# Salinization alters fluxes of bioreactive elements from stream ecosystems across land use

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## Abstract

There has been increased salinization of fresh water over decades due to the use of road salt deicers, wastewater discharges, saltwater intrusion, human-accelerated weathering, and groundwater irrigation. Salinization can mobilize bioreactive elements (carbon, nitrogen, phosphorus, sulfur) chemically *via* ion exchange and/or biologically *via* influencing of microbial activity. However, the effects of salinization on coupled biogeochemical cycles are still not well understood. We investigated potential impacts of increased salinization on fluxes of bioreactive elements from stream ecosystems (sediments and riparian soils) to overlying stream water and evaluated the implications of percent urban land use on salinization effects. Two-day incubations of sediments and soils with stream and deionized water across 3 salt levels were conducted at 8 routine monitoring stations across a land-use gradient at the Baltimore Ecosystem Study Long-Term Ecological Research (LTER) site in the Chesapeake Bay watershed. 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. Biogeochemical responses to salinization varied between sediments and riparian soils in releases of DOC and DIC, and nitrate transformations. The differential responses of riparian soils and sediments to increased salinization were likely due to differences in organic matter sources and composition. 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 in urban watersheds. Given that salinization of fresh water will increase in the future due to human activities, significant impacts on carbon and nutrient mobilization and water quality should be anticipated.

## 1 Introduction

Salt concentrations in freshwaters are rapidly increasing at a regional scale in the United States and worldwide (e.g., Nielsen et al., 2003; Kaushal et al., 2005; Rengasamy, 2006; Findlay and Kelly, 2011; Steele and Aitkenhead-Peterson, 2011; Kaushal et al., 2014a; 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, saltwater inundation caused by sea-level rise, and human-accelerated weathering (e.g., Findlay and Kelly, 2011; Aitkenhead-Peterson et al., 2009; Ardón et al., 2013; 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). Moreover, salinization is difficult if not impossible to reverse, thus, remediation is unlikely. Recent studies have further shown that increased salinization can influence biogeochemical cycles of bioreactive elements such as carbon and nitrogen (Green et al., 2008; Green and Cresser, 2008; Green et al., 2009a, b; Compton and Church, 2011; Lancaster, 2012; Steele and Aitkenhead-Peterson, 2013) as well as phosphorus and sulfur (Nielson et al., 2003; Kulp et al., 2007; Compton and Church, 2011; Kim and Koretsky, 2011, 2013). Chemically, salinization affects mobilization of these bioreactive elements through its direct influences on ion exchange and sorption capacity of sediments/soils (e.g., for ammonium and SRP), as well as *via* indirect effects due to changes in pH and sodium-induced dispersion (e.g., for DOC) (Nielsen et al., 2003; Green et al., 2008; Compton and Church, 2011; Ardón et al., 2013). Biologically, salinization can be a stressor to some microorganisms in fresh water but may also enhance the activities of other microorganisms due to nutrient releases (Kulp et al., 2007; Srividya et al., 2009; Kim and

Koretsky, 2011, 2013). Evidence is accumulating that increased salinization is an important process during the urban evolution of geochemical cycles in watersheds globally from decades to centuries (Kaushal et al., 2014a; Kaushal et al., 2015). Furthermore, 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, more work needs to be done regarding the effects of increased salinization on coupled biogeochemical cycles. Prior studies have commonly investigated the effects of salinization on fluxes and transformations of individual bioreactive elements (e.g., Green et al., 2008, 2009; Green and Cresser, 2008; Green et al., 2009a, b; Compton and Church, 2011; Kim and Koretsky, 2011; Lancaster, 2012; Steele and Aitkenhead-Peterson, 2011). However, biogeochemical cycles of bioreactive elements are generally linked in sedimentary diagenesis (Middelburg and Levin, 2009), and transformations of nitrogen, phosphorus and sulfur are highly dependent on availability of organic carbon (Duan and Kaushal, 2013). For example, organic carbon provides an energy source for microbes responsible for biogeochemical transformations (e.g., Newcomer et al., 2012), and decomposition of organic carbon can facilitate certain redox reactions of bioreactive elements including denitrification, iron reduction and release of soluble reactive phosphorus, and sulfate reduction (Sobczak et al., 2003; Middelburg and Levin, 2009). Regarding organic carbon, prior studies generally investigated the effects of salinization on bulk concentrations of dissolved organic carbon (DOC). However, DOC within aquatic systems consists of not a single compound but a broad suite of organic molecules of varied origin and composition, which may respond differently to salinization. Until recently, relatively little work has been done to improve our conceptual understanding of the effects of salinization on coupled biogeochemical cycles.

Previous studies have shown freshwater salt concentrations vary across land use, with highest concentrations of salt occurring in urban watersheds (e.g., Kaushal et al., 2005). Green et al. (e.g., 2008, 2009) reported that soils in urban watersheds that have already experienced exposure to road salting were less responsive to salinization in DOC release than unexposed soils in rural areas. On the other hand, urbanization may increase stream sediment organic matter (Duan and Kaushal, 2013) *via* algal and wastewater inputs (Daniel et al., 2002; Kaushal et al., 2014a), and influence other physical, chemical and biological characteristics of stream ecosystems (Paul and Meyer, 2001). Despite these two competing impacts of urbanization, biogeochemical impacts of salinization across watershed land use are still less recognized. Moreover, most current studies regarding the effects of salinization focus on soils or anaerobic lake sediments. Very little work has been done to examine stream sediments that may be exposed to high salt concentrations under more aerobic conditions. It is known that stream sediments and soils differ in particle size, structure, and organic matter composition and sources (e.g., Hedges and Oades, 1997). Thus, insights learned from studying the biogeochemical effects of salinization in soils may not always directly apply to stream sediments.

Our primary objective was to investigate the effects of increased salinization on potential fluxes (release or retention) of bioreactive elements (carbon, nitrogen, phosphorus, sulfur) from stream ecosystems, and how the effects of salinization change with watershed land use and/or stream substrates (sediments and riparian soils). Sediments and riparian soils collected from sites across a rural-urban land use gradient were incubated in salt solutions to mimic the effects of runoff with high levels of road salt deicers. Changes in water chemistry were monitored as a function of salt concentrations and land use. Three hypotheses were tested: 1) the effect of salinization on soil leaching and sediment retention/release of bioreactive elements change with watershed urbanization, 2) retention/release of nitrogen, phosphorus, and sulfur in response to salinization can be abiotically and/or biologically coupled with carbon biogeochemistry, and 3) salinization effects on release/transformation of bioreactive elements vary between stream sediments and riparian soils. We expected significant release of organic carbon and coupled transformations with nitrogen, phosphorus and sulfur as salinity increased.  Additionally, we expected experimental salinization increases biogeochemical fluxes with increasing watershed urbanization due to more carbon availability. 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 improve water quality by benefitting our assessment and management of salt use.

# 2 Methods

## 2.1 Site Description

Surface sediments from stream channels and top soil in riparian zones were collected from 8 long-term monitoring sites across a rural-urban land use gradient. All 8 sites are routinely sampled as part of the US National Science Foundation supported Baltimore Ecosystem Study (BES) Long-Term Ecological Research (LTER) site. Land use var~~y~~ies 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).

## 2.2 Sample Collection and Processing

Stream water, sediments, and soils for laboratory salinization experiments were collected on March 8, 2013, one day before a snow storm in the Baltimore-Washington D.C. metropolitan region. Three litres of stream water were collected at each of the 8 sites for the experiments and water quality analyses. The surface sediments and top soils (approximatly 15 cm) were collected at these same sites with a shovel. 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 composite soil sample was collected to represent these two sites. So, laboratory salinization experiments with soils were conducted at 7 rather than 8 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). The homogenized sediments and soils were sampled for determination of ash free dry weight (AFDW). In addition, approximately 100 mL aliquots of steam water were filtered through pre-combusted GF/F Whatman filters, and the filtrates were used for water quality analyses.  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 of dissolved organic carbon (DOC), nutrients, and major anions. The remainder of the stream water, sediments, and soils were temporarily stored at 2-4°C for 2 days prior to laboratory experiments.

