United States have increased nearly an order of magnitude in ∼60 years (Corsi et al 2010) coinciding with an accumulation of road salt ions in soils and groundwater (Kaushal et al 2005, 2018b, Moore et al 2017), a phenomenon that may be exacerbated by long (over 50 year) residence times of road salts in watersheds (Shaw et al 2012). FSS mobilizes chemical cocktails of metals, nutrients, organics, and other ions through shifts in ion exchange, solubility, and microbial activity (Amrhein et al 1992, Green and Cresser 2008, Miller et al 2008, Duan and Kaushal 2015, Haq et al 2018, Kaushal et al 2019). The indirect and direct effects of major ion pollution on water quality, ecosystems, and urban infrastructure are not well known, a concerning gap in knowledge.

Increased urbanization and impervious surface cover in the Mid-Atlantic have increased the quantity of salt ions applied to a watershed but also amplify ‘pulses’ of salinization due to decreased infiltration and transport time (Daley et al 2009, Kaushal et al 2014b). Stream and river channelization and the use of storm drains increase the ‘hydrological connectivity’ between roadways and aquatic ecosystems (Elmore and Kaushal 2008, Kaushal and Belt 2012), increasing the ‘hydrologic flashiness’ of storm hydrograph responses, and the magnitude and frequency of road salt pulses (Trowbridge et al 2010, Kaushal et al 2015, Moore et al 2020). Increased SC from episodic road salt pulses can last for days, weeks, and months, with associated chemical cocktails of metals and cations sometimes remaining elevated for longer (Haq et al 2018, Kaushal et al 2019).

Increased major ion loading from road salts enhances base cation exchange and mobilization of trace metals in both stream sediments and soils to surface waters (Amrhein et al 1992, Shanley 1994, Löfgren 2001, Kaushal et al 2019). For example, monovalent and divalent cations can displace and mobilize trace metals from exchange sites on negatively charged colloids, such as Mn, Sr2+, Cu, Hg and Zn, (throughout this paper we do not include charges on some trace metals due to their complex multiple oxidation states) into the dissolved load (D’Itri 1992, Nelson et al 2009, Fay and Shi 2012, Kaushal 2016, Kaushal et al 2019). Though research on this topic is only just beginning, increased Na+, for example, can displace metals from their exchange sites on stream sediments and soil particles and into solution (Kaushal et al 2019, Lazur et al 2020). Higher valence base cations including Mg2+, and Ca2+, sometimes found in deicers or mobilized through cation exchange, are even more efficient than Na+ at displacing metals in soils (Kaushal et al 2019). Ca2+ outcompetes Zn, Pb, and Cd in soil cation exchange sites (Kaushal et al 2019). Similarly Mg2+ outcompetes Cu, with Cu concentrations often being the highest at the soil surface (Kaushal et al 2019). Following these ion exchange reactions, trace metals are often transported as aqueous complexes. These complexes are made up of a central metal ion bound to an ion or molecule, forming a metal–ligand bond order (Gaillardet et al 2003). Cl− is known to increase the solubility of Cd and Pb, which increases solubility through chloro-complexation (Norrström and Bergstedt 2001, Kaushal et al 2019). Because most research has been conducted on mobilization of individual element mobilization knowledge gaps still exist regarding the full suite of metals released by FSS.

One of the key challenges in understanding the magnitude and scope of FSS is characterizing peaks and lag times in SC and elemental concentrations as a result of road salting events and associated geochemical processes. Here we use high-frequency sensor data, coupled with bi-weekly grab sampling of streamwater chemistry to test the hypothesis that FSS has substantial, negative impacts on urban freshwater systems and to characterize the chemical cocktails formed due to FSS in urban streams across seasons. Changes in the composition of these chemical cocktails are thought to be most significant during and after instances of winter precipitation events. Knowledge of seasonal changes in the magnitudes and mixtures of chemical cocktails mobilized by FSS has implications for protection of aquatic life, safe drinking water, and how the public and government can best mitigate this emerging environmental issue (James et al 2003, Corsi et al 2010, Herbert et al 2015, Kaushal 2016, Hintz and Relyea 2017). Most research has focused on documenting increasing long-term annual trends in SC, Cl−, and Na+ in streams, rivers, lakes, and reservoirs (Kaushal et al 2005, 2018b, Corsi et al 2010, Dugan et al 2017a, 2017b, Stets et al 2020). However, with increased availability of high-frequency sensor data in streams, episodic salt pulses can be detected in real time and quantified in urban and suburban watersheds (Trowbridge et al 2010, Haq et al 2018, Kaushal et al 2019, Moore et al 2020, Morel et al 2020).

