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ABSTRACT

Stormwater control measures (SCMs) are designed to mitigate the deleterious impacts of urban runoff on the water quality of receiving waters. To assess the cumulative effects of SCMs at the watershed scale, we monitored longitudinal changes in storm discharge and stream water chemistry at high temporal resolution in a suburban headwater stream in Charlotte, NC. SCMs significantly decreased or stabilized instream concentrations of reactive solutes (nitrate, soluble reactive phosphorus, and dissolved organic carbon) relative to the upstream control site. However, SCM outflows minimally influenced concentrations of less reactive solutes (major ions) which increased with urbanization. Additionally, instream concentration variability correlated with antecedent moisture conditions – representative of watershed storage availability – highlighting the role that SCM storage availability plays in the timing of solute delivery to the stream. Our results show that SCMs decrease instream concentrations of biogeochemically reactive solutes but the mitigation potential is temporally dynamic and influenced by antecedent conditions.

Introduction

Urban runoff has been identified as a significant cause of water quality impairment and degraded ecosystem function in receiving waters (e.g. Klein 1979; Meyer, Paul, and Taulbee 2005; O'Driscoll et al. 2010). In particular, excess reactive nitrogen (N) and phosphorus (P) from urban land uses contribute to eutrophication of rivers, lakes, and coastal estuaries (Carpenter et al. 1998; Howarth et al. 2000). Elevated instream concentrations of other anthropogenic pollutants, such as major ions, can be toxic to aquatic food webs (Clements and Kotalik 2016). Macroinvertebrate community structure is a function of salinity (Kefford 1998; Timpano et al. 2018); increased salinity causes stark declines in richness and abundance of sensitive taxa such as mayflies (Timpano et al. 2018). In particular, increased magnesium and sulfate concentrations correlate with a decrease in macroinvertebrate community metabolism (Clements and Kotalik 2016).

Conventional stormwater infrastructure quickly conveys runoff directly to receiving waters with little to no treatment. Such practices cause increased discharge volume and intensity, and increased pollutant concentrations and loads in urban streams compared to pre-development conditions. These changes, and their ecological consequences, are collectively referred to as the 'urban stream syndrome' (Walsh et al. 2005). However, urban watersheds can also be transformative ecosystems that retain some of the hydrological, geochemical, and ecological properties of undeveloped watersheds (Utz et al. 2016), such as N retention (Groffman et al. 2004; Kaushal et al. 2011).

Extensive research has suggested that limiting the impervious area directly connected to the stream by artificial drainage is key to restoring hydrological and ecological regimes to predevelopment conditions (e.g. Lee and Heaney 2003; Hatt et al. 2004; Taylor et al. 2004; Burns et al. 2015). Hydrologic buffers are defined as landscape features that moderate hydrologic connectivity between the terrestrial landscape and the stream by storing runoff and promoting water and solute losses through processes such as evapotranspiration and denitrification. Buffering capacity is the extent to which water is retained in storage zones or subsurface pathways (Herron and Wilson 2001). High buffering capacity occurs when greater fractions of runoff are redirected to slow flowpaths, and low buffering capacity occurs when runoff delivery is slowed but runoff volume is unaffected. Without a biogeochemically active buffer of urban runoff, we often see ecological degradation with increasing urbanization (Comings, Booth, and Horner 2000), and increased solute concentrations with increasing urbanization (e.g. Brett et al. 2005; Hatt et al. 2004; Smucker et al. 2016; Tu et al. 2007; Campo, Flanagan, and Robinson 2003; De Jesús-Crespo and Ramírez 2011).

Stormwater control measures (SCMs) such as constructed ponds, wetlands, and rain gardens are designed to increase the buffering capacity in urban landscapes by restoring some elements of the natural flow regime (Burns et al. 2012). In the watershed in this study, SCMs were shown to redistribute stormflows to baseflow periods (Jefferson et al. 2015). SCMs mitigate flashiness of urban hydrological regimes as they are

designed to intercept, store, and slowly release stormwater runoff to the stream (Bell et al. 2016). In turn, hydrologic regimes can influence solute regimes by altering the timing and delivery of essential nutrients to the stream (Harms and Grimm 2010), and the potential for stream bed scouring – which affects plant and microbial ability to assimilate nutrients (Rivers et al. 2018). However, the coupled response of instream water quality to watershed-scale implementation of SCMs is seldom evidenced. We monitored stream discharge and water quality at high temporal resolution (0.5–1.5 hour intervals) in a SCM-mitigated watershed to capture the rapid water quality response to hydrological events and characterize the role of SCMs in this response.

