Biogeosciences Discuss., 12, 7411–7448, 2015
www.biogeosciences-discuss.net/12/7411/2015/
doi:10.5194/bgd-12-7411-2015

Biogeosciences Discussions
Open Access

Salinization alters fluxes of bioreactive elements from streams and soils across land use

S.-W. Duan and S. S. Kaushal

Department of Geology and Earth System Science Interdisciplinary Center, University of Maryland, College Park, MD, USA

Received: 1 April 2015 – Accepted: 12 April 2015 – Published: 20 May 2015

Correspondence to: S.-W. Duan (sduan@umd.edu)

Published by Copernicus Publications on behalf of the European Geosciences Union.

Abstract

There has been increased salinization of fresh water over decades due to the use of road salt deicers, wastewater discharges, human-accelerated weathering, and groundwater irrigation. The effects of increased salinization on biogeochemical cycles in freshwater ecosystems are still not well understood. We investigated potential impacts of increased salinization on fluxes of bioreactive elements from stream sediments and riparian soils to overlying stream water. Two-day incubations of sediments and soils with stream and deionized water across 3 salt levels were conducted at 8 routine monitoring stations at the Baltimore Ecosystem Study Long-Term Ecological Research (LTER) site in the Chesapeake Bay watershed. Ambient stream chemistry was also monitored before and after a snow event coinciding with road salt additions. Results indicated: (1) salinization typically increased sediment releases of labile dissolved organic carbon (DOC), dissolved inorganic carbon (DIC), total dissolved Kjeldahl nitrogen (TKN) (ammonium + ammonia + dissolved organic nitrogen), and sediment transformations of nitrate, (2) salinization generally decreased DOC aromaticity and fluxes of soluble reactive phosphorus (SRP) from both sediments and soils, (3) the effects of increased salinization on sediment releases of DOC and TKN and DOC quality increased with percentage watershed urbanization. The differential responses of riparian soils and sediments to increased salinization were likely due to differences in organic matter amounts and composition. Results of the sediment and soil incubations were used to interpret changes in ambient stream chemistry before and after a snow event. Our results suggest that short-term increases in salinization can cause releases of significant amounts of labile organic carbon and nitrogen from stream substrates and organic transformations of nitrogen and phosphorus. Given that salinization of fresh water will increase in the future, potential impacts on coupled biogeochemical cycles and water quality should be expected.

BGD
12, 7411–7448, 2015

1 Introduction

Salt concentrations in freshwaters are rapidly increasing at a regional scale in the United States, especially in urban watersheds with high population density (e.g., Kaushal et al., 2005; Findlay and Kelly, 2011; Steele and Aitkenhead-Peterson, 2011; Corsi et al., 2015). Most of the increased salinization can typically be attributed to road salt deicers and other industrial uses, wastewater discharges, groundwater irrigation, and human-accelerated weathering (e.g., Findlay and Kelly, 2011; Aitkenhead-Peterson et al., 2009; Kaushal et al., 2013). Increased salinization can have important environmental consequences for drinking water supplies, freshwater biodiversity, degradation of soils and groundwater, degradation of vehicles and infrastructure, and mobilization of inorganic and organic contaminants (Nielson et al., 2003; Kaushal et al., 2005; Findlay and Kelly, 2011; Corsi et al., 2015). Recent studies have further shown that increased salinization can influence biogeochemical cycles of bioreactive elements such as carbon and nitrogen (Green et al., 2008, 2009a, b; Green and Cresser, 2008; Compton and Church, 2011; Lancaster, 2012; Steele and Aitkenhead-Peterson, 2013) as well as phosphorus and sulfur (Compton and Church, 2011; Kim and Koretsky, 2011, 2013). Evidence is accumulating that increased salinization is an important process during the urban evolution of watersheds globally from decades to centuries (Kaushal et al., 2014a), and salinization has significant ecosystem effects over broader spatial and temporal scales (e.g., Findlay and Kelly, 2011; Kaushal and Belt, 2012; Corsi et al., 2015).

Although there has been increasing research, much more work needs to be done regarding the effects of increased salinization on biogeochemical cycles (Green et al., 2008, 2009a, b; Green and Cresser, 2008; Compton and Church, 2011; Kim and Koretsky, 2011; Lancaster, 2012; Steele and Aitkenhead-Peterson, 2013). Prior studies have commonly investigated the effects of salinization on fluxes and transformations of individual bioreactive elements or bulk concentrations of dissolved organic carbon (DOC) (e.g., Green et al., 2008, 2009; Steele and Aitkenhead-Peterson, 2011),

BGD
12, 7411–7448, 2015

but relatively little work has been done to improve our conceptual understanding of the effects of salinization on coupled biogeochemical cycles. The differential biogeochemical impacts of salinization across watershed land use are still less recognized, although urbanization and agriculture can influence physical, chemical and biological characteristics of watershed soils and stream substrates (Paul and Meyer, 2001; Kaushal et al., 2014a).

Our primary objective was to investigate the interactive effects of increased salinization and land use on potential fluxes (release or retention) of bioreactive elements (carbon, nitrogen, phosphorus, sulfur) from stream sediments and riparian soils, which are critical for managing stream water quality (Gilliam, 1994). We tested two hypotheses: (1) soil leaching and sediment retention/release of bioreactive elements in urban watersheds are more sensitive to increased salinization than rural watersheds, (2) retention/release of carbon, nitrogen, phosphorus, and sulfur can be abiotically and/or biologically coupled. An improved understanding of the effects of increased salinization on release/retention of bioreactive elements can contribute to our understanding of urban drivers of changes in water quality, microbial communities and ecosystem functions (Kaushal and Belt, 2012; Kaushal et al., 2014a), and benefit our assessment and management of salt use for water quality improvement.

2 Methods

Combined approaches of laboratory salinization experiments and field monitoring of stream water quality were used to test the above hypotheses. Surface sediments from stream channels and top soil in riparian zones were collected from 8 long-term monitoring stations across a rural-urban land-use gradient. The soils and sediments were leached or incubated in the laboratory with stream water or deionized water amended with 3 levels of salinization. Fluxes of bioreactive elements from sediments and soils were calculated and organic matter quality was characterized using optical properties. In order to investigate the potential impacts of salinization on biogeochemical cycles in

BGD
12, 7411–7448, 2015

sediments and soils under ambient and field conditions, similar water quality measurements were conducted before and after a snow event to compare with the laboratory salinization experiments.

2.1 Site description

The 8 stations were located at the US National Science Foundation supported Baltimore Ecosystem Study (BES) Long-Term Ecological Research (LTER) site, with land use varying from forest to low-density residential, agricultural, to suburban and urban (Table 1). The main focal watershed of the BES LTER site is the Gwynns Falls, a 17 150 ha watershed in the Piedmont physiographic province that drains into the northwest branch of the Patapsco River that flows into the Chesapeake Bay (Fig. 1). The Gwynns Falls sites traverse a rural/suburban to urban gradient from Glyndon (GFGL), Gwynnbrook (GFGB), Villa Nova (GFVN) to Carroll Park (GFCP) (Table 1). An agricultural stream (MCDN) is a small tributary to the Gwynns Falls draining a watershed dominated by row crop agriculture (corn, soybeans), while Dead Run (DRKR) is an urbanized tributary of the Gwynns Falls between GFVN and GFCP. Samples were also taken from a small urban tributary to the Gwynns Falls (GFGR), approximately 700 m above GFCP, which is highly contaminated with sewage (Kaushal et al., 2011). Baisman Run (BARN) is a low-density residential watershed located in the nearby Gunpowder Falls watershed that drains primarily forest land cover (Table 1; Fig. 1). The BES LTER site provides access to extensive background information and long-term monitoring of major anions, nutrients, and carbon concentrations and fluxes in streams (www.beslter.org; Groffman et al., 2004; Kaushal et al., 2008, 2011). Previous work has shown that watersheds of the BES LTER site can have considerably elevated levels of chloride and sodium (Kaushal et al., 2005; Kaushal and Belt, 2012).

BGD
12, 7411–7448, 2015

2.2 Sample collection and processing

Stream water, sediments, and soils for laboratory salinization experiments were collected on 8 March 2013, one day before a snow storm in the Baltimore-Washington D.C. metropolitan region. Three litres of stream water were collected at each site for the experiments and water quality analyses. Sediment samples were taken simultaneously along 4 cross-sections perpendicular to stream flow within 50 m of the primary sampling site (Duan and Kaushal, 2013). Along each stream cross section, surface sediments at three sites (left, middle and right) were collected. All sediments collected at these sites were well-mixed to make a composite sample. Soil samples from the riparian zone were also collected similar to sediment samples. Because the sites GFCP and GFGR were located very close to each other, only one soil sample was collected to represent these two sites. The sediment and soil samples were transferred to glass jars, and placed immediately into a cooler and brought back to lab. In the lab, sediments were sieved through a 2 mm sieve, and the < 2 mm fractions of sediments and soils were homogenized for incubation experiments (e.g., plant roots were picked from soils and discarded). Stream water was re-sampled 2 days later, when snow was melting, in order to examine the changes in water quality before and after the snow storm. Stream waters were temporarily stored at 2–4 °C along with sediments and soils prior to laboratory experiments. Approximately 100 mL aliquots of steam water were filtered through pre-combusted GF/F Whatman filters, and the filtrates were stored in a refrigerator for analyses of optical properties and dissolved inorganic carbon (DIC) measurements. Another aliquot was similarly filtered but frozen prior to analyses for concentrations of dissolved organic carbon (DOC), nutrients, and major anions.