## 2.3 Laboratory Salinization Experiments

For each laboratory salinization experiment, 60-g sub-samples of homogenised sieved sediments (< 2mm) 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 a pipette in order to not disturb the sediments. In order to evaluate the potential effects of salinization, pure NaCl salt (J.T.Baker) 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 $L^{-1}$). Molar concentrations of $Na^+$ were assumed to be the same as $Cl^-$ because pure NaCl was used. 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 per study site to account for analytical variability during laboratory salinization experiments. Simultaneously, streamwater samples without sediments were also incubated at the same 3 levels of salinization as sediment-free controls, in order to separate potential contributions of sediments *vs.* stream water. The laboratory salinization experiments were conducted in the dark in the lab with minor variations in temperature (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 of a stream. Deionized waters without soils were incubated at the 3 levels of salinization as soil-free controls. This experimental design 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 incubation waters were filtered through pre-combusted GF/F Whatman filters for water chemistry analyses.

## 2.4 Chemical Analyses

All filtrates were analyzed for major forms of bioreactive elements - nitrate, total dissolved nitrogen (TDN), soluble reactive phosphorus (SRP), sulfate, DOC, dissolved inorganic carbon (DIC), and optical properties of DOC (absorbance and fluorescence). DOC, TDN and DIC concentrations were measured on a Shimadzu Total Organic Carbon Analyzer (TOC-V CPH/CPN) (Duan and Kaushal 2013). Nitrate and sulfate concentrations were measured with a Dionex ion chromatograph (ICS-1500, Dionex INC., USA), with an eluent of 3.5 mM of $Na_2CO_3$ and 1.0 mM $NaHCO_3$ and a flow rate of 0.3 mL $min^{-1}$. Analyses of the water samples showed that $NO_3^-$-N/$NO_2^-$-N concentrations were almost entirely $NO_3^-$-N(> 99%), and we therefore referto this fraction as $NO_3^-$-N throughout thispaper. 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 composition and lability. Filtrates were scanned for absorbance from 200 nm 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 $^{13}C$ 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). A 1 cm quartz cuvette with slit widths set to 5 nm was used. 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.

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 hours (APHA 1998). Prior to combustion, sediments were dried at 105˚C for 4 hours to remove water. Ash free dry weights were determined in triplicates.

## 2.5 Data Analyses and Statistics

Sediment fluxes were calculated as the net changes in the concentrations of DOC, nitrate, SRP or sulfate during the two-day incubations. The values for nitrate and sulfate are presented as nitrate-N and sulfate-S. The changes in the control flasks (with water only), occurring in water without sediments or soils, were subtracted to obtain the fluxes that were released from sediments or soils. Positive or negative values represent net release from sediments or retention by sediments, respectively.

Effects of salinzation on sediment/soil biogeochemical fluxes were examined by performing linear regressions of these fluxes with salinity, using data from 6 salinization experimental manipulations (3 salinity levels with duplicates). If the $p$-value was $< 0.05$ for the regression, we assumed that there was a significant salinization effect. Otherwise, differences between two adjacent salinization levels were tested using a t-test of two-samples assuming equal variances. The slopes of above linear regressions with salinity, representing changes in biogeochemical fluxes per unit salinity, were regressed with watershed impervious surface cover (ISC) at the 8 study sites to examine changes in salinization effects across watershed urbanization. Differences in ash free dry weight, biogeochemical fluxes or salinization effect between sediments and soils were tested also using t-test of two-samples assuming equal variances. Meanwhile, relationships between sediment/soil fluxes of DOC (or SUVA and fluorescence indices representing DOC composition) and any of sediment/soil fluxes of DIC, TKN, nitrate, and sulfate were examined to test the coupling of nitrogen, phosphorus and sulfur with carbon biogeochemistry during salinization experiments. For linear relationships, Spearman's correlation was used in cases where assumptions of normality were not met. Data are reported in mean ± standard error.

# 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 concentrations 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 ($r^2 = 0.56$, $p < 0.05$, $n = 7$). AFDW of the riparian soils (6.17-8.84%) were considerably higher than the sediments ($p < 0.05$, t-test) but did not vary with watershed ISC (Table 2).

## 3.2 Influence of salinization on C fluxes and DOC composition across land use

Sediments were consistently a net source of both DOC and DIC. Net DOC releases from sediments consistently increased with increasing salinization (all positive slopes and statistically significant in 7 out of 8 cases; $r^2 = 0.64-0.99$, $p <0.05$) (Fig. 2), and DOC releases at 4 g Cl $L^{-1}$ were 7.8 ± 1.9 times (mean ± standard error, same below) higher than those at 0 g Cl $L^{-1}$. Salinization also increased the net releases of DIC (postive slope with one exception at GFCP), and the increases were at a statistically significant level at 6 out of 8 sites (Fig. 2). In contrast to DOC (which showed highest net releases at 4 g Cl $L^{-1}$), the highest net DIC releases at these sites occurred at 2 g Cl $L^{-1}$. The values at 2 g Cl $L^{-1}$ were generally higher than the values at 0 g Cl $L^{-1}$ ($p < 0.05$, t-test), although differences between 2 g Cl $L^{-1}$ and 4 g Cl $L^{-1}$ were not always significant. In addition, the highest DIC values were only 1.4 ± 0.02 times higher than those at 0 g Cl $L^{-1}$.

Moreover, the effects of salinization on sediment net releases differed among DOC fractions. Salinization consistently and considerably increased net releases of the protein-like fluorophore (all positive slopes; $r^2 = 0.77-0.95$, $p < 0.05$), showing considerable 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. 2). The effects of salinization on net humic-like fluorophore releases, however, were not consistent (showing both positive and negative slopes, and only 3 out of 8 cases showed a statistically significant level) and were much less (increased by 1.2 ± 0.1 times) (Fig. 2). As a result, salinization consistently and significantly (by 5.9 ± 0.7 times) increased (all positive slopes; $r^2 = 0.72-0.97$, $p < 0.05$) the protein to humic (P/H) ratio (Fig. 2) - 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 (6 out of 8 cases with negative slopes; $r^2 = 0.69-0.98$, $p < 0.05$; Fig. 2).

Effects of laboratory salinization on net DOC and DIC releases from soils were relatively more complex and not as consistent (both positive and negative slopes). As mentioned earlier, laboratory salinization experiments with soils were conducted only at 7 sites, because GFCP and GFGR are very close were considered as one site for soil experiments (same below). In 4 out of 7 cases, net DOC releases from soils decreased as experimental salinization increased from 0 g Cl $L^{-1}$ to 2 g Cl $L^{-1}$ ($p < 0.05$, t-test), followed by a slight increase as experimental salinization increased from 2 g Cl $L^{-1}$ to 4 gCl $L^{-1}$ (Fig. 3). The effects of laboratory salinization experiments on net DIC releases from soils were also complex (both positive and negative slopes), and 3 out of 7 cases showed decreasees with salinization ($r^2$ = 0.69-0.73, $p < 0.05$; Fig. 3). In spite of the complex effects of salinization on net releases of total DOC, salinization almost consistently decreased SUVA of leached DOC across all sites ($r^2$ = 0.72-0.96, $p < 0.05$ in 6 out of 7 cases) by a factor of 40 ± 4% (Fig. 3).

Effects of laboratory salinization experiments on biogeochemical carbon fluxes from sediments (indicated by changes in their standardized fluxes per g of $Cl^-$) exhibited clear patterns across the rural-urban gradient (Fig. 4). In general, the effects of salinization on sediment net releases of DOC, DIC and protein-like fluorophore, and DOC lability (indicated by P/H ratio) increased with ISC – an index for watershed urbanization ($r^2$ = 0.57-0.84, n= 7, $p < 0.05$; Fig. 4a-4d). The exception was the urban site GFCP with the highest ash free dry weight (Fig. 4f), showing unexpected large, positive salinization effects on net DOC releases, protein-like DOC releases and P/H ratio, but unexpected negative salinization effects on net DIC releases. No consistent urbanization influence was observed for SUVA (Fig. 4g) or the humic-like fluorophore (not shown). The effects of laboratory salinization on DOC and DIC leaching from soils were different from those observed in sediments, however. Effects of salinization on soil leaching were generally less than those on sediment retention/release (not shown). In addition, effects of salinization on soil leaching did not show considerable changes with increasing watershed ISC ($p > 0.05$).