Monitoring elemental flux in highly dynamic urban streams is very time and resource intensive; therefore proxies can be developed using high frequency SC data to estimate other elemental concentrations (Haq et al 2018, Kaushal et al 2018b, 2020, Moore et al 2020, Morel et al 2020). Previous
work using SC as a proxy for Cl$^-$ has shown that Cl$^-$ pulses during road deicing events are difficult to capture using traditional grab sampling methods (Trowbridge et al 2010, Moore et al 2020). Less work has focused on characterizing the dynamics of metals that are also mobilized by deicing events (Haq et al 2018, Kaushal et al 2019, Morel et al 2020). Due to these knowledge gaps, the main research goals answered in this study are to: (a) identify what metals are mobilized during snow events, and (b) develop proxies to predict the mobilization of these metals.

2. Methods

2.1. Study sites

All five study watersheds (381 cumulative km$^2$) were located throughout the Baltimore and Washington D.C. metropolitan areas and within the greater Chesapeake Bay watershed (figure 1). Sampling locations were chosen at USGS gauge stations, providing higher temporal resolution data (5–15 min) than could be obtained via grab-sampling (USGS NWIS 2020). USGS monitoring stations utilize multiparameter datasondes which take instantaneous measurements of SC, dissolved O$_2$, turbidity (TB) and NO$_3^−$/NO$_2^−$ (USGS NWIS 2020). Watersheds were delineated via the StreamStats USGS web application and remotely sensed watershed characteristics, including land use and impervious surface cover, were obtained from a 30 m resolution datasets provided by the 2016 National Land Cover Database (MRLC 2020, StreamStats 2020). Site characteristics were analyzed via ArcMap 10.4 and Microsoft Excel.

Five urban streams were sampled for this study (figure 1 and table 1): Rock Creek, a stream with large riparian buffer and the lowest proportion of impervious surface cover; Sligo Creek, an urbanized stream with a walking trail and road that follows much of its length; Scotts Level Branch, a stream influenced by suburbanization and a small riparian buffer abutted by houses; Herring Run, a heavily urbanized stream which has a small water treatment plant about two miles upstream (Jones 1996, Parks 2016); and Jones Falls, a mainly buried, heavily polluted tidal stream flowing directly into the inner harbor of the Chesapeake Bay (table 1).

2.2. USGS continuous monitoring data

High frequency (5–15 min resolution) data for SC, in micro-Siemens per centimeter at 25 °C, discharge
Table 1. Site characteristics for all sampling sites and their accompanying USGS stations (‘USGS NWIS’, ‘MRLC’).

| Study site | Metro area | Latitude   | Longitude   | USGS site # | Drainage area mi² | NLCD 2016 impervious surface cover % |
|------------|------------|------------|-------------|-------------|-------------------|--------------------------------------|
| Rock Creek | D.C.       | 38°57′36″′″ | 77°00′31.4″′″ | 1648 010    | 63.7              | 18.35                                |
| Sligo Creek | D.C.       | 38°59′10.4″′″ | 77°00′17.5″′″ | 1650 800    | 6.45              | 27.19                                |
| Scotts Level Branch | Baltimore | 39°21′41.7″′″ | 76°45′42.3″′″ | 1589 290    | 3.23              | 22.24                                |
| Herring Run | Baltimore | 39°19′04.7″′″ | 76°33′18.5″′″ | 1585 219    | 16.3              | 32.76                                |
| Jones Falls | Baltimore | 39°17′02.8″′″ | 76°36′13.1″′″ | 1589 485    | 57.5              | 21.28                                |

(Q) in cubic feet per second, and temperature (T) in degrees Celsius, TB and pH were obtained from the USGS National Water Information System for the duration of the study (October 2017–October 2019). SC is measured using contact sensors with electrodes, which are T compensating and have an accuracy greater than 0.5 ± 0.5% of readings, or ±2 μS cm⁻¹ (Wagner et al 2006, Gibs et al 2012). T is measured with a thermistor with an accuracy of ±0.1 °C and Q is accurate to the nearest 0.01 ft or 0.2% stage height, or whichever is larger (Wagner et al 2006, Usgs 2020). Instrumental error, calibrations, and accuracy of USGS multiparameter datasondes are further described in Gibs et al (2012) and Wagner et al (2006).

2.3. Bi-weekly grab sampling and targeted snow event sampling

Water samples were collected approximately bi-weekly from all five sites across the Washington D.C. and Baltimore metropolitan areas (red triangles in figure 1). Two 125 ml acid-washed HDPE Nalgene bottles of stream water were collected from each site after being triple rinsed with stream water before sample collection. Samples were kept on ice until being transported back to the University of Maryland College Park for analysis. Grab samples were filtered through pre-combusted 0.7 μm glass fiber filters to separate dissolved and suspended load. A 60 ml aliquot of the filtered sample was stored in acid-washed HDPE Nalgene bottles with 0.5% high-purity nitric acid. Acidified samples were analyzed within 6 months via inductively coupled plasma optical emission spectrometry (ICP-OES) on a Shimadzu Elemental Spectrometer (ICPE-9800; Shimadzu, Columbia, Maryland, USA) (Haq et al 2018). ICP-OES analysis determined elemental concentrations of Na⁺, Ca²⁺, Mg²⁺, K⁺, Cu, Sr²⁺, and Mn. The remaining unacidified samples were kept at 4 °C for up to 2 weeks before being analyzed on a Shimadzu Total Organic Carbon Analyzer (TOC-V CPH/CPN; Shimadzu, Columbia, Maryland, USA) (Haq et al 2018). The TOC-V analyzer uses a combustion-catalytic-oxidation-NDIR method to dissolved inorganic carbon (DIC) content. The Jones Falls site often exhibited brackish water due to its tidal nature, due to this all samples were diluted with four parts high purity Milli-Q water (conductivity below detection limit) to one-part sample before analysis as to not damage the instrument. In addition to bi-weekly sampling, hourly sampling was also conducted in response to two road deicing events (during the peak and directly following snow events) at Sligo Creek in the winter of 2019.