2.3 Laboratory salinization experiments

For each laboratory salinization experiment, 60 g sub-samples of homogenised sieved sediments (< 2 mm) were inserted into a series of 125 mL glass flasks to cover the bottom of the flasks, and 100 mL of unfiltered stream waters were carefully added with

BGD
12, 7411–7448, 2015

a pipette in order to not disturb the sediments. In order to evaluate the potential effects of salinization, pure NaCl salt was amended to unfiltered stream water to obtain 3 concentration levels (0 g Cl L^{-1}, 2 g Cl L^{-1}, and 4 g Cl L^{-1}). These concentration levels were within the range reported for salt concentrations in ambient stream water at the Baltimore LTER site (Kaushal et al., 2005). All laboratory salinization experiments were conducted in duplicate. Simultaneously, streamwater samples without sediments were also incubated at the same 3 levels of salinization as controls, in order to separate potential contributions of sediments from that of stream water. The laboratory salinization experiments were conducted in the dark and at ambient temperatures (19–22 °C), and the flasks were gently stirred for 2 days with a shaker table to simulate water movement in streams. During the 2 day incubations, the flasks were loosely capped to avoid external contamination while allowing for air entry. Laboratory salinization experiments for riparian soils were conducted similar to stream sediments, except that (1) deionized (DI) water (rather than stream water) was used for soil leaching, and (2) the samples were not stirred during the incubations assuming much slower hydrologic flow rates during soil infiltration than those for a stream. These experimental designs may have introduced potential artefacts such as no soil infiltration, constant temperature and no exposure to sunlight, which could influence results. However, previous studies investigating the potential impacts of salinization on soil biogeochemistry have used similar approaches (e.g., Green et al., 2008, 2009a; Compton and Church, 2011; Kim and Koretsky, 2013; Steele and Aitkenhead-Peterson, 2013). At the end of the incubations, the incubated stream water and DI water were filtered through pre-combusted GF/F Whatman filters for water chemistry analyses.

2.4 Chemical analysis

All filtrates were analyzed for major anions, nitrate, soluable reactive phosphorus (SRP), DOC, dissolved inorganic carbon (DIC), total dissolved nitrogen (TDN), and optical properties (absorbance and fluorescence). DOC, TDN and DIC concentrations were measured on a Shimadzu Total Organic Carbon Analyzer (TOC-V CPH/CPN)

BGD
12, 7411–7448, 2015

(Duan and Kaushal, 2013). Chloride, nitrate, and sulfate concentrations were measured with a Dionex ion chromatograph (ICS-1500, Dionex INC., USA), with an eluent of 3.5 mM of Na_2CO_3 with 1.0 mM $NaHCO_3$ and a flow rate of 0.3 mL min^{-1}. SRP was measured on an automated QuikChem 8500 Series 2 FIA System, using the ascorbic acid-molybdate blue method (Murphy and Riley, 1962). Total Kjeldahl nitrogen (TKN), including dissolved organic nitrogen, ammonia, and ammonium, was calculated by subtraction of nitrate-N from TDN.

Ultraviolet (UV) absorbance and fluorescence spectroscopy were used in characterization of DOC source and lability. Filtrates were scanned for absorbance from 200 to 800 nm with a Shimadzu UV-1800 Spectrophotometer. UV absorbance at 254 nm was used to calculated specific UV absorbance (SUVA) by normalizing for DOC concentration. SUVA is strongly correlated with percent aromaticity of organic matter as determined by 13C NMR (Weishaar et al., 2003), and thus can be a useful parameter for estimating terrestrial organic carbon sources in aquatic systems. Fluorescence measurements were made on a FluoroMax-4 Spectrofluorometer (Horiba Jobin Yvon, Edison NJ, USA) using the method that was described previously by Duan and Kaushal (2013). Basically, we used a 1 cm quartz cuvette with slit widths set to 5 nm. Excitation emission matrix scans (EEMs) were obtained by collecting a series of emission wavelengths ranging from 300 to 600 nm (2 nm increments) at excitation wavelengths ranging from 240 to 450 nm (5 nm increments). EEMs data were corrected for instrument biases, inner filtering and scatter removal, and calibrated values of fluorescence intensities at excitation/emission = 275 nm/340 nm and 350 nm/480 nm were recorded as protein-like and humic-like fluorophores (Coble, 1996; Stolpe et al., 2010). Relative to the humic-like fluorophore, the intensity of the protein-like fluorophore is generally higher in labile DOC sources (e.g., wastewater; Hudson et al., 2007) and positively correlated with DOC bioavailability (Balcarczyk et al., 2009; Lønborg et al., 2010). Thus, the ratio of the protein-like to the humic-like fluorophore (P/H) was calculated here as an index of organic carbon lability.

BGD
12, 7411–7448, 2015

Ash free dry weight (AFDW) of the sediment and soil samples was analyzed as an index of organic matter content. Sediment and soil ash weights were calculated as the difference in weights before and after combustion at 550 °C for 4 h (APHA, 1998). Prior to combustion, sediments were dried at 105 °C for 4 h to remove water. Ash free dry weights were determined in triplicates.

2.5 Data analysis and statistics

Changes in concentrations of DOC and other water quality variables in stream water and DI water during the two-day incubations were calculated, and the changes were calibrated with the controls (incubations with unfiltered water or DI water only) to obtain fluxes from sediments or soils. Differences in chemical fluxes between incubations at the three salinization levels were tested using one-way ANOVA. Relationships between water quality variables and land use or between two sediment/soil fluxes were examined using Spearman's rank correlation. For all statistical tests, significance was accepted at $\alpha = 0.05$. Analyses were performed using SPSS version 17.0 (2014).

3 Results

3.1 Water and sediment chemistry

In stream waters that were used for laboratory salinization experiments, water chemistry varied considerably (Table 2). In general, concentrations of chloride ion (Cl^-), sulfate-S (SO_4^{2-}-S) and DOC, and protein-like to humic-like fluorophore (P/H) ratios of DOC in stream water increased with watershed impervious surface cover (ISC) ($r^2 = 0.77$–0.83, $p < 0.05$, $n = 8$). SUVA showed an opposite trend and decreased with watershed ISC ($r^2 = 0.79$, $n = 8$, $p < 0.05$). Cl^- concentrations also increased with ISC, but the coefficient was not significant ($r^2 = 0.40$, $n = 8$, $p > 0.05$), and the highest value was not observed at the site GFGR with highest ISC. Nitrate-N (NO_3^--N) and SRP con-

BGD
12, 7411–7448, 2015

centrations did not vary with watershed ISC, and the highest concentrations occurred at the agricultural site (MCDN; Table 2).

Sediment ash free dry weight (AFDW) also displayed an increasing trend with ISC (from 0.61 to 1.90 %) except one surprisingly high value (3.98 %) observed at GFCP. AFDW of the riparian soils (6.17–8.84 %) were significantly higher than the sediments ($p < 0.05$, one-way ANOVA) but did not vary significantly with watershed ISC (Table 2).

3.2 Influence of salinization on C fluxes and DOC composition

Sediments were a net source for both DOC and DIC. DOC release from sediments consistently increased with increasing salinization (Fig. 2a), and DOC values at 4 g Cl L^{-1} were 7.8 ± 1.9 times higheer than those at 0 g Cl L^{-1}. Although salinization also increased the release of DIC (with one exception at GFCP), the highest DIC releases generally occurred at 2 g Cl L^{-1} (6 in 8 cases), and the highest DIC values were only 1.4 ± 0.02 times higher than those at 0 g Cl L^{-1} (Fig. 2b). Meanwhile, maximal sediment releases of DOC and DIC were 3.9 ± 0.8 and 0.51 ± 0.12 times higher than their ambient concentrations in streamwater.

Moreover, the effects of salinization on sediment releases differed among DOC fractions. Salinization consistently and considerably increased releases of the protein-like fluorophore, showing significant increases that were 6.7 ± 1.0 times higher at 4 g Cl L^{-1} relative to those at at 0 g Cl L^{-1} (Fig. 2c). The effects of salinization on humic-like fluorophore releases, however, were not consistent and were much less (increase by 1.2 ± 0.1 time) (Fig. 2d). As a result, salinization consistently and considerably increased (by 5.9 ± 0.7 times) the protein to humic (P/H) ratio (Fig. 2e) – an index of DOC lability (Lønborg et al., 2010; Duan and Kaushal, 2013). The effects of salinization on DOC lability using fluorescence spectroscopy were further supported by absorbance measurements. Absorbance measurements showed a general decreasing trend in SUVA changes with increasing salinization (7 out of 8 cases; Fig. 2f).

Effects of laboratory salinization on DOC and DIC releases from soils were relatively more complex and not as consistent. In 4 out of 7 cases (POBR, MCDN, GFGB and

BGD
12, 7411–7448, 2015

DRKR), DOC releases from soils decreased as experimental salinization increased from 0 g Cl L^{-1} to 2 g Cl L^{-1}, followed by slight increases as experimental salinization increased from 2 g Cl L^{-1} to 4 g Cl L^{-1} (Fig. 3a). Similar results were also reported by Green et al. (2008). The effects of laboratory salinization experiments on DIC releases from soils were similar to that of DOC (Fig. 3b). In spite of the complex effects of salinization on releases of total DOC, salinization consistantly decreased SUVA of leached DOC across sites (by 40 ± 4 %; Fig. 3c).

3.3 Influence of salinization on fluxes of TKN, nitrate, SRP, and sulfate

Sediments were generally a source of TKN (ammonium + ammonia + dissolved organic nitrogen) and SRP but a sink of nitrate during the salinization experiments (Fig. 4). Laboratory salinization experiments consistently increased TKN releases from sediments, and the TKN releases at 4 g Cl L^{-1} were 13.3 ± 5.1 times higher than that at 0 g Cl L^{-1} (Fig. 4a). Meanwhile, salinization experiments consistently increased nitrate retention (negative fluxes). Nitrate retention at 4 g Cl L^{-1} was 1.6 ± 0.4 time higher than nitrate retention at 0 g Cl L^{-1} (Fig. 4b). For SRP, 6 out of the 8 sites showed that salinization experiments decreased sediment SRP releases (by 81 ± 7 %), and the exceptions occurred at the two urban sites GFCP and GFGR (showing increases by 1.3 to 3.5 times, respectively; Fig. 4c). Salinization effects on sulfate were even more complex. However, the agricultural site and 2 urban sites (MCDN, GFCP and GFGR) showed strong decreases in sulfate fluxes (by 90 ± 23 %) when the level of salinization increased from 0 g Cl L^{-1} to 4 g Cl L^{-1} (Fig. 4d). Meanwhile, the maximal sediment releases of TKN during the 2 day experiments were 4.9 ± 1.7 times greater than its ambient concentrations in stream water; approximately 80 ± 11 % of ambient stream water nitrate was retained during the salinization experiments. On the other hand, the maximum fluxes of SRP and sulfate during the salinization experiments represented only 1.16±0.16 and 0.20±0.07 of their ambient concentrations in stream water, respectively.