## 3.3 Influence of salinization on fluxes of TKN, nitrate, SRP, and sulfate across land use

Sediments were generally a net source of TKN (ammonium + ammonia + dissolved organic nitrogen) and SRP but a net sink of nitrate during the salinization experiments (Fig. 5). Laboratory salinization experiments consistently and considerably increased net TKN releases from sediments ($r^2$ = 0.72-0.95, n = 6, $p < 0.05$; Fig. 5), and the net TKN releases at 4 g Cl $L^{-1}$ were 13.3 ± 5.1 times higher than at 0 g Cl $L^{-1}$. Meanwhile, salinization experiments consistently increased net nitrate retention (all negative fluxes) and the increases were significant at 6 out of 8 sites (except POBR and GFCP; $r^2$ = 0.73-0.91, n = 6, $p < 0.05$; Fig. 5). Net nitrate retention at 4 g Cl $L^{-1}$ was 1.6 ± 0.4 times higher than net nitrate retention at 0 g Cl $L^{-1}$. For SRP, 5 out of 8 sites (all forest, agricultural and suburban sites) showed that salinization experiments considerably decreased sediment net SRP releases (by 81 ± 7%; $r^2$ =

0.79-0.90, n = 6, $p < 0.05$; Fig. 5). However, two urban sites GFCP and GFGR showed salinization increased sediment net SRP releases by 1.3 to 3.5 times ($r^2$ = 0.71-0.81, n = 6, $p < 0.05$). Salinization effects on sulfate were even more complex, showing both postive and negative slopes. However, the agricultural site MCDN and 2 urban sites (GFCP and GFGR) showed strong decreases in sulfate fluxes (by 90 ± 23%; $r^2$ = 0.73-0.74, n = 6, $p < 0.05$, or $p < 0.05$, t-test) when the level of salinization increased from 0 g Cl $L^{-1}$ to 4 g Cl $L^{-1}$ (Fig. 5).

Similar to sediments, salinization consistently increased net TKN releases from soils and the increases were significant at 6 out of 7 sites ($r^2$ = 0.64-0.95, n = 6, $p < 0.05$; Fig. 6), and the values at 4 g Cl $L^{-1}$ increased by 93 ± 25% relative to 0 g Cl $L^{-1}$. Laboratory salinization increased nitrate releases at 4 out of 7 sites (Fig. 5), showing positive relationship between nitrate releases and salinity ($r^2$ = 0.71-0.76, n = 6, $p < 0.05$) or significantly higher nitrate releases at 2 g $Cl^{-1}$ than that at 0 g $Cl^{-1}$ ($p < 0.05$, t-test). The maximal net 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 $L^{-1}$. Similar to sediments, 6 out of 7 sites showed that experimental salinization suppressed net SRP releases from soils, 5 of which showed inverse relationship between SRP release and salinity ($r^2$ = 0.67-0.97, n = 6, $p < 0.05$; Fig. 6). Net SRP releases at 4 g Cl $L^{-1}$ decreased by 40 ± 9% relative to those at 0 g Cl $L^{-1}$. Similar to the sediments, the effects of salinization on net sulfate releases from soils were complex and inconsistent (Fig. 6).

Effects of laboratory salinization on sediment biogeochemical fluxes of TKN (indicated by changes in their standardized fluxes per g of $Cl^-$) also exhibited clear patterns across the rural-urban gradient. That is, the effects of salinization on sediment releases of TKN increased with ISC – an index for watershed urbanization ($r^2$ = 0.57, n = 7, $p < 0.05$), with one exception at site GFCP that showed highest ash free dry weight (Fig. 4e-4f). No consistent urbanization effects were observed for nitrate, SRP (Fig. 4h-4i) or sulfate (not shown). Furthermore, none of the salinization effects on leaching of TKN, nitrate, SRP or sulfate from soils showed significant correlations with watershed ISC ($p > 0.05$).

### 3.4 Biogeochemical coupling between the fluxes of chemical species

Correlation analyses suggested that there were links of the fluxes of the measured chemical species of bioreactive elements. Here, the term flux was used to mean net retention or net release of a chemical species based on site. For example, there was a correlation between net releases of DIC flux and net releases of DOC. Across soil laboratory salinization experiments, DIC net releases linearly increased with DOC releases, and the correlations were significant at 4 out of 7 sites ($r^2 = 0.66$-$0.99$, $p < 0.05$, $n = 6$; Table 3). Across laboratory salinization experiments with sediments, sites showing linear increase in DIC net releases with DOC was less - 3 out of 8 ($r^2 = 0.70$-$0.99$, $p < 0.05$, $n = 6$; Table 3). Different from DIC, net releases of TKN were all positively correlated with net releases of DOC fluxes in salinization experiments using sediments across the 8 sites ($r^2 = 0.71$-$0.93$, $p < 0.05$, $n = 6$; Table 3). In general, there was no significant relationship (one exception) between net releases TKN and net releases of DOC across soil laboratory salinization experiments (Table 3).

There was an inverse relationship between nitrate fluxes (release in soils or retention in sediments) and DOC fluxes from sediments and soils. Specifically, nitrate fluxes linearly decreased with increasing DOC fluxes from sediments and soils, and the increases were statistically sigificant at 6 of 8 sites for sediment incubation experiments and at 4 out of 7 sites for soil leaching experiemnts ($r^2 = 0.66$-$0.99$, $p < 0.05$, $n = 6$; Table 3). A fourth correlation was between net SRP releases and changes in SUVA of DOC. There were positive correlations between net SRP releases and changes in SUVA values during both sediment incubations and soil leaching. Significant correlations were observed in 6 out of 8 cases during sediment incubations ($r^2 = 0.67$-$0.91$, $p < 0.05$, $n = 6$; Table 3). Five out of 7 sites showed this positive relationship during soil leaching ($r^2 = 0.86$-$0.97$, $p < 0.05$, $n = 6$; Table 3).

# 4 Discussion

## 4.1 Changes in salinization effects with watershed urbanization

Our study shows that the effects of salinization on retention and release of bioreactive elements in sediments changes with watershed urbanization. Thus, Hypothesis 1 regarding changes in salinization effects with watershed urbanization was partially supported by the data from sediment incubation experiments. Overall, our results suggest that the effects of increased salinization on sediment releases of DOC, protein-like fluorophore, TKN and DIC increased with impervious surface cover (ISC) – an index for watershed urbanization (Fig. 4; linear regressions, all $p < 0.05$). These results seem to contradict previous results of soil salinization experiments. Those previous experiments suggest that soils that have already experienced higher degrees of exposure to road salting (e.g., in urban watersheds) respond less to salinization than controls (like in forest watersheds) regarding organic matter mobilisation (e.g., Green et al., 2008, 2009). The reason is that “once the organic matter has been solubilized and/or mineralised under the influence of road salt, and thereafter leached, it is gone from the system”. However, the results from our lab experiments were different from those of Green et al. (2008, 2009) probably for two reasons. First, stream sediments were used in our laboratory experiments and not just soils, and the response of stream sediments to salinization might be somewhat different (potential mechanisms discussed later). Second, the degree of watershed urbanization may not exactly correspond to the degree of exposure to road salt. For example, the highest streamwater $Cl^-$ concentrations in this study were not observed at the GFGR site with highest ISC but at DRKR with a smaller ISC value (Table 2). Thus, our results suggest that urbanization impacts biogeochemical responses to salinization (i.e, the net release and retention of chemicals), but it may not always be related to the degree of watershed impervious surface cover.

Instead, the interactive effects of watershed urbanization and salinization on sediment releases of DOC, protein-like fluorophore, TKN and DIC fluxes may be explained by coinciding changes in stream sediment organic matter content (indicated by ash free dry weight), which also showed an increase with increasing watershed ISC (Table 2 and Fig. 4f). The outlier site GFCP, which had unexpected larger salinization effects, was also highest in sediment ash free dry weight. The reason for the outlier GFCP is not clear, but a much better correlation between sediment ash free dry weight and watershed ISC was reported in our previous study at the same Baltimore LTER sites (Duan and Kaushal et al., 2013). In any case, organic matter content in urban stream sediments was generally higher than in rural streams (also reported in Sloane-Richey et al. 1981; Paul and Meyer, 2001), probably due to additional organic matter inputs from algal (Kaushal et al. 2014b) and anthropogenic sources (e.g., wastewater; Daniel et al., 2002). Our recent work showed that gross primary production and organic matter lability increased with watershed urbanization (Kaushal et al., 2014b). 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 matter increase across the rural-urban land use gradient, we hypothesize that the releases of labile DOC (indicated by protein-like fluorophore), total DOC, TKN and DIC increase in response to salinization.

### 4.2 Potential effects of increased salinization on DOC/DIC mobilization coupled with carbon biogeochemistry

This study suggests that mechanisms responsible for salinization effects on DOC mobilization differ between soils and sediments, as we proposed in Hypothesis 3. Previous studies have shown contrasting 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 concept (pH suppression vs. sodium dispersion) can be used here to interpret the inconsistent effects of salinization on DOC retention/release from riparian soils across sites or across salinities in this study (Fig. 3). However, neither this concept nor the flocculation/microbial-suppression mechanism can explain the consistent observation of enhanced DOC mobilization from sediments in our laboratory salinization experiments (Fig. 2). As we hypothesized, differences in DOC mobilization between soils *vs.* stream sediments may have been primarily due to diffferences in DOC composition and sources.