2.4. Synoptic sampling

Longitudinal, synoptic surveys of Sligo Creek and Rock Creek were conducted during July of 2018. Samples were collected via the bi-weekly methodology described above along the length of both streams at approximately 1–1.6 km intervals. Samples were intentionally collected above or at least 100 m below any large tributaries to increase the likelihood obtaining a homogenized sample (Kaushal et al 2014a). Impervious surface cover was calculated upstream of the sampling point to determine how anthropogenic ground cover might affect analytes (MRLC 2020, StreamStats 2020). Patterns in streamwater chemistry measurements were then evaluated and related to the drainage area above each point.

2.5. Statistical analyses

Regression relationships were developed among elemental concentrations and ancillary variables. All ICP-OES data were analyzed in triplicate to improve data quality. The relative standard deviation (RSD) of these three samples was divided by a calculated RSD derived from sample concentration to determine the error acceptability (Horwitz et al 1980, Burgess 2000, Horwitz and Albert 2006). The acceptable error threshold is based upon the assumption that RSD increases as analyte concentration decreases (Horwitz et al 1980, Burgess 2000). Equation (1) below was used to determine the calculated RSD.

\[
\text{RSD calculated} = 2^{1-0.5\text{log} C}
\]

Where

\[C = \text{relative concentration}\]

Equation 2 determines the Horwitz ratio or HORRAT. If the HORRAT is <2 it is generally an acceptable value. If it the HORRAT is >2, the corresponding measurement is excluded from the results (Burgess 2000).
HORRAT = \frac{\text{RSD observed}}{\text{RSD calculated}} \quad (2)

The Nash–Sutcliffe model efficiency coefficient (NSE) (equation 3) was utilized to determine the predictive power of the model relating concentrations of metals to SC (Nash and Sutcliffe 1970, Moriasi et al. 2007). Samples were arranged by date and alternating data points (odd) were used to develop the linear relationships. The NSE test was then performed on the half of the dataset (even data points) not used for model calibration.

\text{NSE} = 1 - \frac{\sum_{i=1}^{n} (Y_{i}^{\text{obs}} - Y_{i}^{\text{sim}})^2}{\sum_{i=1}^{n} (Y_{i}^{\text{obs}} - Y_{\text{mean}})^2} \quad (3)

Where

- $Y_{i}^{\text{obs}}$ = the $i$th observation of the data being tested
- $Y_{i}^{\text{sim}}$ = the $i$th simulated value of the data being tested
- $Y_{\text{mean}}$ = the mean of the observed data
- $n$ = the number of observations in the dataset

Principal component analysis (PCA) was used to quantify more complex multivariate patterns in metals mobilization. PCA analysis was performed in MATLAB with normalized datasets in order to correct for the different scales and units of the data used (e.g. $\mu$S cm$^{-1}$ and mg L$^{-1}$) in the analysis. PCA was able to illustrate the changing correlations between major and trace elements as a result of FSS across seasons and in response to road salt events.

3. Results

3.1. Linear relationships between SC and metals across sites

There were seasonal trends, with greater concentrations of base cations and metals during winter than the rest of the year (figure 2 and table 2). Winter 2019 had the most significant snowfall and summer 2018 received the most rain across all sites (supplementary figure 1 (available online at stacks.iop.org/ERL/16/035017/mmedia)). The estuarine nature of Jones Falls diminished the site's relationship to winter storms, as brackish water would frequently interact with the sensor. This saltwater intrusion likely does not affect the entire Jones Falls watershed however, with more upstream areas mainly being affected by road salt application. We typically observed significant positive linear relationships between SC, base cations and select trace metals across all sites (figure 3 and supplementary figure 2). $R^2$ values differed among sites and elements, but relationships remained positive and significant across all sites (except for Fe at most sites and Mn at Jones Falls) ($p < 0.05$) (table 3). Though the data appears to be skewed towards low concentrations at some of the sites represented in figure 3, additional data collected at Sligo Creek further supports the trends observed (supplementary figure 3). Q integrated daily loads were explored as an alternative but provided less favorable results (supplementary figure 4). Alternate trends were also explored including power and logarithmic but models which had the best fit varied across sites and analytes (supplementary figure 5). As expected, Na$^+$ exhibited the strongest relationships with SC, with $R^2$ values up to 0.94. Mn and Cu also exhibited strong positive linear relationships with SC ($R^2$ values up to 0.61 and 0.67 respectively) (table 3). Across all sites, Fe was not significantly related to SC, potentially due to higher sensitivity to redox conditions than stream salinity. Mn can also be sensitive to changes in redox but its mobilization does not follow that of Fe. Concentrations of base cations also exhibited significant positive relationships with watershed impervious surface cover at Sligo Creek; with K$^+$ and DIC showing similar trends at Rock Creek (figure 4 and supplementary table 1). There was some variability in the goodness of fit in the regressions due to tributary inputs influencing concentrations, but there were statistically significant relationships for base cations ($p < 0.05$).