Similar to sediments, salinization consistently increased TKN releases from soils, and the values at 4 g Cl L^{-1} increased by 93 ± 25 % relative to 0 g Cl L^{-1} (Fig. 5a). Lab-

BGD
12, 7411–7448, 2015

oratory salinization increased nitrate releases in 5 out of 7 cases. The maximal nitrate releases with salinization (generally occurred at 2 g Cl L^{-1}) were 1.73 ± 0.19 times greater than those at 0 g Cl L^{-1} (Fig. 5b). Similar to sediments, 6 out of 7 cases showed that experimental salinization suppressed SRP releases from soils, and SRP releases at 4 g Cl L^{-1} decreased by 40 ± 9 % relative to those at 0 g Cl L^{-1} (Fig. 5c). Similar to the sediments, the effects of salinization on sulfate releases from soils were complex and inconsistent (Fig. 5d).

3.4 Biogeochemical coupling between the fluxes of chemical species

Correlation analysis suggested links between the fluxes of the measured chemical species of bioreactive elements. The first correlation was DIC flux to releases of DOC. Across laboratory salinization experiments with sediments, DIC flux initially increased with DOC releases but the increases did not continue with further DOC increases (Fig. 6a). Across soil laboratory salinization experiments, DIC flux linearly increased with DOC releases, however (Fig. 6b). There was also a correlation between nitrate retention (negative values) to DOC releases. Specifically, nitrate retention linearly increased with increasing DOC releases from both sediments and soils in 6 out of 8 cases (Fig. 6c and d). A third correlation was with SRP releases to the changes in SUVA of DOC. There were positive correlations between SRP releases and changes in SUVA values during both sediment incubations and soil leaching. This correlation occurred in 4 out of 8 cases during sediment incubations (Fig. 6e), while more cases (5 out of 7) showed this positive relationship during soil leaching (Fig. 6f).

3.5 Interactive effects of watershed land-use

Effects of laboratory salinization on sediment biogeochemical fluxes, indicated by changes in their standardized fluxes per g of Cl^-, exhibited clear patterns across the rural-urban gradient (Fig. 7). In general, the effects of salinization on DOC lability (indicated by P/H ratio and SUVA) and releases of DOC, the protein-like fluorophore, and

BGD
12, 7411–7448, 2015

TKN increased along this gradient (Fig. 7b–d and f, g). These changes were consistent with changes in sediment ash free dry weight (Fig. 7a and Table 2). Salinization effects on DIC releases generally followed a similar pattern, but there was large variability at the urban sites (Fig. 7e). In contrast, the effects of salinization on nitrate retention or SRP releases were larger at agricultural and suburban sites (Fig. 7h and i).

The effects of laboratory salinization on C, N, P and S leaching from soils was different from those observed in sediments, however (Fig. 7). Effects of salinization on soil leaching were generally less than those on sediment retention/release (except DIC, SUVA and SRP). In addition, effects of salinization on soil leaching did not show any consistent patterns along the rural-urban land use gradient.

3.6 Changes in water quality before and after a snow event

Changes in ambient Cl^- concentrations in stream water before and 2 days after the snow event differed site from site. The largest increase occurred at the Gwynns Falls headwater suburban site GFGL, which is the most distant from the center of Baltimore City (Fig. 5a and b). Increases in Cl^- concentrations also occurred at 3 downstream sites of the Gwynns Falls main stem (by 150–200 %). Surprisingly, only minor changes were observed at the two urban tributaries of DRKR and GFGR, although these sites were highest in Cl^- concentrations before the snow event.

Significant changes in concentrations of DOC (increase) and nitrate (decrease) in streams following the snow storm event were observed across the sites (Fig. 8c and i). These changes were consistent with results from laboratory salinization experiments using sediments, showing releases of DOC and retention of nitrate in response to laboratory salinization. The changes in DOC showed gradual decreases along the Gwynns Falls, whereas the changes in nitrate did not show any longitudinal trends along the land use gradient (Fig. 8d and j). Although there was no consistent changes in other water quality parameters, DIC and P/H ratio increased, whereas SRP decreased at GFGL (Fig. 8e–h, k and l), which was the site showing the largest increase in Cl^- concentration. These observed changes in DIC, P/H ratio and SRP concentrations

BGD
12, 7411–7448, 2015

before and after the snow storm event at GFGL were also consistent with the results of laboratory sediment salinization experiments (Figs. 2 and 4). However, there were no significant correlations between changes in Cl^- concentrations and changes in any other water quality parameter in ambient stream water during field observations.

4 Discussion

4.1 Effects of increased salinization on carbon retention and release

Previous studies have shown different effects of salinization (e.g., suppression, or inconsistent effects) on DOC mobilization in soils (Amrhein et al., 1992; Evans et al., 1998; Green et al., 2008, 2009a; Compton and Church, 2011; Ondrašek et al., 2012). These variations were attributed to soil types (Amrhein et al., 1992; Evans et al., 1998), water to soil ratios (Amrhein et al., 1992), water chemistry (Evans et al., 1998), leaching time (Compton and Church, 2011), and historical exposure to road salt deicers (Green et al., 2008, 2009a). Two competing effects of salts have been suggested upon which solubilisation of organic matter is dependent: sodium dispersion and pH suppression (Amrhein et al., 1992; Bäckström et al., 2004; Green et al., 2008, 2009a). That is, upon salt additions, the replacements of Ca^{2+} and Al^{3+} of soils by Na^+ would be expected to increase DOC solubility, because trivalent Al^{3+} and divalent Ca^{2+} reduce organic carbon solubility far more than monovalent Na^+ (Amrhein et al., 1992; Skyllberg and Magnusson, 1995). On the other hand, salinization suppresses pH in solution over shorter time scales due to the mobile anion effect, and therefore decreases DOC leaching from soils (Bäckström et al., 2004; Li et al., 2007; Green et al., 2008). In addition to pH suppression, flocculation/sorption or inhibitory effects on microbial activity have also been suggested as possible mechanisms for DOC retention upon increased salinization (e.g., Compton and Church, 2011; Ondrasek et al., 2012). It seems the above two-competing effect model (pH suppression vs. sodium dispersion) can be used here to interpret the inconsistent salinization effect on DOC retention/release from riparian

BGD
12, 7411–7448, 2015

soils in this study (Fig. 3). However, neither this model nor the flocculation/microbial-suppression mechanism can explain the consistent observation of DOC mobilization from sediments in our laboratory salinization experiments (Fig. 2), probably owing to differences in organic carbon composition and sources between stream sediments and riparian soils.

Our results from DOC characterization can provide further information for interpreting the differences in salinization effects on DOC releases between sediment and soils. Our results showed that only protein-like fluorophores were consistently and significantly remobilized from sediments with salinization (Fig. 2), which suggested that the increased DOC releases from sediments were mainly attributed to the releases of protein-like labile DOC fractions. Similar findings were also reported by Li et al. (2013), which showed that KCl can significantly increase the mobility of microbially-derived labile organic matter (indicated by the fluorescence index). Meanwhile, chemical analyses suggest that the protein-like fluorophores consist primarily of proteinaceous materials (e.g., proteins and peptides; Yamashita and Tanoue, 2003; Maie et al., 2007), and this DOC fraction is generally hydrophilic and low molecular weight (LMW) compounds (e.g., Sommerville and Preston, 2001). Results of Chen et al. (1989) and Fuchs et al. (2006) showed that solubility of the proteinaceous materials in LMW is generally neither affected by pH within normal range 6–9 nor by colloid coagulation. Therefore, increasing ionic strength (or salinization) can enhance the solubility of the proteinaceous materials via sodium dispersion (Green et al., 2008, 2009a) or through nonspecific electrostatic interactions at low salinities (called a "salting in" effect) (Tanford, 1961; Chen et al., 1989). Furthermore, because stream sediments are generally enriched in these labile, proteinaceous materials derived from biofilms (algae and microbes) and wastewater organics in urban watersheds (Kaushal et al., 2011, 2014b; Kaushal and Belt, 2012; Newcomer et al., 2012; Duan et al., 2014b), it is reasonable that salinization can mobilize a large amount of protein-like labile dissolved organic matter from stream sediments.

Relative to the proteinaceous materials, humic substances are larger hydrophobic molecules occurring in the colloidal size range (e.g., Aiken et al., 1985). This DOC

BGD
12, 7411–7448, 2015

fraction is readily subjected to flocculation (e.g., Sholkovit, 1976), sorption to mineral surfaces (Fox, 1991; Hedges and Keil, 1999), and pH suppression (Kipton et al., 1992; Li et al., 2007, 2013) with increasing ionic strength or salinization. The potential instability of the humic-like DOC fraction upon salinization was further supported by our present results and previous studies (e.g., Li et al., 2013), which showed that salinization consistently decreased SUVA of DOC released from soils and sediments (Figs. 2 and 3) – a parameter indicating DOC aromaticity (Weishaar et al., 2003). Relative to stream sediments, soil organic matter consists primarily of humic substances (up to 60–70 %; Griffith and Schnitzer, 1975). In this study, we also observed much higher SUVA values in DOC leached from soils (around 10 $L(mg\ C)^{-1}\ m^{-1}$) than from sediments ($< 2\ L(mg\ C)^{-1}\ m^{-1}$) (Fig. 7). Due to larger fractions of humic substances, the effects of salinization on DOC leaching from soils were not consistent (Fig. 3), but depended on the relative importance of sodium dispersion and pH suppression (Green et al., 2008).

The effects of salinization on DIC fluxes from sediments and soils may involve organic carbon mineralization, dissolution of carbonate minerals, and CO_2 exchange with the atmosphere. The potential importance of organic carbon mineralization and its influence on DIC releases during laboratory salinization experiments were supported by the observed increases in DIC concentrations with DOC releases (Fig. 6a and b). This mechanism seemed to fit better for soils, considering the strong linear relationship between DIC and DOC across soil salinization experiments (Fig. 6b). The complex relationships between DOC and DIC for sediment incubations (Fig. 6a) indicated the importance of other potential controls as well – e.g., CO_2 efflux to the atmosphere. It is known that the solubility coefficient for CO_2 decreases with salinity (Weiss et al., 1974; Duan and Sun, 2003) and pH suppression, both of which could occur during salinization experiments (Green et al., 2008). Thus, CO_2 efflux to the atmosphere may become a dominant control at higher salinities (e.g., 2–4 $g\ Cl\ L^{-1}$), and further increases in salinization may decrease DIC releases despite of continuous releases of DOC (Fig. 2). Relative to organic carbon mineralization and CO_2 efflux to the atmosphere, the ef-

BGD
12, 7411–7448, 2015

fects of salinization on carbonate mineral solubility seemed relatively less important because crystalline rocks of igneous or metamorphic origin characterize the surface geology in the region (http://www.mgs.md.gov/esic/geo/bal.html). Additional evidence suggests that the solubility of carbonate minerals increases with salinization (Akin and Lagerwerff, 1965), but DIC releases from soils in laboratory salinization experiments of the present study did not follow this trend (Fig. 3).