Nitrogen and phosphorus retention and load reduction have been observed in individual SCM monitoring studies (Collins et al. 2010) and small-scale drainage areas (i.e. sampling of inlet and outlet runoff from street-scale watersheds) (Dietz and Clausen 2008; Line and White 2016). However, at larger scales, solute retention is variable and dependent on contaminant type (Pennino, Mcdonald, and Jaffe 2016), urban form (Bell et al. 2017), and mitigation level (Bell et al. 2017; Pennino, Mcdonald, and Jaffe 2016). Observed high variability of instream water quality response to SCMs is likely due to regional confounding influences (Jefferson et al. 2017), such as spatial heterogeneity in fertilizer application across urban and suburban landscapes (Zhou, Troy, and Grove 2008), leaky urban infrastructure (Kaushal et al. 2011), and legacy pollutants from historical land use (Basu et al. 2010). We evaluated water quality changes across nested sites to minimize these potentially confounding factors.

While much of the research on urban stream water quality has focused on N and P, major ions such as magnesium and calcium are also affected by urbanization and stormwater management. Elevated base ion concentrations are observed in urbanized watersheds compared to their forested counterparts (Siver et al. 1996; Rose 2002), and concentrations of anions and cations tend to increase with impervious surface cover (Kaushal et al. 2017; Moore et al. 2017). The positive correlation between imperviousness and major ion concentrations is increasingly associated with the dissolution of concrete (Conway 2007; Kaushal et al. 2017; Tippler et al. 2014; Davies et al. 2010), however studies often include confounding factors that contribute to major ion concentration such as wastewater effluent, road salt applications, and bedrock weathering in carbonate lithology (Kaushal et al. 2013). Additionally, many studies report the positive relationship between urbanization and major ion concentrations during baseflow, but the trends during stormflows are indeterminate. Our study design isolated the effects of imperviousness and stormwater mitigation on major ion concentration during stormflow by observing changes in concentration across nested sites overlying uniform lithology and lacking both significant point sources of these ions and carbonate minerals.

Our study tests whether SCMs add significant buffering capacity to decrease the impacts of urbanization on solute concentration and transport dynamics at the watershed scale. We address the following questions: (1) Do increases in SCM-mitigated area decrease instream solute concentrations relative to an upstream control reach? (2) How does runoff storage in SCMs affect instream concentration variability? To answer these questions, we collected storm discharge and solute concentrations along a longitudinal gradient of SCM treatment in a small suburban watershed. Monitoring nested sites eliminates confounding influences of heterogeneity (e.g. soils, land use, and climate) on water quality which are problematic in comparisons of geographically separated watersheds.

Materials and methods

Site description

We sampled a series of nested sites in Beaverdam Creek, a watershed in southwest Charlotte, North Carolina, USA. Site locations were placed immediately downstream of confluences between the stream and SCM outlets (Figure 1). Development within the watershed is primarily suburban residential with separated stormwater sewers and multiple roadways. There are no identified point sources to the stream. There is extensive riparian forest throughout the watershed, and the middle reaches are dominated by mixed hardwood forests. Underlying lithology is granodiorite and gabbro (Goldsmith, Milton, and Horton 1988), and soils are fine sandy loams with low pH (USDA-NRCS 2010).

Water quality and flow monitoring sites were established at four locations – SCM-A, SP-1, SP-2, and SP-3 – and we compared these to our upstream control site, SP-US (Figure 1). The upstream control has the lowest percentage of impervious area and highest fraction of forested landcover compared to the downstream sites (Table 1). Most runoff from additional impervious surfaces draining towards the upstream site is directed towards the large forested riparian buffer present in the middle reaches which dampens the influence of impervious area at this monitoring site. SCMs include two wet ponds (SCM-A and D), a wetland (SCM-B), and a bioretention cell (SCM-C). SP-1 is immediately downstream of SCM-A, which collects runoff from residential housing. SP-2 captures the drainage area upstream of SCM-B in addition to that of SP-1, and SP-3 captures the drainage area of the entire watershed, including outflow from SCM-C and SCM-D (Figure 1). As watershed area increases, proportion of the watershed treated by SCMs increases from 8.7% to 19.6% (Table 1).