Using the linear relationships from figure 3 and table 3, SC values were used to predict Mn and Cu concentrations. Data from Sligo Creek were selected, as it was the only site where (high frequency) hourly metals data was collected during snowstorms, giving it the most robust dataset for this analysis. NSE and root mean square error (RMSE) results for the dataset containing regular bi-weekly measurements were mixed with an NSE of 0.5 for Cu and 0.06 for Mn (table 4). By incorporating high frequency (hourly data) collected during a snowfall event into the regression, overall predictability improved, with an NSE of 0.4 for Cu and 0.3 for Mn (table 4). However, observed data after peak snowfall were harder to predict using the relationships developed from regular sampling combined with hourly snowfall data, resulting in negative NSE values, and suggesting a deviation between predicted and observed values after snow events (figure 5 and table 4). This lag time in metals concentrations returning to baseline levels with SC is most noticeable for Mn during March and April of 2019 (figure 5). There also may be Mn lag times evident in November 2018 and January 2019 associated with a snowstorm on 15 November. However, due to the limited size of the dataset, it is unclear if these are outliers or caused by another mechanism.

3.2. Changes in composition of chemical cocktails across seasons and snow events

Across seasons at Sligo Creek, there was a general pattern where distinct chemical cocktails were more correlated with SC during winter deicer use. During the spring and summer (figure 6(A)) a weak clustering of Cu and Sr$^{2+}$ and some base cations (Na$^+$, K$^+$, Mg$^{2+}$) is present. During the peak of an episodic salinization event however (figure 6(B)) Mn, Sr$^{2+}$, and all base
Figure 2. Time series of major and trace elements (mg l$^{-1}$) plotted against SC (µS cm$^{-1}$). Discharge is also included for each site (cfs) (‘USGS NWIS’).

cations (Na$^+$, Ca$^{2+}$, Mg$^{2+}$ and K$^+$) were correlated with SC. As SC begins to slowly return to baseline levels (figures 6(C) and (D)) base cations and trace metals remain correlated but Na$^+$ and SC are anti-correlated.

All PCA biplots illustrate correlations between base cations and trace metals throughout the year with the strongest groupings (highest correlation between co-mobilized elements) occurring at the peak of episodic salinization events. Less distinct
groupings of elements were observed in spring and summer of 2019, and less variability was explained on the primary axis (55%), meaning co-mobilization was less distinct (figure 6(A)). All metals, except Cu and Fe, were tightly clustered during a snowstorm salinity spike along with base cations and SC (figure 6(B)). A large proportion of the data was explained by principal component 1 (∼72%) in this plot, suggesting that co-mobilization was strong. Figure 6(C) illustrates a similar biplot to figure 6(B), but is taken from a dataset collected during the descending SC limb of a snow event following deicer use. There was a looser cluster of major and trace elements, with two smaller sub groups therein. SC was not correlated to mobilized base cations and trace metals in this plot. As SC reached a temporary elevated baseline a day after the peak of the storm, (figure 6(D)) clustering of base cations and trace metals remained strong though Na⁺ was also found to be anti-correlated with SC.

4. Discussion

Although there are multiple causes and sources of FSS in urban environments (Kaushal et al 2017, 2019, 2020), episodic road salting events can be a driver of ‘winter’ chemical cocktails in temperate regions (Löfgren 2001, Kaushal et al 2019). Our results show that chemical cocktail mobilization of base cations and trace metals begins within an hour of the start of snowstorms (supplementary figure 6), which correlates with the addition of large quantities of road salt (Snodgrass et al 2017, Haq et al 2018, Kaushal et al 2018b, Moore et al 2020). These chemical cocktails evolve in concentration and composition quickly over time, mobilizing Mn, Cu, Sr²⁺, and potentially other metals into solution (figures 3 and 6); this mobilization may occur on exchange sites on colloids present in stream and bank sediment (Kaushal et al 2019). Some of the mechanisms behind metal and base cation mobilization are thought to be a combination of base cation exchange and chloro-complexation among other mechanisms of chemical cocktail formation in urban environments (Kaushal et al 2017, 2019, 2020).