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 considerably 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 (or labile) fractions. Similar findings were also reported by Li et al. (2013), which showed that KCl can considerably 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 (Daniel et al. 2002; Kaushal et al., 2011; Kaushal and Belt, 2012; Newcomer et al., 2012; Duan et al., 2014b; Kaushal 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 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; Li et al., 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 (Fig. 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 our study, although humic substances were not measured, much higher SUVA values were observed in DOC leached from soils (around 10 $\mathrm{Lmg^{-1}\ m^{-1}}$) than from sediments (< 2 $\mathrm{L\ mg^{-1}\ m^{-1}}$). This suggested that soils were higher in humic substances. Because of large differences in organic matter composition, we speculate that the effects of salinization on DOC leaching from sediments and soils were different (Fig. 2 and 3).

Our laboratory experiments suggests that simultaneous net releases of DIC and DOC were examples of coupled biogeochemical cycles in response to salinization, as predicted in Hypothesis 2. The effects of salinization on DIC fluxes from sediments and soils may involve shifts in carbonate chemistry (e.g., dissolution of carbonate minerals), or organic carbon mineralization and $CO_2$ efflux that are coupled with DOC biogeochemistry. The effects of salinization on carbonate chenistry seems like a less important control in this study, becausee the solubility of carbonate minerals increases with salinization (Akin and Lagerwerff, 1965) while DIC releases from sediment or soils in our laboratory salinization experiments did not always follow this trend (Fig. 2 and 3). In our study region, crystalline rocks of igneous or metamorphic origin characterize the surface geology and there are almost no carbonate rocks (http://www.mgs.md.gov/esic/geo/bal.html). 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 (Table 3). The coupling of DIC with organic carbon mineralization seemed to fit better for soils, considering the strong linear relationship between DIC and DOC across soil salinization experiments (Table 3). The complex relationships between DOC and DIC for sediment incubations (Table 3) indicated the importance of other potential controls as well - likely, efflux of $CO_2$, the product of mineralization of labile protein-like DOC released from sediments. It is known that the solubility coefficient for $CO_2$ decreases with salinity (Weiss et al., 1974; Duan and Sun, 2003). We hypothesize that $CO_2$ efflux to the atmosphere may become a dominant control on DIC release at higher salinities (e.g., 2 - 4 g Cl $L^{-1}$), and further increases in salinization may decrease net DIC release despite increased release of DOC (Fig. 2b).

## 4.3 Potential effects of salinization on N, P, and S transformation coupled with C biogeochemistry

We observed consistent mobilization of TKN (e.g., $NH_4^+$ and DON) in response to salinization in both sediments and soils (Fig. 5-6), and the mobilization of TKN was coupled with DOC release in sediments but not coupled in soils (Table 3). These observations support Hypothesis 2 and 3. Mobilization of $NH_4^+$ has been observed in several previous studies (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). Several previous studies have also shown DON leaching from plant litter or soils along with DOC upon increased salinization (Steele and Aitkenhead-Peterson, 2013; Green et al., 2008, 2009; Compton and Church, 2011). In this study, despite similarities between enhanced TKN release in response to increased salinization of sediments and soils, there were much stronger relationships between TKN and DOC during sediment incubation experiments than with soil leaching experiments (Table 3). The decoupling of TKN mobilization and DOC during soil leaching suggests that TKN mobilization was largely attributed to mobilization of inorganic $NH_4^+$, due to $Na^+$ dispersion. The coupling of TKN with DOC during sediment incubations, however, indicates that TKN release could be associated with mobilization of dissolved organic nitrogen (DON). This was consistent with far more release of nitrogen-enriched protein-like dissolved organic matter or DON from sediments than from soils (0.11 ± 0.01 RU vs 0.033 ± 0.004 RU).

Our results further suggest that nitrate transformation and DOC remobilization were also coupled during salinization experiments with both sediments and soils, which supports Hypothesis 2. In contrast to DOC, DON, or $NH_4^+$, 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 in soils, salinity can decrease the rates of both nitrification and denitrification 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 from positive to no effects, as a combined result of availability of ammonium and nitrate removal *via* denitrification (Duckworth and Cresser, 1991; Green and Cresser, 2008b; Compton and Church, 2011). Our results from soils suggested positive effects of salinization at some sites (Fig. 6), probably due to nitrification of released TKN (including ammonium; e.g., Compton and Church, 2011). For sediments, we found that laboratory salinization experiments consistently increased nitrate retention, however, although there was increasing release of TKN with higher salinity (Fig. 5). These salinization effects in sediments may be related to the remobilization of labile DOC in sediments, based on the consistent inverse relationship between nitrate and DOC (Table 3).

That is, although salinization may directly influence denitrification rates of in-stream sediments (Hale and Groffman, 2006), it may also cause mobilization of considerable amounts of protein-like dissolved organic matter into streams (Fig. 2). 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 actually enhance nitrate retention in stream sediments (Fig. 4). However, the effects of increased salinization on DON and ammonium mobilization warrant further research.

Our results suggest that SRP release from sediments or soils during laboratory salinization experiments was associated with changes in DOC aromaticity (indicated by SUVA), supporting Hypothesis 2. Different from N, 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 SRP per unit mass is about 5,000 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 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 (Fig. 5 and 6) and a coupling between SRP and SUVA (Table 3). However, biological controls such as temporary inhibition of microbial activity at higher salinities could provide an alternative explanation (Srividya et al., 2009). An explanation for the increased releases of SRP from sediments at higher salinities at two urban sites (GFGR and GFCP) is not clear. Probably, these SRP increases was related to the release of large amounts of labile DOC and resulting changes in redox condition favorable for SRP release. In summary, decreases in SRP fluxes from sediments and soils in response to salinization were likely a result of colloid coagulation and microbial inhibition at higher salinities, while the increases in SRP fluxes from sediments at urban sites warrant further evaluation within the context of redox changes.

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 large variability in the effects of salinization on net sulfate release from either sediments or soils (Fig. 5 and 6), and sulfate reduction seems to not be dominant in free-flowing streams. Effects of increased salinization on sulfate releases warrant further investigation in future studies, however.

## 5 Conclusions

The potential effects of salinization on biogeochemical fluxes from soils and stream sediments are summarized in Fig. 7. As shown in this figure, releases of labile DOC (thus total DOC) and TKN (primarily DON and ammonium) 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 (primarily DON and ammonium) 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 TKN (DON and ammonium) 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 suggests 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 couple them together as a whole.

## Acknowledgements

This research was supported by NSF Awards EAR 1521224, DBI 0640300, CBET 1058502, EAR-1426844 and DEB-0423476, NASA grant NNX11AM28G, and Maryland Sea Grant Awards SA7528085-U and R/WS-2.

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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) of 2006. Both land cover and impervious statistics were based on 30-m resolution land cover data.

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

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

- : samples were not taken. Legends DOC, P/H, DIC, SUVA, SRP and AFDW stand for dissolved organic carbon, protein to humic ratio of DOC, dissolved inorganic carbon, specific ultraviolent absorption, soluble reactive phosphorus and ash-free weight.

Table 3. Correlations between ΔDIC, ΔTKN or Δnitrate and ΔDOC, and between ΔSRP and ΔSUVA during the sediment/soil salinization incubations with NaCl-amendments. The data with significant correlations ($p < 0.05$) are in bold font.