4.2 Potential effects of salinization on N, P, and S leaching and transformation

We observed mobilization of TKN in response to salinization in both sediments and soils (Figs. 3 and 4), and this has also been observed in previous studies (mainly NH_4^+; Duckworth and Cresser, 1991; Compton and Church, 2011; Kim and Koretsky, 2011). The consistent NH_4^+ releases with salinization can be attributed to Na^+ dispersion (Green and Cresser, 2008). That is, as a positively-charged ion, NH_4^+ can be adsorbed on negatively-charged particles of soils and sediments (Nieder et al., 2011); NH_4^+ retained on the cation exchange sites can be greatly reduced by the presence of sodium ions, causing flushing of NH_4^+-N with salinization (Duckworth and Cresser, 1991; Compton and Church, 2011; Kim and Koretsky, 2011). For DON releases from stream sediments or soils, it is reasonable to argue that the effects of salinization on DON are similar to those of the protein-like fluorophores for the reasons we discussed previously. However, previous studies have shown no consistent effects of salinization on DON leaching from soils or plant litter (Steele and Aitkenhead-Peterson, 2013; Green et al., 2008, 2009; Compton and Church, 2011). Thus, the increased TKN fluxes from sediments or soils in response to increased salinization (Fig. 4 and 5) were more likely attributed to NH_4^+ mobilization.

In contrast to DOC, DON, and NH_4^+, nitrate is a highly soluble, negatively-charged ion. Mechanisms such as pH suppression, Na^+ dispersion/exchange, and colloid coagulation do not apply for nitrate to interpret the salinization effects, while biologically-mediated transformations may play a relatively more important role. According to previous studies on soils, salinity can decrease the rates of both nitrification and denitri-

BGD
12, 7411–7448, 2015

fication during short time periods (hours to days; Dincer and Kargi, 2001; Hale and Groffman, 2006; Aminzadeh et al., 2010; Lancaster et al., 2012) due to biological inhibition. However, effects of salinization on nitrate releases from soils varied considerably (Hahn et al., 1942; Duckworth and Cresser, 1991; Green and Cresser, 2008; Compton and Church, 2011), and our results from soils also suggested considerable variability (Fig. 5b). For sediments, we found that laboratory salinization experiments consistently increased nitrate retention, however (Fig. 4b). These salinization effects might be related to the remobilization of labile DOC in sediments (Fig. 2c). That is, although salinization may directly influence denitrification rates of instream sediments (Hale and Groffman, 2006), it may also cause mobilization of significant amounts of protein-like dissolved organic matter into streams (Fig. 2c). We speculate that this mobilized labile dissolved organic matter may stimulate nitrate biological uptakes via denitrification and/or microbial immobilization because it provides an energy source for microbes (Newcomer et al., 2012). Furthermore, decomposition of labile dissolved organic matter can lead to anoxic conditions for N removal via denitrification (Sobczak et al., 2003; Duan et al., 2014a). So, when the effects of released labile dissolved organic matter override the inhibitory effects of salinization on nitrate transformations, we speculate that salinization may enhance nitrate retention in stream sediments (Fig. 4b).

Decreases in SRP fluxes from sediments and soils in response to salinization in the present study (Figs. 4 and 5) were likely a result of colloid coagulation at higher salinities (e.g., Compton and Church, 2011). Different from nitrate, P is primarily a particle reactive element, and a large fraction of dissolved P (e.g., up to 88 %; Cai and Guo, 2009) is in the form of colloids, or humic- Fe (Al-) phosphate complexes (Hens and Merckx, 2001; Turner et al., 2004; Regelink et al., 2013). This is because the sorption capacity for P per unit mass is about 5000 times larger for colloids than for the immobile soil matrix (McGechan and Lewis, 2002). However, the stability of colloids decreases with increasing ionic strength and decreasing pH (e.g. Bunn et al., 2002; Saiers et al., 2003), both of which can be induced by salinization (e.g., Green et al., 2008). An example of this salinization effect is rapid flocculation of freshwater SRP and

BGD
12, 7411–7448, 2015

colloids in estuaries in response to mixing of fresh water with seawater (e.g., Sholkovit, 1976). Thus, increased salinization may decrease stability of the colloidal humic- Fe (Al-) phosphate complexes, leading to reduced releases of SRP from sediments and soils (Figs. 4 and 5) and a coupling between SRP and SUVA (Fig. 6). In addition to abiotic controls, inhibition of microbial activity at higher salinities (Srividya et al., 2009) could provide an alternative explanation for observed decreases in SRP mobilization with salinization.

Relative to C, N and P, effects of salinization on sulfur transformations are relatively less known. Kim and Koretsky (2011, 2013) reported salinization inhibited porewater sulfate reduction in lake sediments. However, our results show that stream sediments were generally a source of sulfate (Figs. 4d and 5d), and thus sulfate reduction seemed to be an unimportant process in free-flowing streams. Effects of increased salinization on sulfate releases warrant further investigation in future studies, however.

4.3 Interactive effects of watershed urbanization and salinization

Overall, our results suggest that the effects of increased salinization on sediment DOC, TKN and DIC fluxes, DOC lability (indicated by P/H ratio and SUVA) increased from rural/agricultural, suburban to urban site (Fig. 7). The interactive effects of land use and salinization on sediment fluxes may be explained by coinciding changes in stream sediment organic matter content (indicated by ash free dry weight), which also showed an increase across the rural-urban gradient (Table 2 and Fig. 7a). Higher sediment organic matter content in urban streams has also been observed in our previous work (Duan and Kaushal, 2013), probably due to additional organic inputs from algal and anthropogenic sources (e.g., wastewater). Our recent work (Kaushal et al., 2014b) showed that gross primary production and organic matter lability increased significantly with watershed urbanization. Wastewater inputs from sewer leaks are common in the urban tributaries in the lower Gwynns Falls (DEPRM and Baltimore City Department of Public Works, 2004; Kaushal et al., 2011). As quantity and quality of sediment organic

BGD
12, 7411–7448, 2015

matter increase across the rural-urban land use gradient, so did the fluxes of labile DOC, total DOC, TKN and DIC in response to increased salinization.

4.4 Comparison of laboratory salinization experiments to field observations

Similar effects of laboratory salinization experiments on DOC and nutrient fluxes from sediments were only partially observed in the field measurements on ambient stream water quality before and after the snow event. The agreements included the consistently higher DOC concentrations and consistently lower nitrate concentrations during post-snow storm conditions than those of pre-snow conditions (Fig. 8c, d, i, j). The difference between laboratory salinization experiments and field observations during the snow event (Figs. 2–5 and 9) may be attributed to the different settings between field processes and laboratory experiments. First of all, the compositions of salts that was used for deicers are different from pure NaCl that was used in our laboratory experiments (Ramakrishna and Viraraghavan, 2005; Shi et al., 2010). The impurities in the deicers may cause increases in pH in soils and sediments – different from pH suppression with pure NaCl. Many studies have observed that soil pH actually increases after use of road deicers or groundwater irrigation (e.g., Aitkenhead-Peterson et al., 2009; Galuszka et al., 2011). In this study, consistent increases in SUVA (not shown) and decreases in P/H ratio at some sites during the snow event might be related to an increase in pH with deicer use (Fig. 8). In addition, snow melt might cause elevated leaching of bioreactive elements or "dilution effects", in addition to increases in salinization (Cameron, 1996; Agren et al., 2012). There are also other major nonpoint sources of organic matter and nutrients (e.g., upland soils and plant litter) from watersheds besides stream sediments and riparian soils (Kaushal et al., 2011), which may respond differently to the episodic salinization. All these uncertainties might contribute to observed differences between laboratory and field observations and should be considered in future research.

BGD
12, 7411–7448, 2015

5 Conclusions

The potential effects of salinization on biogeochemical fluxes from soils and stream sediments are summarized in Fig. 9. As shown in this figure, releases of labile DOC (thus total DOC) and TKN from sediments can potentially increase during episodic stream salinization, due to "salting-in" effects (or Na dispersion) of proteinaceous organic matter and NH_4^+ mobilization. The increased releases of labile DOC and TKN can result in increases in sediment releases of DIC and sediment retention of nitrate as a result of organic carbon mineralization and associated N transformations (e.g., denitrification and nitrate microbial immobilization). Moreover, the effects of salinization on sediment releases of labile DOC and TKN also increased with watershed urbanization (indicated by watershed ISC) due to higher sediment organic content at urban sites. DOC aromaticity (indicated by SUVA) and releases of SRP, however, decreased with stream salinization, likely due to coagulation of colloidal humic- Fe (Al-) complexes and pH suppression, which were associated with ion exchange. The sediment releases of labile DOC and TKN with increased salinization probably represents a significant, previously unrecognized flux of labile DOC and nitrogen in urban streams, which might have a large influence on carbon and nutrient biogeochemical cycles and water quality in urban waters. For soils, salinization effects on DOC leaching were not consistent, and there were no interactive effects of land use and salinization. Differences in effects of salinization on sediments and soils are likely attributed to differences in organic matter sources and lability. Nonetheless, our work suggest that increased salinization can have major effects on concentrations and fluxes of bioreactive elements in human-impacted watersheds and streams, and it is critical to conduct comprehensive investigations of the effects of salinization on all major bioreactive elements and also couple them together as a whole.

Acknowledgements. This research was supported by NSF Awards DBI 0640300, CBET 1058502, and Coastal SEES (NSF-1426844), NASA grant NASA NNX11AM28G, Maryland Sea Grant Awards SA7528085-U, R/WS-2 and NA05OAR4171042, and Baltimore Ecosystem Study LTER project (NSF DEB-0423476).

BGD
12, 7411–7448, 2015

References

Agren, A. M., Haei, M., Blomkvist, P., Nilsson, M. B., and Laudon, H.: Soil frost enhances stream dissolved organic carbon concentrations during episodic spring snow melt from boreal mires, Global Change Biol., 18, 1895–1903, 2012.