Monitoring and data collection

We collected hydrological and water quality data for 8 storms during 2013. Precipitation data were obtained from USGS gauge (#350842080572801) CRN-21, located 2 km southwest of the study sites (Figure 1). We monitored stream stage every 10 minutes at SP-1, SP-2 and SP-3 from January to December 2013 using Solinst Leveloggers attached to an ISCO autosampler. We surveyed short reaches (~15 m) for cross-sectional geometry in 2012 at all monitoring locations and conducted a continuous survey of the entire reach in 2017. We checked for geomorphic changes by comparing the cross-sectional geometry between 2012 and 2017. We observed minor differences between cross-sectional area at our monitoring sites (0.12–0.19 m^2), and the channel slope remained 0.02. We used the 2017 survey to create rating curves at each monitoring site using HEC-RAS software
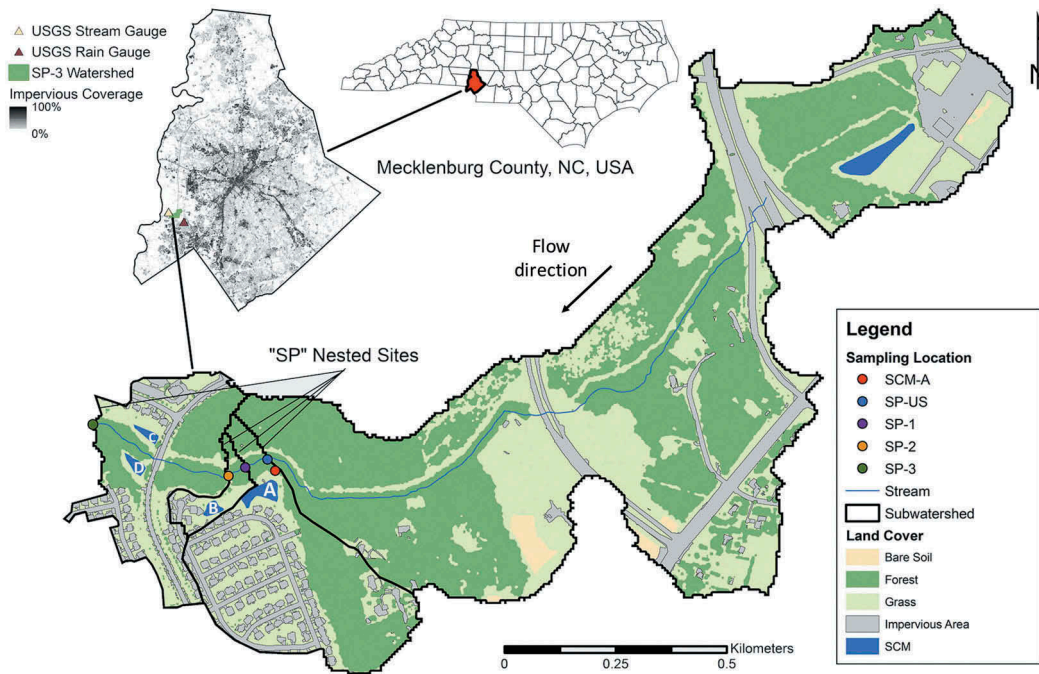
Figure 1. Map of nested sampling locations along Beaverdam Creek, the rain gauge, and the USGS stream gauge. SCMs are labeled A, B, C, and D.

Table 1. Site descriptions.