|  | DIC vs DOC |  | TKN vs DOC |  | $NO_3$ vs DOC |  | SRP vs SUVA |  |
|---|---|---|---|---|---|---|---|---|
|  | $r^2$ | *p* | $r^2$ | *p* | $r^2$ | *p* | $r^2$ | *p* |
| Sediments |  |  |  |  |  |  |  |  |
| BARN | 0.04 | 0.71 | **0.89** | **0.00** | **0.90** | **0.00** | **0.67** | **0.05** |
| MCDN | 0.25 | 0.31 | **0.75** | **0.02** | **0.90** | **0.00** | **0.91** | **0.00** |
| GFGB | 0.58 | 0.08 | **0.89** | **0.00** | **0.82** | **0.01** | **0.79** | **0.02** |
| GFGL | **0.78** | **0.02** | **0.93** | **0.00** | **0.86** | **0.01** | 0.01 | 0.87 |
| GFVN | **0.70** | **0.04** | **0.94** | **0.00** | **0.84** | **0.01** | **0.85** | **0.01** |
| DRKR | 0.47 | 0.13 | **0.93** | **0.00** | 0.00 | 0.95 | **0.75** | **0.03** |
| GFCP | **0.99** | **0.00** | **0.98** | **0.00** | **0.99** | **0.00** | **0.70** | **0.04** |
| GFGR | 0.25 | 0.31 | **0.71** | **0.03** | **0.74** | **0.03** | 0.05 | 0.68 |
| Soils |  |  |  |  |  |  |  |  |
| BARN | 0.18 | 0.40 | 0.04 | 0.71 | **0.65** | **0.05** | **0.96** | **0.00** |
| MCDN | **0.90** | **0.00** | 0.06 | 0.64 | **0.95** | **0.00** | **0.96** | **0.00** |
| GFGB | **0.99** | **0.00** | 0.30 | 0.26 | 0.56 | 0.09 | 0.57 | 0.08 |
| GFGL | 0.16 | 0.43 | 0.10 | 0.55 | 0.01 | 0.86 | 0.38 | 0.20 |
| GFVN | 0.39 | 0.18 | 0.05 | 0.68 | 0.54 | 0.10 | **0.86** | **0.01** |
| DRKR | **0.99** | **0.00** | 0.36 | 0.21 | **0.93** | **0.00** | **0.97** | **0.00** |
| GFCP | **0.66** | **0.05** | **0.91** | **0.00** | **0.77** | **0.02** | **0.95** | **0.00** |

Legends DIC, DOC, TKN, SRP and SUVA stand for dissolved inorganic carbon, dissolved organic carbon, total Kjeldahl nitrogen, soluble reactive phosphorus and specific ultraviolent absorption.

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/).

Figure 2. Changes in DOC, DIC, protein-like fluorophore, humic-like fluorophore, protein to humic (P/H) ratio and specific ultraviolet absorption (SUVA) with salinization ($Cl^-$) for sediment incubations with NaCl-amended stream water. Changes in stream water only (controls) were subtracted to obtain the contributions from sediments. A linear regression line was added (6 experiment with 3 NaCl levels) only if the regression was significant. For the panel without significant correlation, * was used to indicate significant difference between two adjacent salinization treatments. Humic- and proten-like fluorescence is in Raman Unit (RU).

Figure 3. Releases of DOC and DIC and changes in specific UV absorption (SUVA) with salinization ($Cl^-$) for soil incubations with NaCl-mended DI water. A linear regression line was added only if the regression was significant. For the panel without significant correlation, * was used to indicate significant difference between two adjacent salinization treatments.

Figure 4. Changes in salinity effects on DOC, DIC, protein-like fluorophore, P/H ratio, SUVA, TKN, nitrate and SRP for sediment incubations, as well as ash-free dry weight (AFDW) with watershed impervious surface cover (ISC). A outlier (urban site GFCP) was identified in sediment incubation for DOC, DIC, protein-like fluorophore, P/H ratio, and TKN and sediment AFDW. A regression line was added to the data only if the correlation with ISC was significant ($p < 0.05$), and the outlier was not counted in the regression.

Figure 5. Changes in TKN (DON + $NH_3$-N + $NH_4^+$-N), nitrate-N, SRP and sulfate with salinization ($Cl^-$) for sediment incubations with NaCl-amended stream water. The changes in stream water only were subtracted to obtain the contributions from sediments. A linear regression line was added only if the regression was significant. For the panel without significant correlation, * was used to indicate significant difference between two adjacent salinization treatments.

Figure 6. Release of TKN (DON + $NH_3$-N + $NH_4^+$-N), nitrate-N, SRP and sulfate with salinization ($Cl^-$) for soil incubations with NaCl-amended DI water. A linear regression line was added only if the regression was significant. For the panel without significant correlation, * was used to indicate significant difference between two adjacent salinization treatments. The scale of x axil of SRP for MCDN was different from other sites.

Figure 7. 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.

**Figure 1**

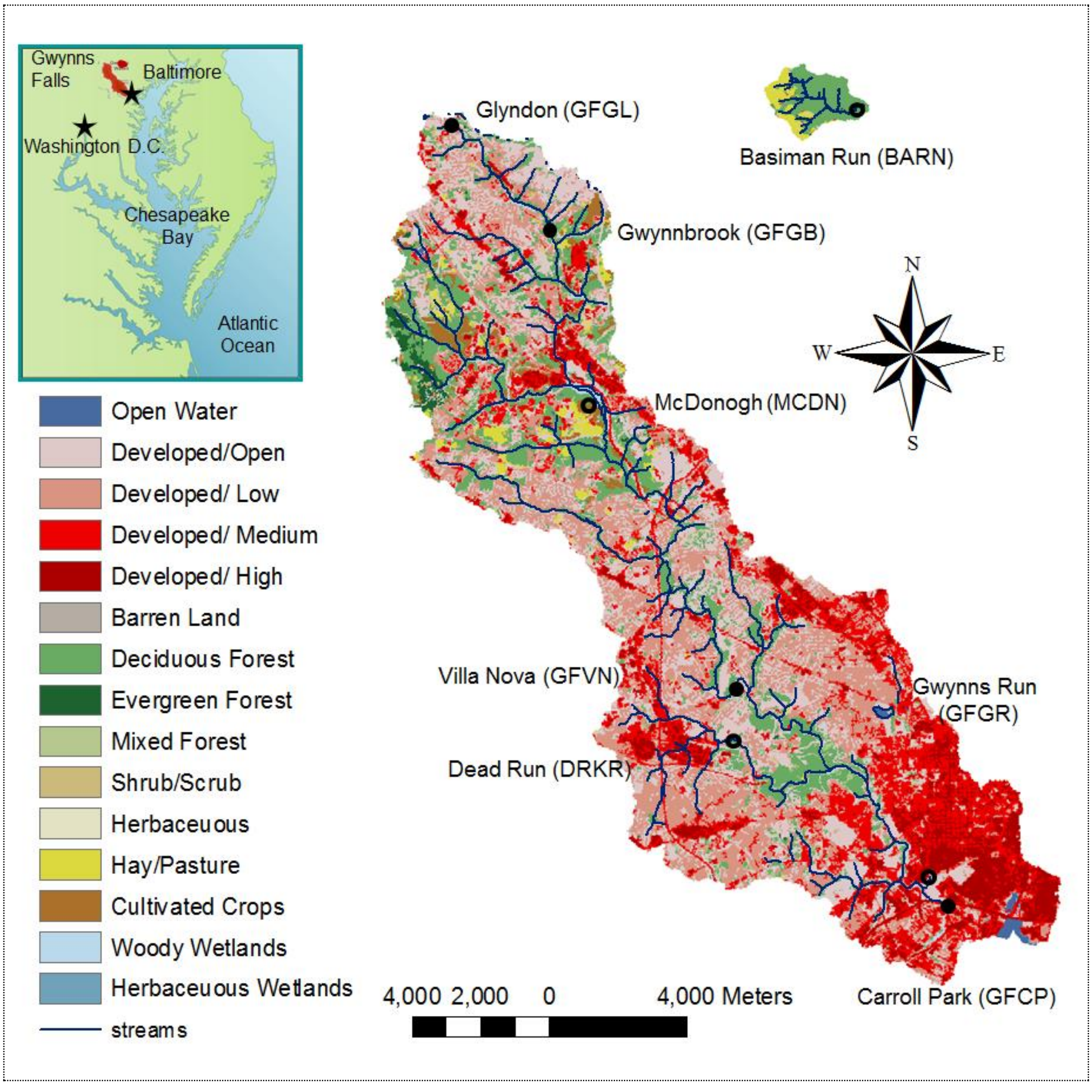

Gwynns Falls
Baltimore
Washington D.C.
Chesapeake Bay
Atlantic Ocean
Open Water
Developed/Open
Developed/ Low
Developed/ Medium
Developed/ High
Barren Land
Deciduous Forest
Evergreen Forest
Mixed Forest
Shrub/Scrub
Herbaceuous
Hay/Pasture
Cultivated Crops
Woody Wetlands
Herbaceuous Wetlands
streams
Glyndon (GFGL)
Basiman Run (BARN)
Gwynnbrook (GFGB)
N
W
E
S
McDonogh (MCDN)
Villa Nova (GFVN)
Gwynns Run (GFGR)
Dead Run (DRKR)
4,000 2,000 0 4,000 Meters
Carroll Park (GFCP)