Aiken, G. R., McKnight, D. M., Wershaw, R. L., and MacCarthy, P.: Humic Substances in Soil, Sediment, and Water: Geochemistry, Isolation and Characterization, Wiley, New York, 1985.

Aitkenhead-Peterson, J. A., Steele, M. K., Nahar, N., and Santhy, K.: Dissolved organic carbon and nitrogen in urban and rural watersheds of south-central Texas: land use and land management influences, Biogeochemistry, 96, 119–129, 2009.

Akin, G. W. and Lagerwerff, J. V.: Calcium carbonate equilibria in aqueous solutions open to the air. I. The solubility of calcite in relation to ionic strength, Geochim. Cosmochim. Ac., 29, 343–352, 1965.

Aminzadeh, B., Torabian, A., Azimi, A. A., Bidhendi, G. R. N., and Mehrdadi, N.: Salt inhibition effects on simultaneous heterotrophic/autotrophic denitrification of high nitrate wastewater, Int. J. Environ. Res., 4, 255–262, 2010.

Amrhein, C., Strong, J. E., and Mosher, P. A.: Effect of deicing salts on metal and organic matter mobilization in roadside soils, Environ. Sci. Technol., 26, 703–709, 1992.

APHA: Standard methods for the examination of water and wastewater, 20th edn., American Public Health Association, Washington D.C., 1998.

Bäckström, M., Karlsson, S., Bäckman, L., Folkeson, L., and Lind, B.: Mobilisation of heavy metals by deicing salts in a roadside environment, Water Res., 38, 720–732, 2004.

Balcarczyk, K. L., Jones, J. B., Jaffe, R., and Maie, N.: Stream dissolved organic matter bioavailability and composition in watersheds underlain with discontinuous permafrost, Biogeochemistry, 94, 255–270, 2009.

Bunn, R. A., Magelky, R. D., Ryan, J. N., and Elimelech, M.: Mobilization of natural colloids from an iron oxide-coated sand aquifer: effects of pH and ionic strength, Environ. Sci. Technol., 36, 314–322, 2002.

Cai, Y. and Guo, L.: Abundance and variation of colloidal organic phosphorus in riverine, estuarine and coastal waters in the northern Gulf of Mexico, Limnol. Oceanogr., 54, 1393–1402, 2009.

Cameron, E. M.: Hydrogeochemistry of the Fraser River, British Columbia: seasonal variation in major and minor components, J. Hydrol., 182, 209–225, 1996.

BGD
12, 7411–7448, 2015

Chen, C. C., Zhu, Y. Z., and Evans, L. B.: Phase partitioning of biomolecules: solubilities of amino acids, Biotechnol. Progr., 5, 111–118, 1989.
Coble, P. G.: Characterization of marine and terrestrial DOM in seawater using excitation-emission matrix spectroscopy, Mar. Chem., 51, 325–346, 1996.
Corsi, S. R., De Cicco, L. A., Lutz, M. A., and Hirsch, R. M.: 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, 2015.
Compton, J. E. and Church, M. R.: Salt additions alter short-term nitrogen and carbon mobilization in a coastal Oregon Andisol, J. Environ. Qual., 40, 1601–1606, 2011.
DEPRM and Baltimore City Department of Public Works: Gwynns Falls water quality management plan: Executive Summary, http://www.cbtrust.org/atf/cf/Beb2a714e-8219-45e8-8c3d-50ebe1847cb8D/GWYNNSFALLSWATERQUALITYMANAGEMENTPLAN-EXEC.SUMMARY.PDF (last access: 8 May 2015), 2004.
Dincer, A. R. and F. Kargi.: Salt inhibition kinetics in nitrification of synthetic saline wastewater, Enzyme Microb. Tech., 28, 661–665, 2001.
Duan, S.-W. and Kaushal, S. S.: Warming increases carbon and nutrient fluxes from sediments in streams across land use, Biogeosciences, 10, 1193–1207, doi:10.5194/bg-10-1193-2013, 2013.
Duan, S. W., Delaney-Newcomb, K., Kaushal, S. S., Findlay, S. E. G., and K. T. Belt.: Potential effects of leaf litter on water quality in urban watersheds, Biogeochemistry, 121, 61–80, 2014a.
Duan, S. W., Amon, R. M. W., and Brinkmeyer, R. L.: Tracing sources of organic matter in adjacent urban streams having different degrees of channel modification, Sci. Total Environ., 485–486, 252–262, 2014b.
Duan, Z. H. and Sun, R.: 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, 257–271, 2003.
Duckworth, C. M. S. and Cresser, M. S.: Factors influencing nitrogen retention in forest soils, Environ. Pollut., 72, 1–21, 1991.
Evans, A., Zelazny, L. W., and Zipper, C. E.: Solution parameters influencing dissolved organic carbon levels in three forest soils, Soil Sci. Soc. Am. J., 52, 1789–1792, 1998.

BGD
12, 7411–7448, 2015

Findlay, S. E. G. and Kelly, V. R.: Emerging indirect and long-term road salt effects on ecosystems, Ann. N.Y. Acad. Sci., 1223, 58–68, 2011.
Fox, L. E.: The transport and composition of humic substances in estuaries, in: Organic Substances and Sediments in Water, Vol. 1, Humic and Soils, edited by: Baker, R. A., Lewis Publishers, Chelsea, MI, 129–162, 1991.
Fuchs, D., Fischer, J., Tumakaka, F., and Sadowski, G.: Solubility of amino acids: influence of the pH value and the addition of alcoholic cosolvents on aqueous solubility, Ind. Eng. Chem. Res., 45, 6578–6584, 2006.
Gilliam, J. W.: Riparian wetlands and water quality, J. Environ. Qual., 23, 896–900, 1994.
Green, S. M. and Cresser, M. S.: Nitrogen cycle disruption through the application of de-icing salts on upland highways, Water Air Soil Poll., 188, 139–153, 2008.
Green, S. M., Machin, R., and Cresser, M. S.: Long-term road salting effects on dispersion of organic matter from roadside soils into drainage water, Chem. Ecol., 24, 221–231, 2008.
Green, S. M., Machin, R., and Cresser, M. S.: Does road salting induce or ameliorate DOC mobilisation from roadside soils to surface waters in the long term?, Environ. Monit. Assess., 153, 435–448, 2009a.
Green, S. M., Machin, R., and Cresser, M. S.: Effect of long-term changes in soil chemistry induced by road salt applications on N-transformations in roadside soils, Environ. Pollut., 152, 20–31, 2009b.
Griffith, S. M. and Schnitzer, M.: Oxidative degradation of humic and fulvic acids extracted from tropical volcanic soils, Can. J. Soil Sci., 55, 251–267, 1975.
Groffman, P. M., Law, N. L., Belt, K. T., Band, L. E., and Fisher, G. T.: Nitrogen fluxes and retention in urban watershed ecosystems, Ecosystems, 7, 393–403, 2004.
Hahn, B. E., Olson, F. R., and Roberts, R. C.: Influence of potassium chloride on nitrification in Bedford silt loam, Soil Sci., 54, 113–121, 1942.
Hale, R. L. and Groffman, P. M.: Chloride effects on nitrogen dynamics in forested and suburban stream debris dams, J. Environ. Qual., 35, 2425–2432, 2006.
Hedges, J. I. and Keil, R. G.: Organic geochemical perspectives on estuarine processes: sorption reactions and consequences, Mar. Chem., 65, 55–65, 1999.
Hens, M. and Merckx, R.: Functional characterization of colloidal phosphorus species in the soil solution of sandy soils, Environ. Sci. Technol., 35, 493–500, 2001.
Hudson, N., Baker, A., and Reynolds, D.: Fluorescence analysis of dissolved organic matter in natural, waste and polluted waters – a review, River Res. Appl., 23, 631–649, 2007.

BGD
12, 7411–7448, 2015

Kaushal, S. S. and Belt, K. T.: The urban watershed continuum: evolving spatial and temporal dimensions, Urban Ecosyst., 15, 409–435, 2012.
Kaushal, S. S., Groffman, P. M., Likens, G. E., Belt, K. T., Stack, W. P., Kelly, V. R., Weathers, K. C., Band, L. E., and Fisher, G. T.: Increased salinization of fresh water in the northeastern U.S., P. Natl. Acad. Sci. USA, 102, 13517–13520, 2005.
Kaushal, S. S., Groffman, P. M., Mayer, P. M., Striz, E., Doheny, E. J., and Gold, A. J.: Effects of stream restoration on denitrification at the riparian-stream interface of an urbanizing watershed of the mid-Atlantic U.S., Ecol. Appl., 18, 789–804, 2008.
Kaushal, S. S., Groffman, P. M., Band, L. E., Elliott, E. M., Shields, C. A., and Kendall, C.: Tracking nonpoint source nitrogen pollution in human-impacted watersheds, Environ. Sci. Technol., 45, 8225–8232, 2011.
Kaushal, S. S., Likens, G. E., Utz, R., Pace, M. L., Grese, M., and Yepsen, M.: Increased river alkalinization in the Eastern U.S., Environ. Sci. Technol., 47, 10302–10311, 2013.
Kaushal, S. S., McDowell, W. H., and Wollheim, W. M.: Tracking evolution of urban biogeochemical cycles: past, present, and future, Biogeochemistry, 121, 1–21, 2014a.
Kaushal, S. S., Delaney-Newcomb, K., Findlay, S. E. G., Newcomer, T. A., Duan, S., Pennino, M. J., Sivirichi, G. M., Sides-Raley, A. M., Walbridge, M. R., and Belt, K. T.: Longitudinal patterns in carbon and nitrogen fluxes and stream metabolism along an urban watershed continuum, Biogeochemistry, 121, 23–44, 2014b.
Kim, S. Y. and Koretsky, C.: Influence of NaCl and $CaCl_2$ on lake sediment biogeochemistry, Appl. Geochem., 26, S198–S201, 2011.
Kim, S. Y. and Koretsky, C.: Effects of road salt deicers on sediment biogeochemistry, Biogeochemistry, 112, 343–358, 2013.
Kipton, H. and Powell, J.: Town, R. M. Solubility and fractionation of humic acid – effect of pH and ionic medium, Anal. Chim. Acta, 267, 47–54, 1992.
Lancaster, N. A.: Impact of salt on denitrification potential in roadside environments, M.S. thesis, University of Connecticut, http://digitalcommons.uconn.edu/cgi/viewcontent.cgi?article=1371&context=gs_theses (last access: 8 May 2015), 337 pp., 2012.
Li, M. T., Zhao, L. P., and Zhang, J. J.: Effect of temperature, pH and salt on fluorescent quality of water extractable organic matter in black soil, J. Integr. Agr., 12, 1251–1257, 2013.
Li, X. G., Rengel, Z., Mapfumo, E., and Singh, B.: Increase in pH stimulates mineralization of "native" organic carbon and nitrogen in naturally salt-affected sandy soils, Plant Soil, 290, 269–282, 2007.