4.1. FSS increases with impervious surface cover: anthropogenic inputs and urban karst

We observed increasing trends in concentrations of base cations with impervious surface cover at Sligo Creek and inorganic carbon and K⁺ with impervious surface cover at Rock Creek (figure 4). Our results are similar to those reported elsewhere when increased chemical weathering of concrete urban infrastructure in the form of buildings, sidewalks, and drainage infrastructure (urban karst), leads to elevated base cations and inorganic carbon (Kaushal et al 2015, 2020, Bonneau et al 2017). Concrete weathering releases carbonates and base cations (CaCO₃ and Ca(OH)₂) into downstream urban waterways (Demars and Benoit 2019). Human-accelerated weathering in urban environments increases the potential for river alkalization as carbonates are released during the chemical weathering process (Kaushal et al 2013, 2017). In Baltimore, MD, USA, drinking water alkalinity has increased by over 50% over almost 50 years due to release of carbonates from weathering of concrete infrastructure (buildings, pavements and pipes) as in other areas (Baker et al 2008, Davies et al 2010, Kaushal et al 2017, Demars and Benoit 2019). The increase in DIC that we observed in our study may also be a function of concrete weathering. The increase in weathering products such as Ca²⁺, Mg²⁺, K⁺, and other ions has also been observed across space and time in other urban watersheds in Maryland (Kaushal et al 2017) and elsewhere (Barnes and Raymond 2009, Moore et al 2017, Demars and Benoit 2019). Increasing pH and alkalinity may also be due to reduced nitrogen and sulfur oxidation emissions due to the implementation of the Clean Air Act and its amendments.

4.2. Episodic salinization: acute mobilization of chemical cocktails due to FSS

We observed increased mobilization of chemical cocktails of base cations and trace metals in response to episodic road salting events (figures 2 and 6). Na⁺, Ca²⁺, Mg²⁺, K⁺, Mn, Cu, Sr²⁺, and Fe were all more elevated during winters than summers, potentially due to ion exchange or chloro-complexation and other geochemical processes (Löfgren 2001, Norrström and Bergstedt 2001, Kaushal et al 2017, 2019). We observed strong seasonal effects in metals (table 2) with Mn and Cu being more than 2.5 and 4.6 times higher respectively in the winter than they were in the summer. Copper is toxic to aquatic organisms (Berntssen et al 1999, Mahrosh et al 2014). Mn pulses during winter storms reached 0.631 mg l⁻¹⁻¹, over 12 times the EPA drinking water standard (Us

| Attribute                  | Ca²⁺  | Cu    | Fe    | K⁺    | Mg²⁺  | Na⁺  | Sr²⁺  | Mn    |
|----------------------------|-------|-------|-------|-------|-------|------|-------|-------|
| Average winter mg⁻¹⁻¹       | 52.7  | 0.0479| 0.122 | 7.28  | 18.5  | 224  | 0.203 | 0.146 |
| Winter std dev              | 18.2  | 0.0578| 0.0973| 4.1   | 10.6  | 251  | 0.151 | 0.137 |
| Average summer mg⁻¹⁻¹       | 40.3  | 0.0104| 0.0914| 4.19  | 13    | 42.3 | 0.122 | 0.0565|
| Summer std dev              | 17.9  | 0.0104| 0.131 | 3.01  | 7.1   | 44.3 | 0.0834| 0.0729|
| % difference                | 131   | 468   | 134   | 174   | 142   | 529  | 166   | 258   |

Table 2. Elemental concentrations for all sampling sites and their accompanying USGS stations ('USGS NWIS').

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Epa 2015). Base cation and metal peaks were found at all sites during both winters immediately after winter storms and road salting. Similar effects may be causing elevated Mn in drinking water (Shaver 2015). Previous work has shown that pure laboratory grade salt ions mobilize the exact same metals and base cations mobilized in this study (Haq et al 2018, Kaushal et al 2019).

Figure 3. Positive linear relationships between base cations, metals and specific conductance in D.C. and Baltimore (‘USGS NWIS’). (Linear trends with a p value < 0.05 shown on the right).
Table 3. Linear trend statistics for all sampling sites and their accompanying USGS stations (‘USGS NWIS’).