**Figure 2**

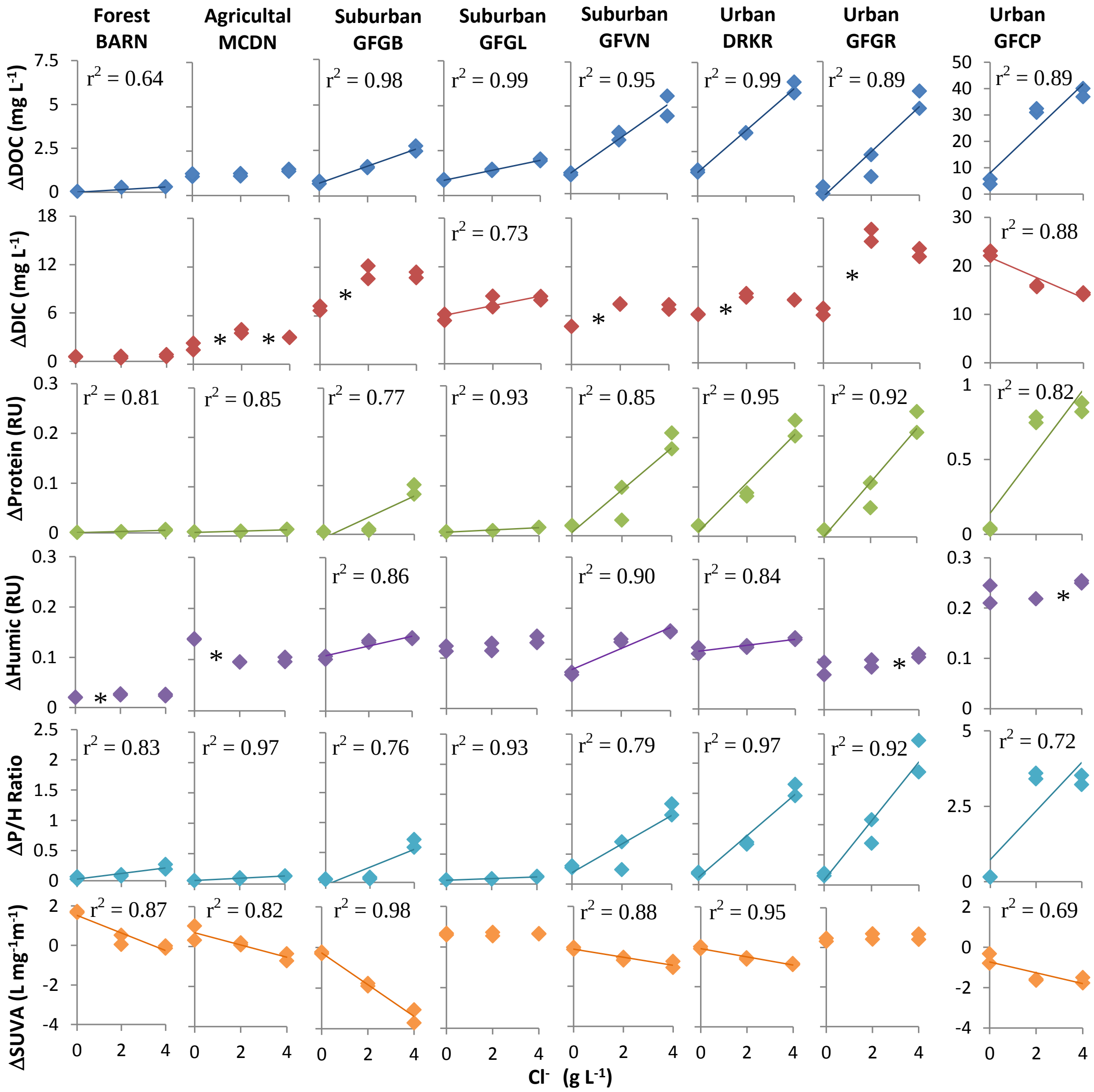

Forest BARN
Agricultal MCDN
Suburban GFGB
Suburban GFGL
Suburban GFVN
Urban DRKR
Urban GFGR
Urban GFCP
ΔDOC (mg L-1)
ΔDIC (mg L-1)
ΔProtein (RU)
ΔHumic (RU)
ΔP/H Ratio
ΔSUVA (L mg-1m-1)
Cl- (g L-1)
0
2
4
7.5
5
2.5
18
12
6
0.3
0.2
0.1
2.5
2
1.5
1
0.5
-2
-4
50
40
30
20
10
1
0.5
5
r2 = 0.64
r2 = 0.98
r2 = 0.99
r2 = 0.95
r2 = 0.99
r2 = 0.89
r2 = 0.89
r2 = 0.73
r2 = 0.88
r2 = 0.81
r2 = 0.85
r2 = 0.77
r2 = 0.93
r2 = 0.85
r2 = 0.95
r2 = 0.92
r2 = 0.82
r2 = 0.86
r2 = 0.90
r2 = 0.84
r2 = 0.83
r2 = 0.97
r2 = 0.76
r2 = 0.93
r2 = 0.79
r2 = 0.97
r2 = 0.92
r2 = 0.72
r2 = 0.87
r2 = 0.82
r2 = 0.98
r2 = 0.88
r2 = 0.95
r2 = 0.69
*

**Figure 3**

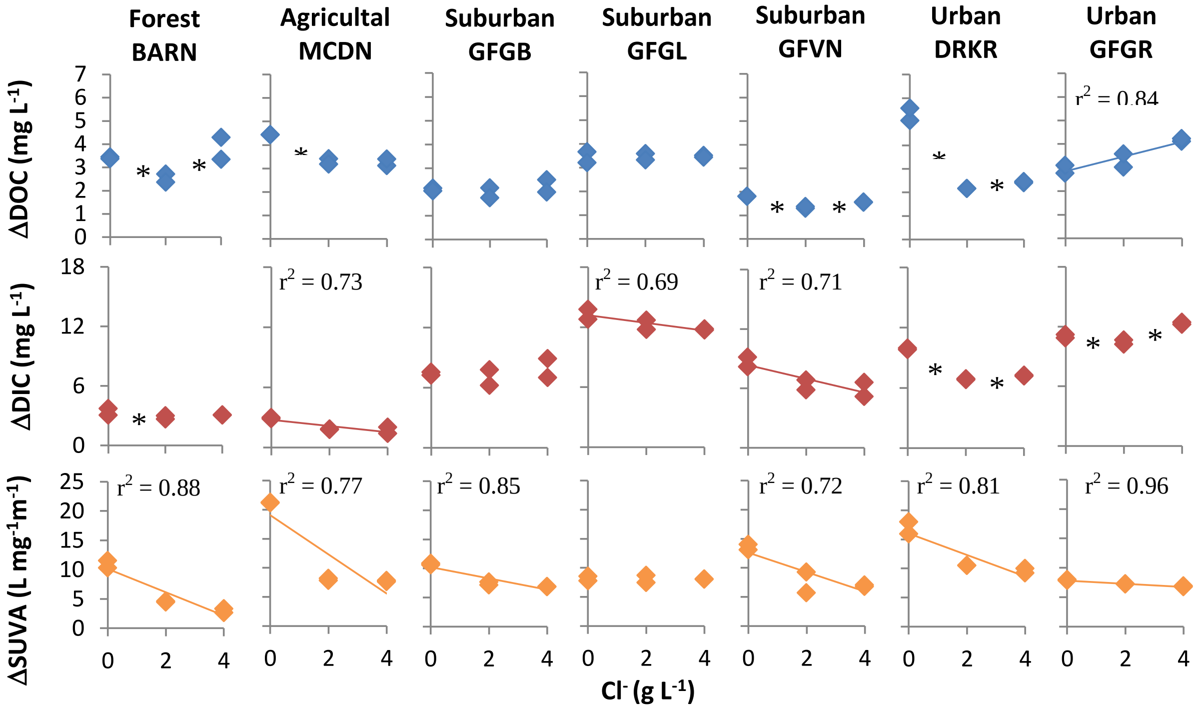

Forest BARN
Agricultal MCDN
Suburban GFGB
Suburban GFGL
Suburban GFVN
Urban DRKR
Urban GFGR
ΔDOC (mg L-1)
ΔDIC (mg L-1)
ΔSUVA (L mg-1m-1)
Cl- (g L-1)
0
1
2
3
4
5
6
7
0
6
12
18
0
5
10
15
20
25
0
2
4
*
r2 = 0.84
r2 = 0.73
r2 = 0.69
r2 = 0.71
r2 = 0.88
r2 = 0.77
r2 = 0.85
r2 = 0.72
r2 = 0.81
r2 = 0.96