BGD
12, 7411–7448, 2015

Lønborg, C., Alvarez-Salgado, X. A., Davidson, K., Martinez-Garcia, S., and Teira, E.: Assessing the microbial bioavailability and degradation rate constants of dissolved organic matter by fluorescence spectroscopy in the coastal upwelling system of the Ria de Vigo, Mar. Chem., 119, 121–129, 2010.

Maie, N., Scully, N. M., Pisani, O., and Jaffé, R.: Composition of a protein-like fluorophore of dissolved organic matter in coastal wetland and estuarine ecosystems, Water Res., 41, 563–570, 2006.

McGechan, M. B. and Lewis, D. R.: Sorption of phosphorus by soil, Part 1: Principles, equations and models (review paper), Biosyst. Eng., 82, 1–24, 2002.

Murphy, J. and Riley, J. P.: A modified single solution method for determination of phosphate in natural waters, Anal. Chim. Acta, 26, 1256, doi:10.1029/2002WR001887, 1962.

Newcomer, T. A., Kaushal, S. S., Mayer, P. M., Shields, A. R., Canuel, E. A., Groffman, P. M., and Gold, A. J.: Influence of natural & novel organic carbon sources on denitrification in forested, degraded-urban, and restored streams, Ecol. Monogr., 82, 449–466, 2012.

Olsen, M. W., Frye, R. J., and Glenn, E. E.: Effect of salinity and plant species on CO_2 flux and leaching of dissolved organic carbon during decomposition of plant residue, Plant Soil, 179, 183–188, 1996.

Ondrašek, G., Rengel, Z., Romić, D., and Savić, R.: Salinity decreases dissolved organic carbon in the rhizosphere and increases trace elements phyto-accumulation, Eur. J. Soil Sci., 63, 685–693, 2012.

Paul, M. J. and Meyer, J. L.: Streams in the urban landscape, Annu. Rev. Ecol. Evol. S., 32, 333–365, 2001.

Ramakrishna, D. M. and Viraraghavan, T.: Environmental impact of chemical deicers – a review, Water Air Soil Poll., 166, 49–63, 2005.

Regelink, I. C., Koopmans, G. F., van der Salm, C., Weng, L., and van Riemsdijk, W. H.: Characterization of colloidal phosphorus species in drainage waters from a clay soil using asymmetric flow field-flow fractionation, J. Environ. Qual., 42, 464–473, 2013.

Saiers, J. E. and Lenhart, J. J.: Ionic-strength effects on colloid transport and interfacial reactions in partially saturated porous media, Water Resour. Res., 39, 1256, 2003.

Shi, X. M., Liu, Y. J., Mooney, M., Berry, M., Hubbard, B., Fay, L., and Leonard, A. B.: Effect of Chloride-based Deicers on Reinforced Concrete Structures, WSDOT Research Report WA-RD 741.1., Transportation Research Board The National Academies, http://www.trb.org/Main/Blurbs/163932.aspx (last access: 8 May 2015), 2010.

BGD
12, 7411–7448, 2015

Sholkovit, E. R.: Flocculation of dissolved organic and inorganic matter during the mixing of river water and seawater, Geochim. Cosmochim. Ac., 40, 831–845, 1976.
Sobczak, W. V., Findlay, S., and Dye, S.: Relationships between DOC bioavailability and nitrate removal in an upland stream: an experimental approach, Biogeochemistry, 62, 309–327, 2003.
Sommerville, K. and Preston, T.: Characterisation of dissolved combined amino acids in marine waters, Rapid Commun. Mass Sp., 15, 1287–1290, 2001.
Srividya, S., Soumya, S., and Pooja, K.: Influence of environmental factors and salinity on phosphate solubilization by a newly isolated Aspergillus niger F7 from agricultural soil, Afr. J. Biotechnol., 8, 1864–1870, 2009.
Steele, M. K. and Aitkenhead-Peterson, J. A.: Long-term sodium and chloride surface water exports from the Dallas/Fort Worth region, Sci. Total Environ., 409, 3021–3032, 2011.
Steele, M. K. and Aitkenhead-Peterson, J. A.: Salt impacts on organic carbon and nitrogen leaching from senesced vegetation, Biogeochemistry, 112, 245–259, 2013.
Stolpe, B., Guo, L., Shiller, A. M., and Hassellöv, M.: Size and composition of colloidal organic matter and trace elements in the Mississippi River, Pearl River and the northern Gulf of Mexico, as characterized by flow field-flow fractionation, Mar. Chem., 118, 119–128, 2010.
Tanford, C.: Physical Chemistry of Macromolecules, Wiley, New York, 1961.
Turner, B. L., Kay, M. A., and Westermann, D. T.: Colloidal phosphorus in surface runoff and water extracts from semiarid soils of the western United States, J. Environ. Qual., 33, 1464–1472, 2004.
Weishaar, J. L., Aiken, G. R., Bergamaschi, B. A., Fram, M. S., Fujii, R, and Mopper, K.: Evaluation of ultraviolet absorbance as an indicator of the chemical composition and reactivity of dissolved organic carbon, Environ. Sci. Technol., 37, 4702–4708, 2003.
Weiss, R. F.: Carbon dioxide in water and seawater: the solubility of a non-ideal gas, Mar. Chem., 2, 203–215, 1974.
Yamashita, Y. and Tanoue, E.: Chemical characterization of protein-like fluorophores in DOM in relation to aromatic amino acids, Mar. Chem., 82, 255–271, 2003.

BGD
12, 7411–7448, 2015

Table 1. Characteristics of study subwatersheds.

Site	BARN	MCDN	GFGB	GFGL	GFVN	GFCP	DRKR	GFGR
Type	forest	agriculture	suburban	suburban	urban	urban	urban	urban
Area (ha)	3.86	0.1	11	0.8	84.2	170.7	14.3	6.5
%ISC	0.3	0.1	15	19	17	24	45	61
Developed/open	25.5	13.6	43.8	41.2	27.4	25.5	22.4	9.2
Developed/low		5.4	28.9	21.5	25.2	28.8	38.8	27.5
Developed/medium		3.6	4.3	8.3	10.5	16.2	18.1	43.6
Developed/high			1.3	3.4	2.5	5.0	7.4	17.4
Barren					0.2	0.1	0.1	0.04
Shrub	0.7	7.9	1.1	6.3	1.4	0.8	0.2	0.05
%Forest	72.6	1.4	19.0	19.2	25.5	19.3	12.7	1.3
Hay/pasture	1.0	30.4	0.9	0.1	3.1	1.7	0.1	
Cultivated Crops		37.1	0.1		3.4	1.8		
Wetland		0.7	0.6		0.8	0.7	0.2	
Open water					0.1	0.1		0.9

Watershed land cover and impervious surface (ISC %) data are from Shields et al. (2008) and the National Land Cover Database (NLCD). Both land cover and impervious statistics were based on 30 m resolution land cover data.

BGD
12, 7411–7448, 2015

Table 2. Water chemistry, sediment and soil ash-free weight prior to salinization incubation experiments.

	Water									Sediment	Soil
	F^-	Cl^-	SO_4-S	DOC	P/H	DIC	SUVA	NO_3-N	SRP	Ash-free weight	Ash-free weight
	$mg\,L^{-1}$	$mg\,L^{-1}$	$mg\,L^{-1}$	$mg\,L^{-1}$	$mg\,L^{-1}$	$mg\,L^{-1}$	$L/(mg\,C\,m^{-1})$	$mg\,L^{-1}$	$\mu g\,L^{-1}$	(%)	(%)
BARN	0.26	75	5	1.2	0.56	3.3	2.26	1.76	16.0	0.61	6.17
MCDN	0.41	57	19	1.5	0.36	12.2	2.64	7.13	48.1	1.23	7.68
GFGB	0.30	95	6	1.2	0.63	12.1	2.11	2.09	16.9	0.92	8.84
GFVN	0.46	116	10	1.5	0.73	16.6	2.24	1.26	13.4	0.89	7.82
GFGL	0.38	124	25	2.3	0.52	32.1	2.31	1.43	38.7	1.35	6.27
GFCP	0.80	159	22	1.9	0.83	18.9	1.94	1.19	10.5	3.98	7.17
DRKR	0.87	557	59	2.5	0.77	34.6	1.96	1.28	30.2	1.22	8.04
GFGR	2.80	187	54	3.5	1.36	32.8	0.95	2.30	20.4	1.90	–

–: samples were not taken.