| Element | Slope of relationship | $p$ value (Element/SC) | $R^2$ (Element/SC) | Slope |
|---------|-----------------------|------------------------|---------------------|-------|
| Rock Creek | | | | |
| Ca$^{2+}$ | Positive | 0.05 | 0.08 | 0.006 |
| Cu | Positive | 4.55E−08 | 0.49 | 1.65E−05 |
| Fe | Negative | 0.54 | 0.01 | −1.59E−05 |
| K$^+$ | Positive | 1.68E−04 | 0.28 | 0.001 |
| Mg$^{2+}$ | Positive | 0.04 | 0.09 | 0.002 |
| Mn | Positive | 7.16E−06 | 0.38 | 4.07E−05 |
| Na$^+$ | Positive | 8E−30 | 0.94 | 0.170 |
| Sr$^{2+}$ | Positive | 0.01 | 0.16 | 4.31E−05 |
| Sligo Creek | | | | |
| Ca$^{2+}$ | Positive | 4.70E−03 | 0.16 | 0.006 |
| Cu | Positive | 1.08E−10 | 0.62 | 1.46E−05 |
| Fe | Positive | 0.81 | 0.04 | 1.59E−06 |
| K$^+$ | Positive | 5.61E−09 | 0.54 | 0.001 |
| Mg$^{2+}$ | Positive | 0.02 | 0.12 | 0.001 |
| Mn | Positive | 6.32E−07 | 0.43 | 2.98E−05 |
| Na$^+$ | Positive | 3.18E−18 | 0.81 | 0.122 |
| Sr$^{2+}$ | Positive | 3.57E−04 | 0.26 | 3.55E−05 |
| Jones Falls | | | | |
| Ca$^{2+}$ | Positive | 5.00E−04 | 0.26 | 0.010 |
| Cu | Positive | 4.46E−03 | 0.19 | 2.12E−05 |
| Fe | Negative | 0.15 | 0.05 | 1.36E−05 |
| K$^+$ | Positive | 7.94E−12 | 0.70 | 0.005 |
| Mg$^{2+}$ | Positive | 1.24E−13 | 0.75 | 0.015 |
| Mn | Positive | 0.40 | 0.02 | 7.65E−06 |
| Na$^+$ | Positive | 2.20E−04 | 0.29 | 0.108 |
| Sr$^{2+}$ | Positive | 7.67E−04 | 0.25 | 7.1E−05 |
| Herring Run | | | | |
| Ca$^{2+}$ | Positive | 7.31E−03 | 0.16 | 0.020 |
| Cu | Positive | 1.94E−10 | 0.67 | 0.000134 |
| Fe | Positive | 4.08E−03 | 0.18 | 5E−05 |
| K$^+$ | Positive | 5.24E−07 | 0.48 | 0.006 |
| Mg$^{2+}$ | Positive | 0.03 | 0.11 | 0.005 |
| Mn | Positive | 3.7E−05 | 0.34 | 0.000104 |
| Na$^+$ | Positive | 5.62E−16 | 0.80 | 0.375 |
| Sr$^{2+}$ | Positive | 2.84E−03 | 0.21 | 0.000208 |
| Scents Level Branch | | | | |
| Ca$^{2+}$ | Positive | 9.75E−05 | 0.28 | 0.006 |
| Cu | Positive | 0.04 | 0.11 | 9.3E−06 |
| Fe | Positive | 0.67 | 0.00 | 4.39E−06 |
| K$^+$ | Positive | 7.78E−07 | 0.43 | 0.001 |
| Mg$^{2+}$ | Positive | 0.02 | 0.11 | 0.001 |
| Mn | Positive | 7.18E−10 | 0.61 | 3.42E−05 |
| Na$^+$ | Positive | 2.87E−09 | 0.55 | 0.092 |
| Sr$^{2+}$ | Positive | 7.96E−05 | 0.30 | 3.05E−05 |

4.3. Episodic salinization shifts mixtures in chemical cocktails
Mixtures of base cations and metals continuously evolve throughout seasons in regions affected by FSS. During the summer (figure 6(A)), SC was weakly associated with metals and cations (Cu, Mg$^{2+}$, and Sr$^{2+}$). SC peaks during the summer were often associated with periods of drought whereas precipitation events had a dilution effect (figure 2). SC peaks associated with road salting (figure 6(B)) were strongly correlated with almost every element (Na$^+$, Sr$^{2+}$, K$^+$, Ca$^{2+}$, Mg$^{2+}$, and Mn); these strong correlations suggest that beyond a salinity threshold, co-mobilization increases dramatically. As SC begins to decrease (figure 6(C)) after a snow event, it becomes less correlated with the metals and base cations. Thus, contaminant mobilization is highly correlated with base cations and metals during the
Figure 4. Synoptic survey results illustrating increasing dissolved inorganic carbon (DIC) and base cations with increasing impervious surface cover ('Data | Multi-Resolution Land Characteristics (MRLC) Consortium').

Figure 5. Estimated metals concentrations using linear relationships developed at Sligo Creek ('USGS NWIS').

rising limb of a SC pulse but not the falling limb, which can remain elevated for weeks afterwards (Kaushal et al. 2019). This may be due to ongoing mobilization of base cations after SC and Na\(^+\) begin to decrease. The main grouping of base cations and trace metals (Ca\(^{2+}\), K\(^+\), Mg\(^{2+}\), Cu, Mn, and Sr\(^{2+}\), circled in figure 6(D)) remain correlated while both Na\(^+\) and SC are anti-correlated. Mn concentrations indicated that metals are mobilized up to 24 h after peak stream salinity. These elevated metals concentrations may persist in urban streams for several months before returning to baseline conditions (Kaushal et al. 2019). The mechanism causing the lag times may be related to salt accumulation in sediments or groundwater (Cooper et al. 2014).