**Figure 4**

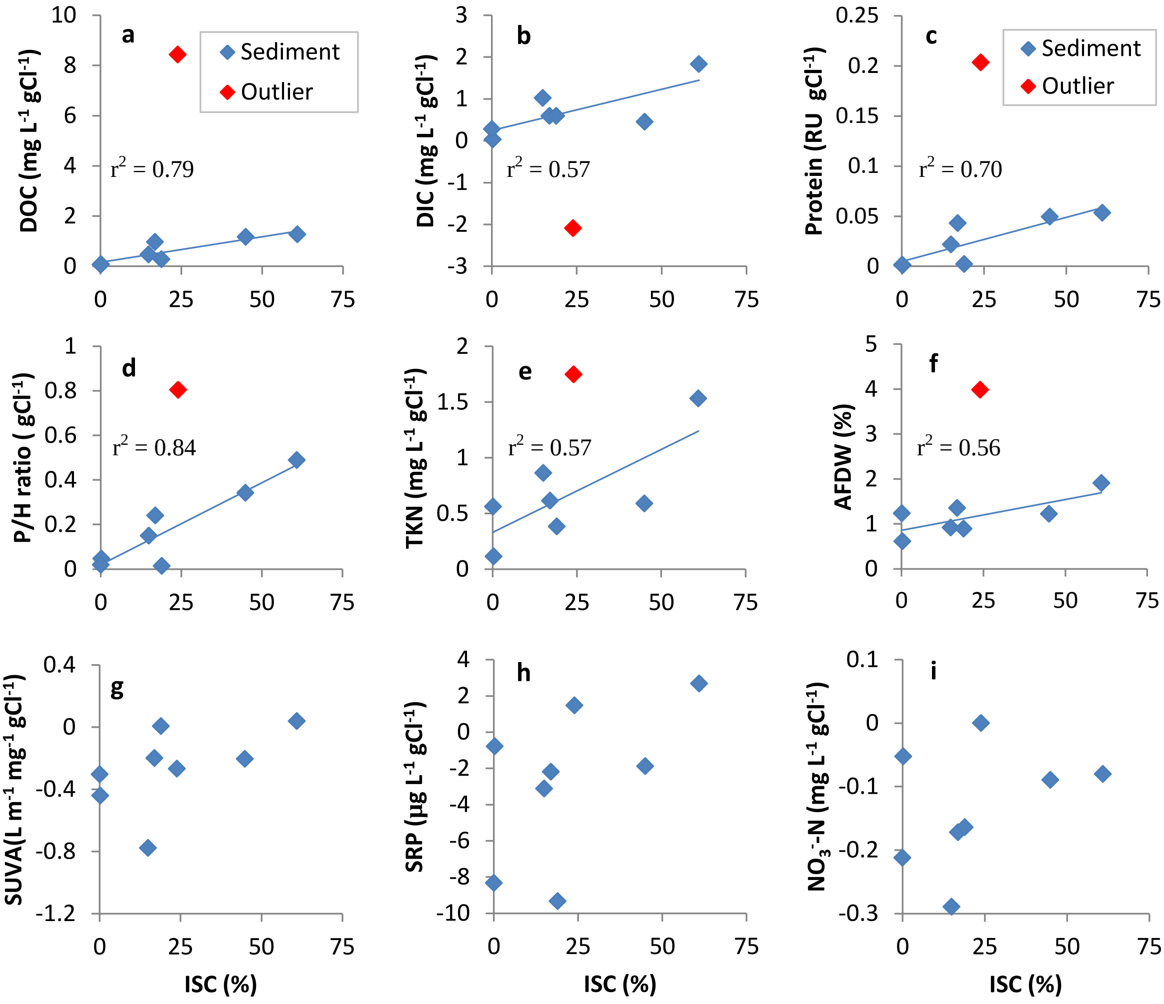

a
Sediment
Outlier
r² = 0.79
DOC (mg L⁻¹ gCl⁻¹)
10
8
6
4
2
0
0
25
50
75
b
r² = 0.57
DIC (mg L⁻¹ gCl⁻¹)
3
2
1
0
-1
-2
-3
c
Sediment
Outlier
r² = 0.70
Protein (RU gCl⁻¹)
0.25
0.2
0.15
0.1
0.05
0
d
r² = 0.84
P/H ratio ( gCl⁻¹)
1
0.8
0.6
0.4
0.2
0
e
r² = 0.57
TKN (mg L⁻¹ gCl⁻¹)
2
1.5
1
0.5
0
f
r² = 0.56
AFDW (%)
5
4
3
2
1
0
g
SUVA(L m⁻¹ mg⁻¹ gCl⁻¹)
0.4
0
-0.4
-0.8
-1.2
h
SRP (µg L⁻¹ gCl⁻¹)
4
2
0
-2
-4
-6
-8
-10
i
NO₃⁻-N (mg L⁻¹ gCl⁻¹)
0.1
0
-0.1
-0.2
-0.3
ISC (%)
ISC (%)
ISC (%)

**Figure 5**

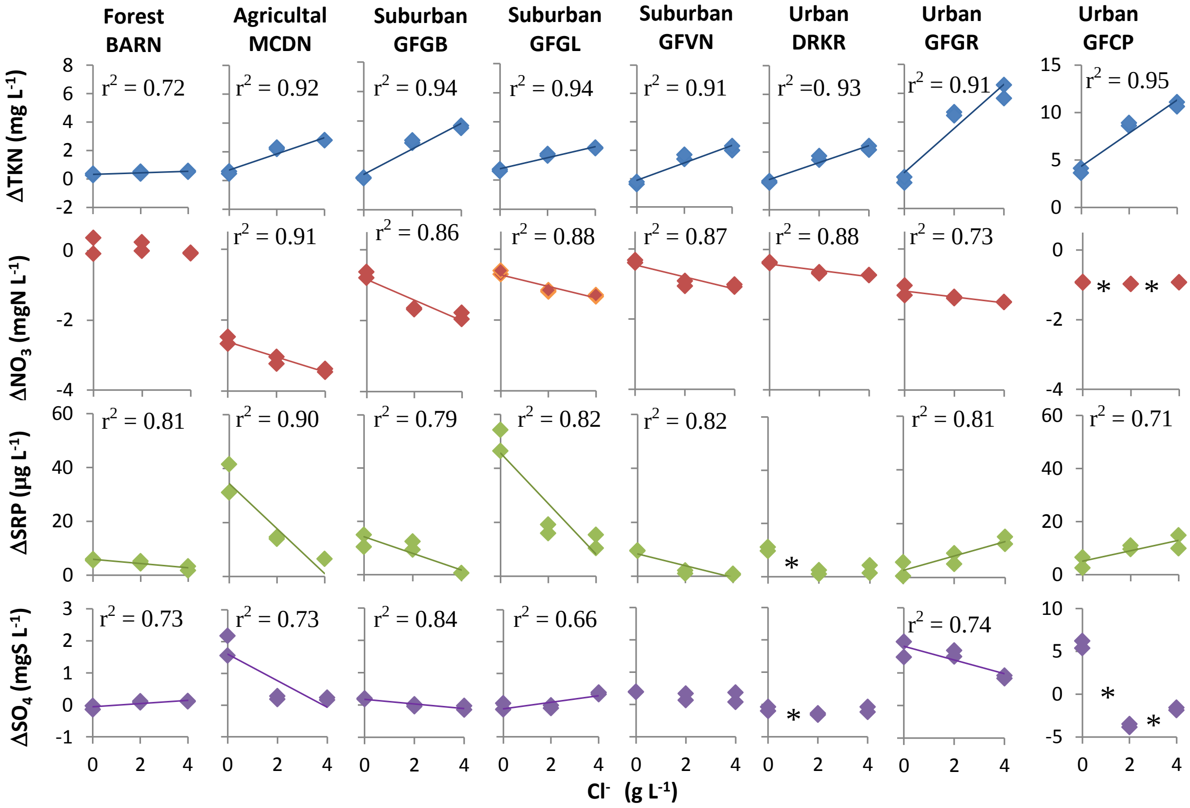

Forest BARN
Agricultal MCDN
Suburban GFGB
Suburban GFGL
Suburban GFVN
Urban DRKR
Urban GFGR
Urban GFCP
ΔTKN (mg L-1)
ΔNO3 (mgN L-1)
ΔSRP (µg L-1)
ΔSO4 (mgS L-1)
r2 = 0.72
r2 = 0.92
r2 = 0.94
r2 = 0.94
r2 = 0.91
r2 =0. 93
r2 = 0.91
r2 = 0.95
r2 = 0.91
r2 = 0.86
r2 = 0.88
r2 = 0.87
r2 = 0.88
r2 = 0.73
r2 = 0.81
r2 = 0.90
r2 = 0.79
r2 = 0.82
r2 = 0.82
r2 = 0.81
r2 = 0.71
r2 = 0.73
r2 = 0.73
r2 = 0.84
r2 = 0.66
r2 = 0.74
*
8
6
4
2
0
-2
15
10
5
0
-2
-4
60
40
20
3
1
-1
-5
0 2 4
Cl- (g L-1)