BGD
12, 7411–7448, 2015

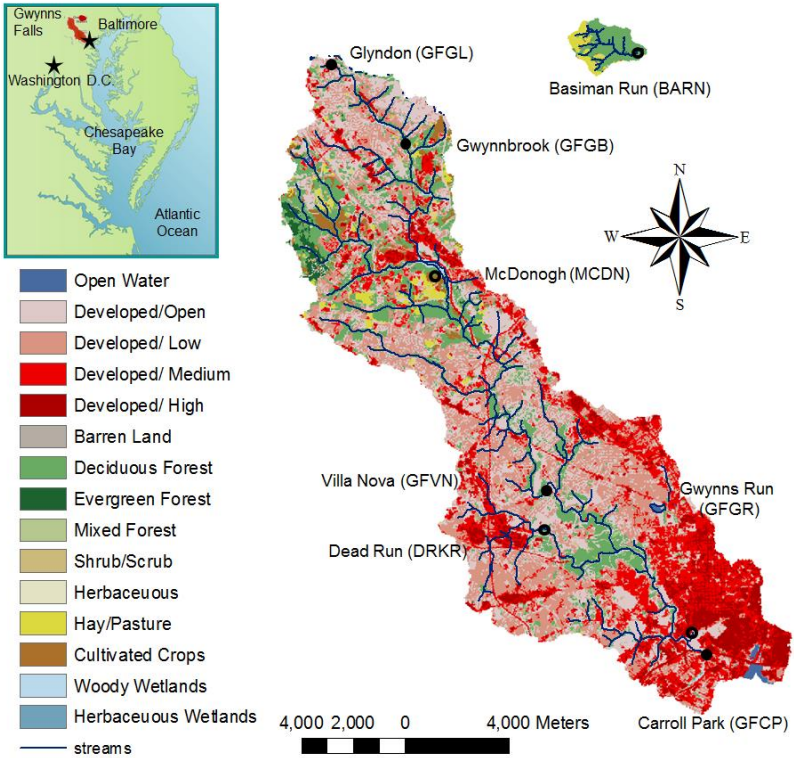

Figure 1. Land use of the Gwynns Falls and Baisman Run watersheds, showing sites from which sediment, soil and stream water were collected for salinization experiments. Baisman Run is a watershed with forest as the dominant land use, and it is located in the nearby Gunpowder River. Solid and open circles represent sites of the main stem and tributaries, respectively. Resolution of the land use data is 30 m, and land use and stream channel location data are from US Department of Agriculture (dtagateway.nrcs.usda.gove) and US Geological Survey (http://datagateway.nrcs.usda.gov/).

BGD
12, 7411–7448, 2015

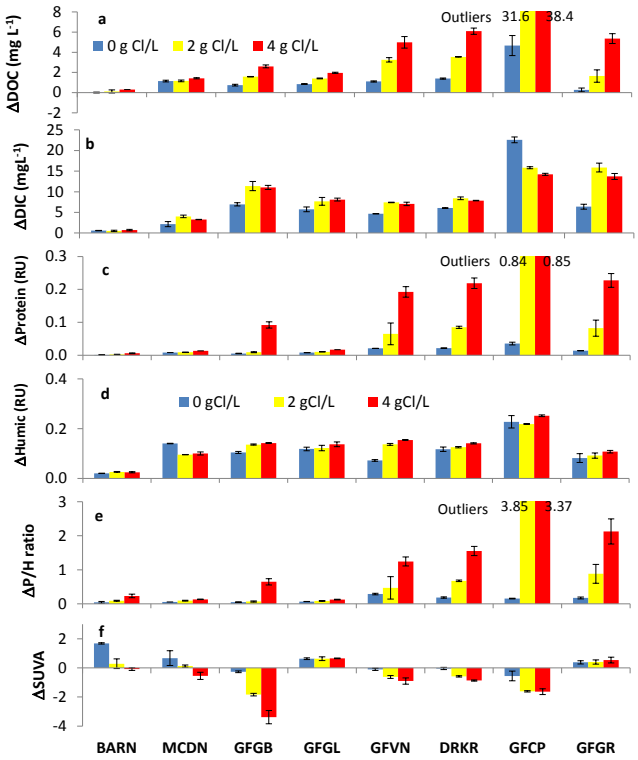

Figure 2. Changes in DOC, DIC, protein-like fluorophore, humic-like fluorophore, protein to humic (P/H) ratio and specific ultraviolet absorption (SUVA) during 2 day sediment incubations with NaCl-amended stream water (in 0, 2 and 4 g Cl L^{-1}). The changes in controls (stream water only) were subtracted to obtain the contributions from sediments. Errors bars stand for SDs of duplicate incubations, and positive and negative values referred to release and retention, respectively. Humic- and proten-like fluorescence is in Raman Unit (RU).

BGD
12, 7411–7448, 2015

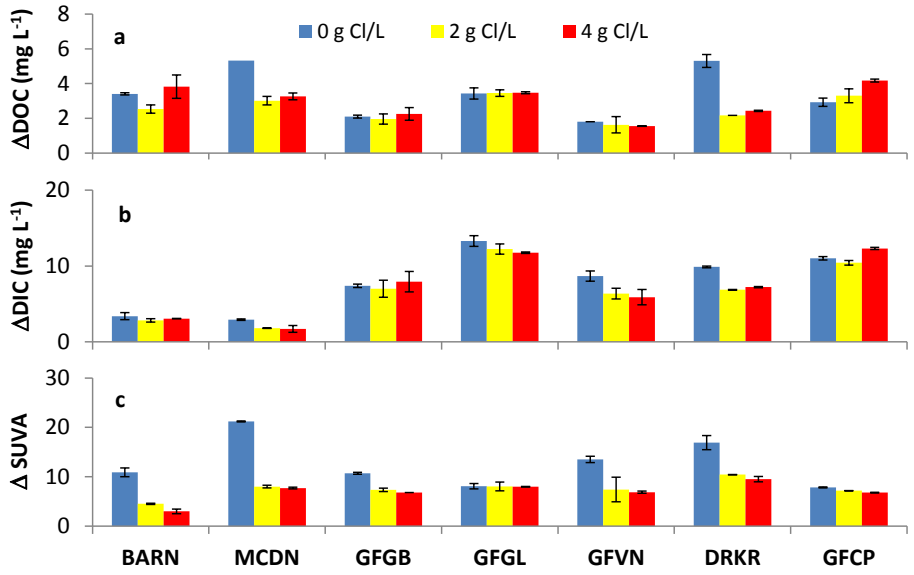

Figure 3. Releases of DOC and DIC and changes in specific UV absorption (SUVA) during 2 day soil incubations with NaCl-mended DI water (in 0, 2 and 4 g Cl L^{-1}). Errors bars stand for SDs of duplicate incubations.

BGD
12, 7411–7448, 2015

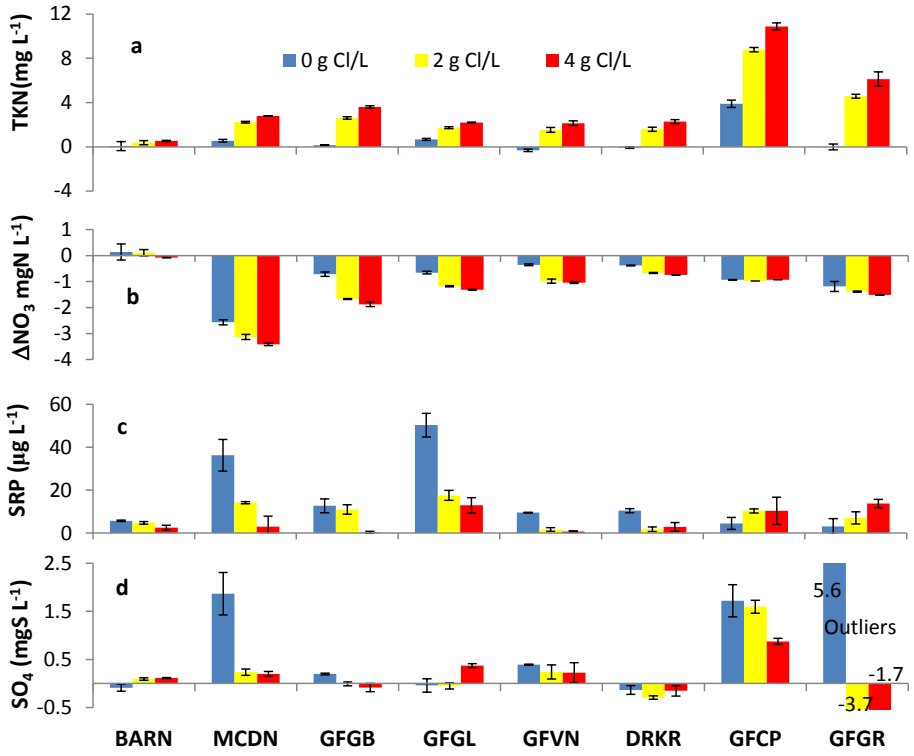

Figure 4. Changes in TKN (DON + NH_3-N + NH_4^+-N), nitrate-N, SRP and sulfate during 2 day sediment incubations with NaCl-amended stream water (in 0, 2 and 4 g Cl L^{-1}). The changes in controls (stream water only) were subtracted to obtain the contributions from sediments. Errors bars stand for SDs of duplicate incubations, and positive and negative values referred to release and retention, respectively.

BGD
12, 7411–7448, 2015

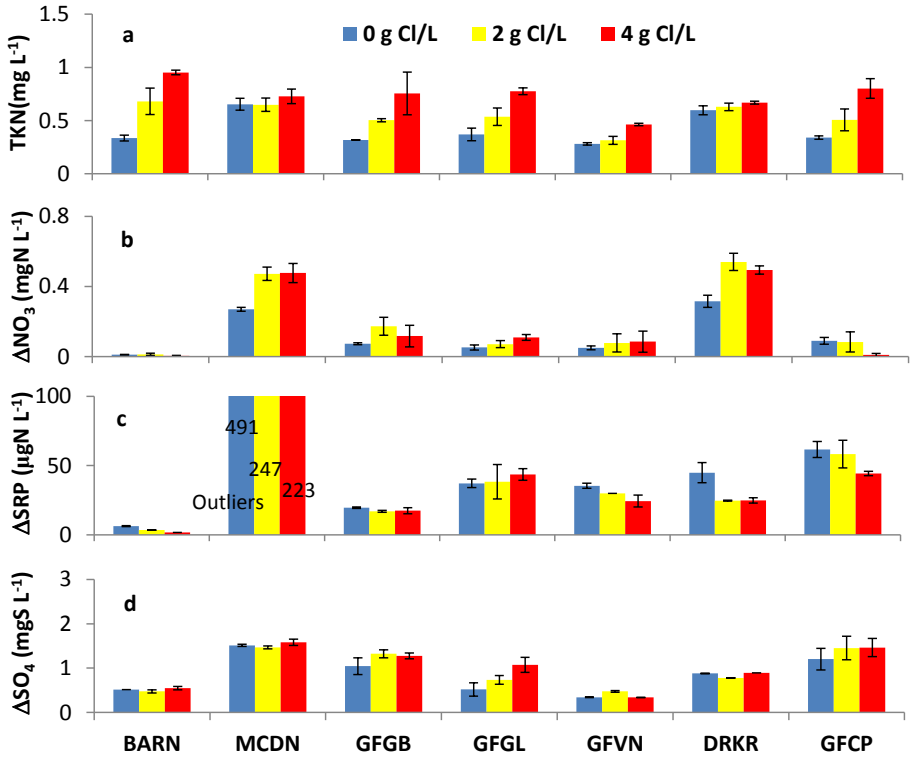

Figure 5. Release of TKN (DON + NH_3-N + NH_4^+-N), nitrate-N, SRP and sulfate in during 2 day soil incubations with NaCl-amended DI water (in 0, 2 and 4 g Cl L^{-1}). Errors bars stand for SDs of duplicate incubations.