4.4. Potential mechanisms of metal mobilization

The concentration of metals in stream soils and sediments is likely due to the extent of watershed impervious surface area and proximity of roadways to streams. Heavy metals are a common pollutant deposited by motor vehicles (Adams et al. 2009). Metals are often ionically bonded in colloids or ligands and therefore can also be mobilized through base cation exchange. The linear relationship between SC and Cu may be caused by indirect mobilization of organic matter present in stream sediments and adjacent soils (often in the form of colloids) (Amrhein et al. 1992, Norrström and Jacks 1998, Nelson et al. 2009). Cu has also been shown to associate with oxides and edge sites of clay silicate minerals (McBride 1994, Nelson et al. 2009). Mobilization of Mn due to road salting may be due to cation exchange through the formation of Cl\(^-\) complexes and other geochemical processes. The amount of organic matter present, pH and redox conditions also may facilitate mobilization (Granato et al. 1995, Wen 2012). Metals are generally less biologically available if they are complexed and more biologically available when dissolved (John and Levanthal 1995). To research the possibility of Mn and Cu being contaminants within the road salt applied, daily loads of Mn and Cu were plotted against daily loads of Na\(^+\) in supplementary figure 7. Best fit lines were mostly logarithmic in nature with Na\(^+\) increasing faster than the metals. This leads us to believe there is little additional of Mn or Cu found in the salt applied. The relationship observed may be controlled by a single high concentration point however so further research should be conducted to rule out this possibility. Cation and metal mobilization
using lab grade NaCl has been shown in previous work however (Haq et al. 2018, Kaushal et al. 2019).

4.5. SC as a proxy for chemical cocktails in road-salt impacted streams

Simple linear regression models of SC and metals showed promise for developing Mn and Cu proxies. NSE appears to be higher for Cu than Mn but both are within acceptable ranges for a natural system as are RMSE values ranging from 0.009 to 0.05. Adding additional data (from targeted snow event sampling), which populates the dataset with higher concentrations of both SC and mobilized metals in response to road salt use, also appears to help overall model validation. Interestingly, the areas of the timeseries in which the model is the least accurate occur immediately after snowfall events where observed metals concentrations remain elevated after SC has decreased to pre-snow event levels (figure 5). This temporal lag time has been noted in other studies as well (e.g. (Kaushal et al. 2019)), with metals remaining elevated for up to a month after a storm. Difficulty modeling post storm metal values are also suggested in table 4 with low RMSE and NSE values for data collected 24 h after a salinization event. Datasets in figure 3 are somewhat skewed towards lower concentrations with only a few winter storms captured at or near their maximum SC. Additional hourly sampling data was collected before and during the peak of a storm at Sligo Creek (supplementary figure 3) which helps illustrate that the slopes derived in figure 3 are valid and not simply being controlled by the sparse high values. Data collection during storms is challenging as SC can increase by >1000 µS cm⁻¹ per hour during a storm necessitating extremely high sampling frequencies or lab experiments to cover the gaps in the data. More research should be done just prior to, during, and after winter snow storms to better constrain proxy models and account for metals release and biogeochemical mechanisms contributing to lag times in metals concentrations returning to baselevel following road salt events. A larger dataset would also allow for developing regression relationships based on weather, Q, precipitation and/or season. Monitoring of a more ‘natural’ catchment would also be beneficial to determine what baseline metal mobilization is without anthropogenic salt application. Data from urban watersheds with differing amounts of deicing salts applied could also help illuminate how much of the metals flux is originating from cation exchange in sediments vs. metals flux from motor vehicle particulate. It appears that SC may not be a simple proxy for metal concentration. A more complex model integrating time dynamics of mobilization may be needed to account for the lag times discovered. Metal mobilization can be predicted with some precision with the current model but it is return to baselevel is not well constrained.

4.6. Future monitoring implications

Information on the concentrations and compositions of chemical cocktails will be key to identifying management strategies for this anthropogenic legacy. SC in streams is a robust proxy for Cl⁻ concentrations in multiple studies (Daley et al. 2009, Corsi et al. 2010, Trowbridge et al. 2010, Perera et al. 2013, Robinson and Hasenmueller 2017, Snodgrass et al. 2017, Haq et al. 2018, Oswald et al. 2019, Moore et al. 2020), but the potential for SC to serve as a proxy for multiple base cations and trace metals in urban streams has not been thoroughly investigated until recently (Löfgren 2001, Haq et al. 2018, Kaushal et al. 2019, 2020, Morel et al. 2020), and less is known regarding applications of sensors to develop proxies. Our analysis suggests