Location	Drainage area (km^2)	Distance from SP-US (m)	Total impervious area (%)	SCM- treated area (%)	Land cover fraction		
					Developed (%)	Forest (%)	Other (%)
Instream							
SP-US	1.01	0	12	8.7	34	57.1	8.9
SP-1	1.11	60	14	16.5	40.1	51.8	8.1
SP-2	1.19	110	14	16.8	38.1	54.3	7.6
SP-3	1.29	490	18	19.6	40.8	52.2	7
SCMs							
A	0.095	25	42	100	100	0	0
B	0.017	110	30	100	100	0	0
C + D	0.053	385	56	100	100	0	0

simulations of discharge under steady flow conditions. A rating curve was not developed for SP-US due to missing cross-sectional data in 2012. The model contained the entire reach (SP-US to SP-3), and Manning's roughness coefficients were calibrated with manual storm discharge measurements at SP-1, which had the most measurements ($n = 7$; $r^2 = 0.90$) (Jefferson et al. 2015). We used the calibrated model to develop rating curves at SP-2 and SP-3, which were validated using a HEC-RAS unsteady flow simulation of stage and matching those to observed stage measurements at SP-2 and SP-3. We validated the stage of two storms, one in April 2013 and one in September 2013 ($r^2_{SP-2, Apr} = 0.94$; $r^2_{SP-2, Sep} = 0.96$; $r^2_{SP-3, Apr} = 0.96$; $r^2_{SP-3, Sep} = 0.70$) (Supplemental Material Figure S1 for simulated vs. observed stage).

We collected water chemistry samples via ISCO autosamplers and manual grabs during 8 storms distributed seasonally (Supplemental Material Figure S2) and baseflow conditions on 6 occasions prior to storms. We analyzed all water samples using standard methods (Eaton et al. 2005) for nitrate (NO_3^--N), ammonium (NH_4^+-N), soluble reactive phosphorus (SRP), dissolved organic carbon (DOC), dissolved organic nitrogen (DON), sulfate (SO_4^{2-}), potassium (K^+), magnesium (Mg^{2+}),

and calcium (Ca^{2+}). We grouped constituents as reactive solutes (NO_3^--N, NH_4^+-N, SRP, DOC, DON, and K^+) and less reactive solutes (SO_4^{2-}, Mg^{2+}, and Ca^{2+}) based on the greater possibility for reactive solutes to be biologically or physically retained in SCMs or riparian zones.

Consecutive storms were treated separately if hydrograph peaks were separated by at least 8 hours or at least 3 hours of no rainfall. For event-scale analysis, we performed a hydrograph separation designed to isolate stormflow using the constant slope method (Bell et al. 2016). Samples were collected at greater frequency on the rising limb and around peak flow of storm event hydrographs (e.g. every 20 minutes) than during hydrograph recession (e.g. every 3–8 hours). In cases of multiple precipitation peaks, we continued to collect samples at 20 minute intervals until the hydrograph recession began. The analysis only includes storms where we collected multiple samples during both the rise and the recession of the storm hydrograph. The 8 individual storms occurred on the following dates: January 30th–February 1st, June 2nd-3rd, June 3rd-4th, June 6th-9th, June 10th-12th, August 17th-18th, November 26th, and November 27th–29th. Event precipitation depths were 18.8, 18.5, 42.4, 20.6, 19.6, 16, 65.3, and 19.3 mm, respectively. Antecedent dry periods ranged

from a few hours to 25 days, and two-day antecedent precipitation depths were 0, 0, 18.5, 40.6, 2.3, 15.2, 0, and 56.1 mm, respectively. Peak storm flows ranged from 3.2 $m^3 s^{-1}$ to 195 $m^3 s^{-1}$ at the Beaverdam Creek USGS gauge station (#0214297160) (Supplemental Material Figure S2), a stream gauge located 0.75 km away from our site with a continuous record throughout our study period (Figure 1). The gauges at our sampling stations have some gaps in flow data outside of our sampling time, hence the USGS gauge record provides a useful context for understanding the magnitude of sampled event responses relative to the overall range of flows during the year. During the sampling period, a series of storms resulted in one of the wettest months of June on record, with twice the average June precipitation between 1948–2017 (measured at the NOAA rain gauge: GHCND:USW00013881). The number of samples collected and sampling sites varied between storms due to variation in sampling techniques (automated sampling and grab sampling) and rapidity of the stream response.

To explore potential sources of solutes to the stream, we collected water samples from one groundwater well, one identified groundwater seep on the bank near SP-2, SCM-A inflow, and SCM-A outflow. A 1.9 m deep groundwater well, punctured and screened for the bottom 0.5 m, was located in the riparian forest near SP-2 approximately 15 meters away from the stream bank. We sampled the groundwater well and seep during stormflow conditions in May-August, October, and November. We collected grab samples from SCM-A extensively during the November storm and at least once per storm otherwise.