BGD
12, 7411–7448, 2015

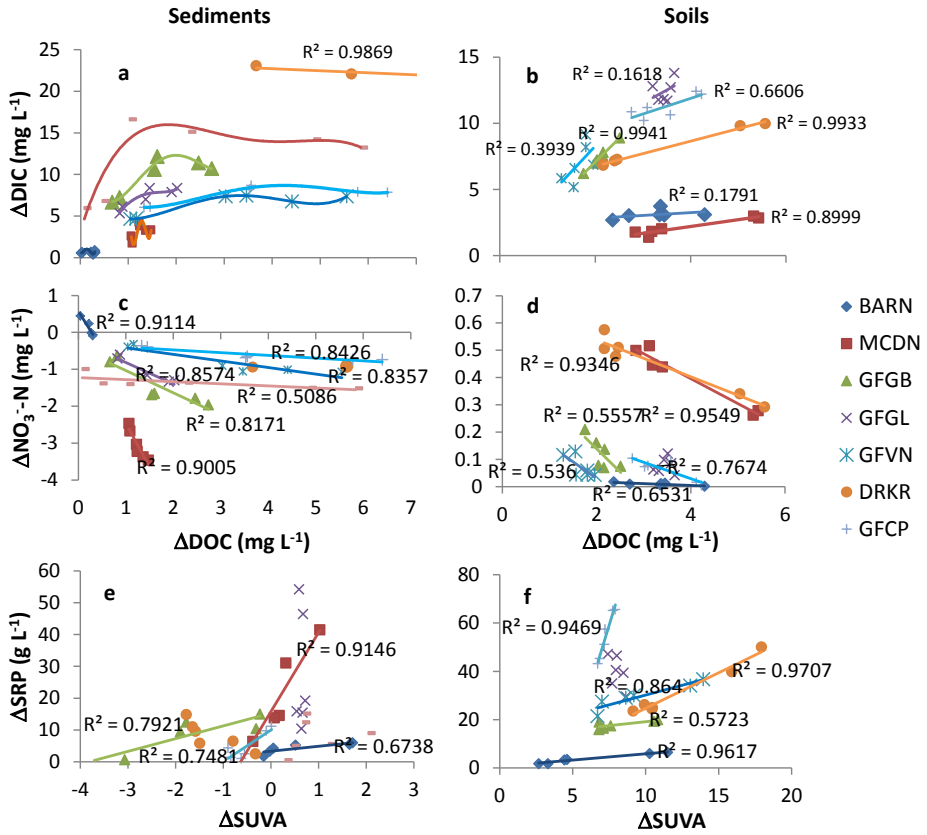

Figure 6. Correlations between changes in DIC or nitrate and changes in DOC, and between changes in SRP and changes in SUVA during the incubations of sediment and soils with NaCl-amended stream or DI water.

BGD
12, 7411–7448, 2015

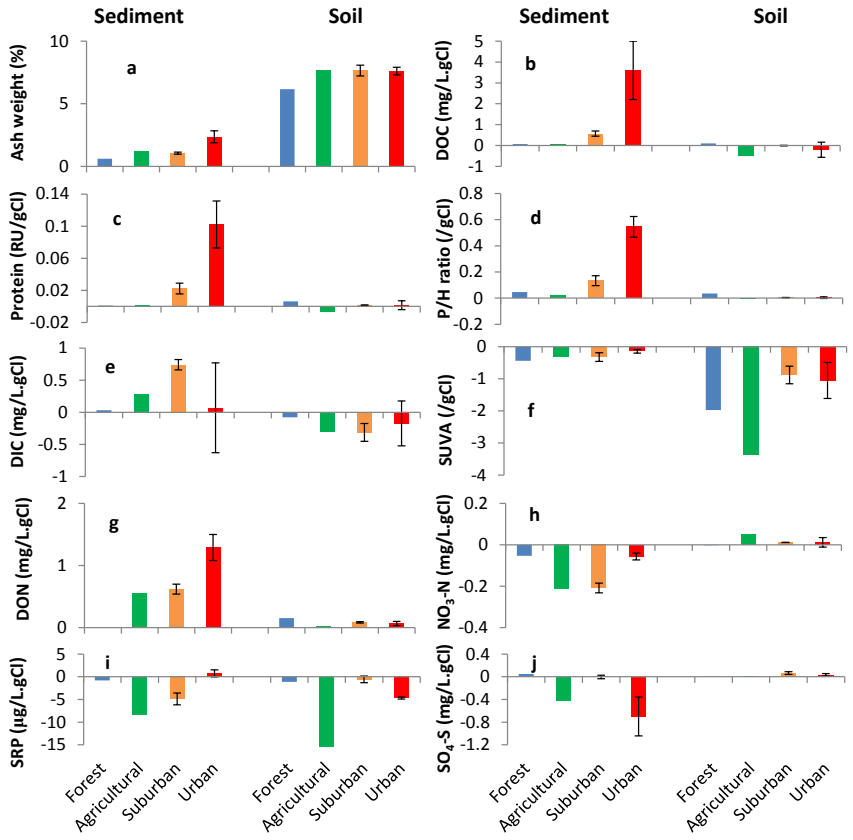

Figure 7. Ash-free dry weight, and salinity effects on DOC, protein-like fluorophore, P/H ratio, DIC, SUVA, TKN, nitrate, SRP and sulfate for sediment and riparian soils at the forested (1), agricultural (1), suburban (3) and urban (3) sites. Salinity effects were estimated from changes in these variables across three different salinities used for the incubations. Positive and negative values represented retention/release in their standardized fluxes (or increases/decreases in P/H ratio) per g of Cl^-.

BGD
12, 7411–7448, 2015

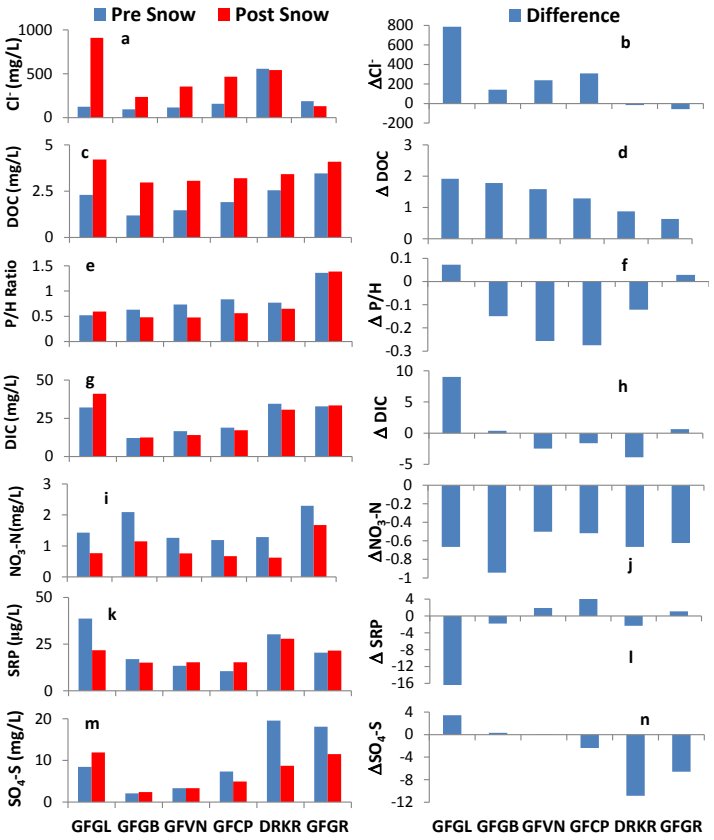

Figure 8. Concentrations of Cl^-, DOC, DOC P/H ratio, DIC, nitrate, SRP and sulfate and their changes in ambient stream water observed in the field before and 2 days after snow storm event.

BGD
12, 7411–7448, 2015

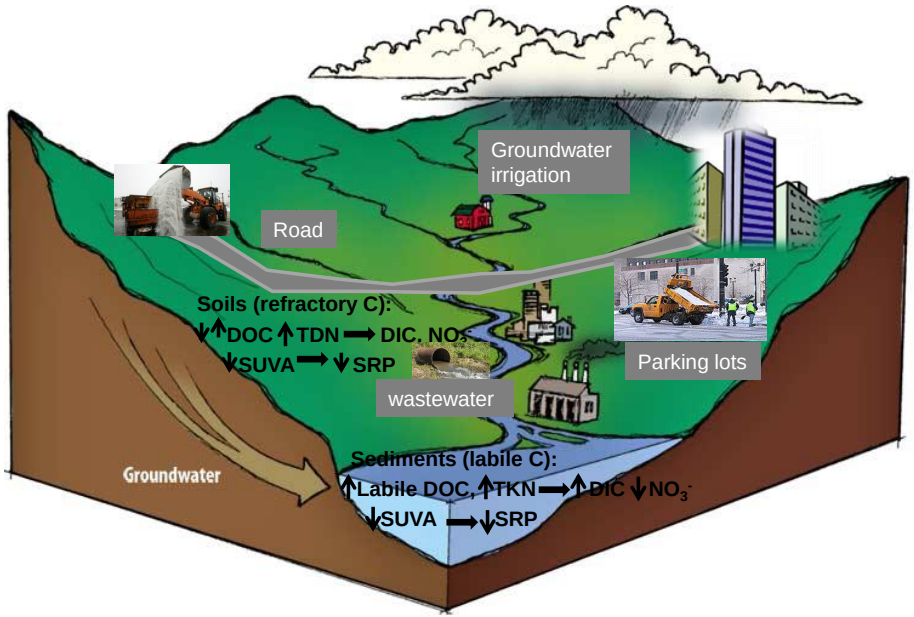

Figure 9. A conceptual diagram summarizing potential effects of salinization on DOC quality, DOC and TKN releases from sediments and soils, as well as linkage to release/retention of DIC, nitrate and SRP during sediment and soil salinization.

BGD
12, 7411–7448, 2015