Table 4. Root mean square error and Nash–Sutcliffe efficiency for predicted values at Sligo Creek ('USGS NWIS'). SC = specific conductance µS cm⁻¹ at each time interval. Samples were arranged by date; odd samples were used to generate the regression and even samples were used as a test of model validity.

| Dataset generated                  | Dataset applied                      | Equation                      | Element | RMSE  | NSE   |
|------------------------------------|--------------------------------------|-------------------------------|---------|-------|-------|
| Regular sampling odd               | Regular sampling even                | 1.1*10⁻⁵ - 5*SC + 0.0045      | Cu      | 0.0093| 0.502 |
| Regular sampling odd               | Regular sampling even                | 2.89*10⁻⁵ - 5*SC + 0.005      | Mn      | 0.0523| 0.059 |
| Regular sampling + high frequency peak odd | Regular sampling + high frequency peak even | 1.9*10⁻⁵ - 5*SC + 0.0016  | Cu      | 0.0255| 0.366 |
| Regular sampling + high frequency peak odd | Regular sampling + high frequency peak even | 3.2*10⁻⁵ - 5*SC + 0.0112  | Mn      | 0.0477| 0.282 |
| Regular sampling + high frequency peak odd | Sampling after peak of storm          | 1.9*10⁻⁵ - 5*SC + 0.0016  | Cu      | 0.1154| -5.006|
| Regular sampling + high frequency peak odd | Sampling after peak of storm          | 3.2*10⁻⁵ - 5*SC + 0.0112  | Mn      | 0.0878| -0.326|
Figure 6. (A)–(D): principal component analysis of data collected from Sligo Creek. The x-axis describes the most variance and y-axis describes the second most variance. In the PCA biplots, a small angle between analytes indicates positive correlation. At 90° of each other, analytes are considered uncorrelated, while diametrically opposed analytes are considered anti-correlated. Figure 6(A) illustrates a PCA for data collected during spring and summer 2019 representing a ‘baseline’ chemical cocktail absent from road salting. The PCA in figure 6(B) shows the peak of a winter storm captured between 29 January 2019 and 30 January 2019 illustrating a very tight grouping of major and trace elements mobilized through base cation exchange. Figure 6(C) illustrates a dataset collected during the descending limb of SC during a storm between 1 March 2019 and 2 March 2019. A grouping of elements similar to #B can be seen in #C as well but with SC and Na\(^{+}\) becoming a less significant portion of the cocktail. Figure 6(D) shows data collected later in the day on 2 March 2019, metal mobilization in this plot appears to be driven primarily by Ca\(^{2+}\), Mg\(^{2+}\) and K\(^{+}\) instead of Na\(^{+}\) or SC. This process is likely cyclic year to year, illustrating the complex and ever-changing nature of chemical cocktails in urban streams (‘USGS NWIS’).

that proxies can be developed to predict concentrations of base cations and trace metals from sensors and characterize seasonal shifts in chemical mixtures or cocktails. SC sensors are becoming relatively inexpensive to install, and could be distributed across many sites, allowing for much higher frequency monitoring over larger spatial areas than grab sampling or automated water samplers. More research is needed to evaluate proxy relationships across sites spanning a wider gradient of environmental conditions and applications, to manage the causes and consequences of FSS. In addition, it is difficult to obtain high-resolution elemental data from expensive and labor-intensive ICP analyses in routine monitoring of streams and during hydrologic events compared to analyses of nutrients and carbon. When additional data is available, more complex models may also be used which create different regressions for baseline and storm events conditions and incorporate insights gained from the literature on concentration–Q(C–Q) relationship variability. For example, the C–Q\(_{\text{quick,slow}}\) model shows particular promise as it is able to consider the possibility that C–Q relationships vary across seasons (Minaudo et al 2019). Nonlinear empirical modeling may also be explored as similar studies have been conducted.
relating phosphorus concentrations to T and Q measurements (Minaudo et al. 2017, Stutter et al. 2017, Villa et al. 2019).

**Data availability statement**

The data that support the findings of this study are available upon reasonable request from the authors.

**Acknowledgments**

Lainey Reed assisted with field work, Shahan Haq and William Nguyen assisted in the lab, and Laura Sammon and Zi Qin Ni helped with statistical analyses. Robert Walter provided thoughtful and constructive reviews of previous drafts. This work was supported by Maryland Sea Grant SA75281870W, NSF EAR 1521224, NSF OIA 2021089, and the US Environmental Protection Agency. Partial support was also provided by the Maryland Department of Natural Resources, the Maryland Department of Transportation State Highway Administration, and the National Fish and Wildlife Foundation through the U.S. Environmental Protection Agency’s Chesapeake Bay Program Office, and Chesapeake Bay Trust GRANT 1619. The information in this document has been subjected to US Environmental Protection Agency (Agency) peer and administrative review, and it has been approved for publication as an Agency document. The views expressed in this article are those of the authors and do not necessarily represent the views or policies of the Agency. Any mention of trade names, products, or services does not imply an endorsement by the US Government or the Agency.

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