**Figure 6**

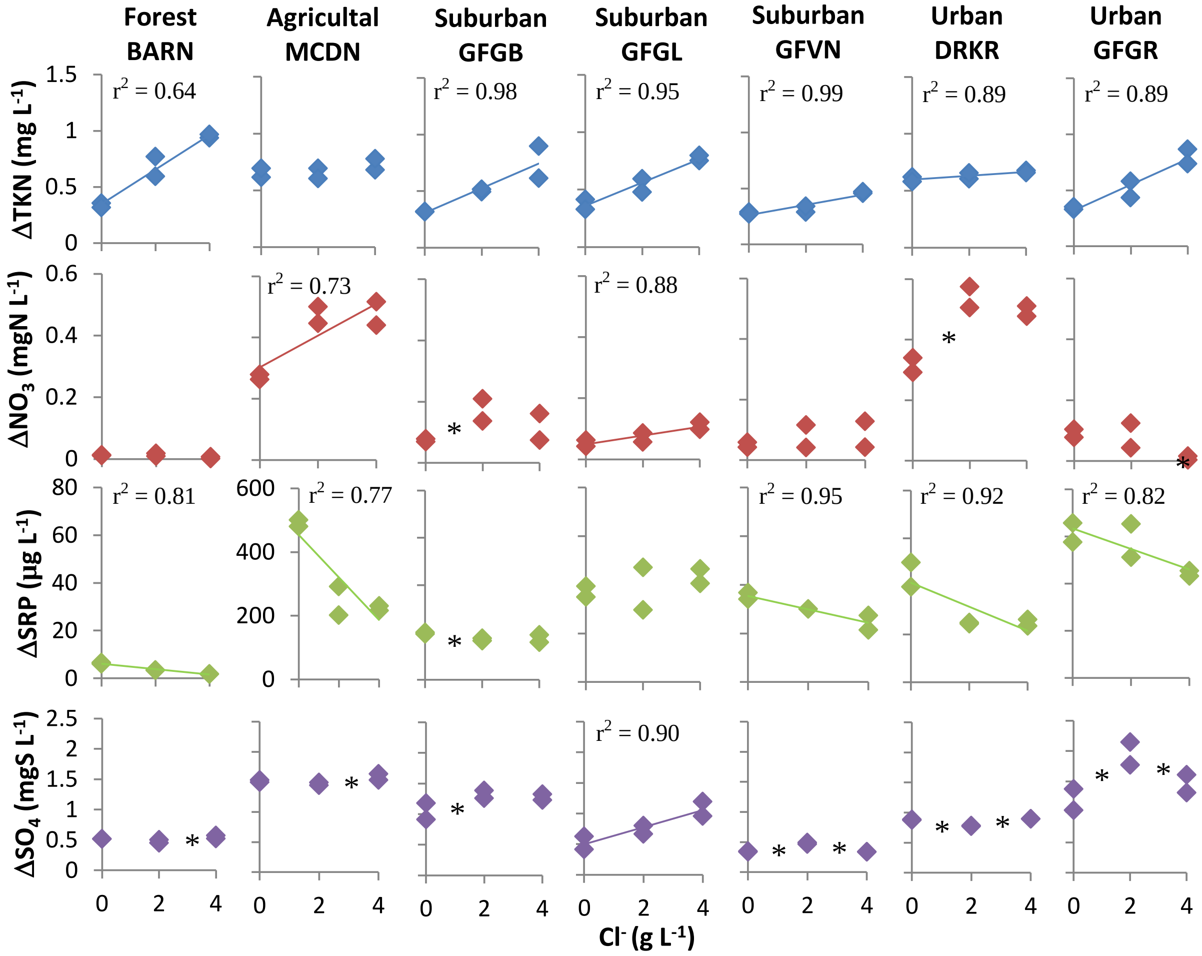
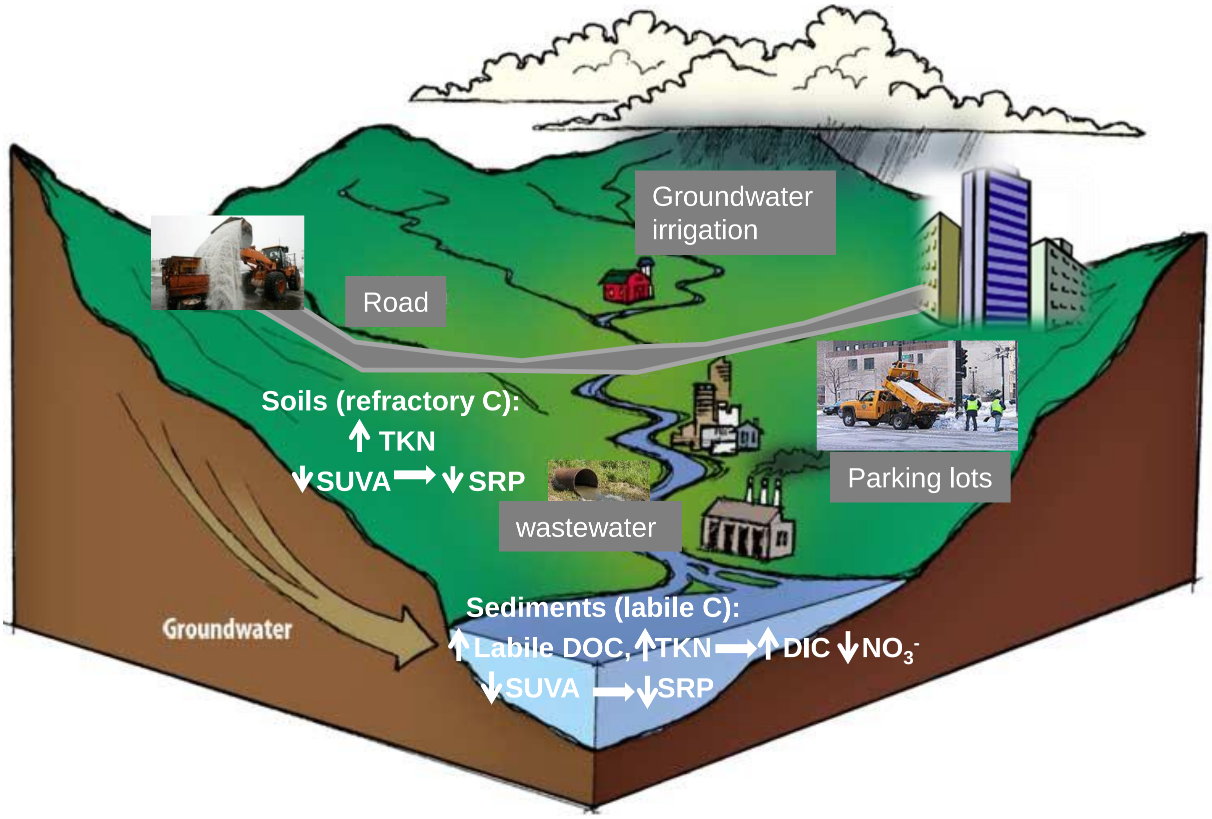

Forest BARN
Agricultal MCDN
Suburban GFGB
Suburban GFGL
Suburban GFVN
Urban DRKR
Urban GFGR
ΔTKN (mg L-1)
ΔNO3 (mgN L-1)
ΔSRP (µg L-1)
ΔSO4 (mgS L-1)
Cl- (g L-1)
r2 = 0.64
r2 = 0.98
r2 = 0.95
r2 = 0.99
r2 = 0.89
r2 = 0.89
r2 = 0.73
r2 = 0.88
r2 = 0.81
r2 = 0.77
r2 = 0.95
r2 = 0.92
r2 = 0.82
r2 = 0.90
*
1.5
1
0.5
0
0.6
0.4
0.2
0
80
60
40
20
0
600
400
200
0
2.5
2
1.5
1
0.5
0
0
2
4

**Figure 7**


Groundwater irrigation
Road
Soils (refractory C):
↑ TKN
↓SUVA ⟶ ↓ SRP
wastewater
Parking lots
Sediments (labile C):
↑Labile DOC, ↑TKN ⟶ ↑DIC ↓$NO_3^-$
↓SUVA ⟶ ↓SRP
Groundwater