We collected near synchronous samples at SCM-A outflow, SP-US, and SP-1 during the November storm period to isolate the impact of SCM outflow on stream chemistry. We consider synchronicity as a set of samples from all three sites being collected within a 30-minute window. Samples were collected at a higher frequency during the November storms than the other storms.

Water quality analysis

To address the first research question, we calculated differences between temporally-matched (within a two-hour window) downstream sampling locations (SP-1, SP-2, and SP-3) and SP-US as

$$\Delta C = C_{DS} - C_{US} \tag{1}$$

where C_{DS} is the solute concentration at downstream locations – SP-1, SP-2, and SP-3; C_{US} is the solute concentration at the upstream site, SP-US. Positive ΔC indicates an increase in concentration; negative ΔC indicates a decrease.

We also tested the effect of runoff storage in SCMs on stream concentration variability by examining changes in solute concentration relative to flow at the event scale. We used $CV_C : CV_Q$ to quantify the relative variability between concentration and flow:

$$CV_C : CV_Q = \frac{\sigma_C}{\mu_C} \times \frac{\mu_Q}{\sigma_Q} \tag{2}$$

where CV_C is the coefficient of variation of concentration, CV_Q is the coefficient of variation of the discharge, σ is standard deviation, and μ is mean. This analysis was conducted for all instream sites except SP-US due to missing discharge data. $CV_C : CV_Q$ has previously been used to describe the spatial distribution and transport processes of solutes in the landscape (Musolff et al. 2017; Thompson et al. 2011). Studies have shown that geogenic (Godsey, Kirchner, and Clow 2009) and legacy (Basu et al. 2010) solutes demonstrate chemostatic behavior – small variation in concentration with respect to discharge ($CV_C : CV_Q < 0.5$). Under chemostatic regimes, solute sources are uniformly distributed across the landscape and through the soils, solute attenuation is negligible, and therefore, solute export behavior is predominantly driven by flow. However, solutes with heterogeneous distribution over the landscape and throughout the soil profile show temporally variable export behavior termed chemodynamic behavior ($CV_C : CV_Q > 0.5$) (Musolff et al. 2017). Such solutes typically exhibit different concentrations on the rising compared to the falling limb of storm hydrographs, reflecting pulses of solute export when sources are mobilized.

All statistical analyses were completed in the R language for statistical computing (R Core Team 2013). Inorganic N and P concentrations at or below the detection limit (detection limits: 0.01 mg NO_3^- -N L^{-1}, 0.3 μg SRP L^{-1}, 0.004 mg NH_4^+-N L^{-1}) were set to the detection limit; all others were above detection. We performed a Wilcoxon matched-pair sign rank test to determine if the change in concentration from the upstream site, ΔC, was significantly different than 0 which would indicate a significant influence of SCMs on receiving water quality. One assumption of this test is that the distribution of differences is symmetric around the mean or median; when invalid the data were log-transformed to ensure symmetry, and the test was performed with the logarithms of the concentration. We tested for correlation between $CV_C : CV_Q$ and antecedent precipitation, a proxy variable for SCM storage, with Spearman's rank correlation. We also tested for differences in median concentration between solute sources – SCM-A outflow, SCM-A inflow, the seep, and groundwater well – with Mood's Median test to identify significant sources of these solutes to the stream.

Results and discussion

Longitudinal patterns of reactive solutes

Our results suggest that SCMs play a significant role in decoupling the positive relationship between reactive solute concentrations and imperviousness. Across a gradient of imperviousness and SCM-mitigated area, we generally observed stable concentrations or a cumulative decrease in stream concentration of reactive solutes, after the initial transition from predominantly forested to urban residential land cover (Figure 2). At the initial transition, the sampling site with the first major increase in imperviousness and mitigation (SP-1), we observed a significant increase in concentration of NO_3^--N, NH_4^+-N, SRP, DON, and K^+ (Figure 2). Mean percent increase in concentration and its standard deviation was 18 ± 37%, 53 ± 106%, 38 ± 74%, 23 ± 34%, and 9 ± 21%, respectively (Supplemental Material Table S1). At this confluence, total imperviousness increases from 12% to 14% because the additional drainage area of SCM-A is 42% impervious (Table 1). Despite the small additional drainage area (0.1 km^2 compared
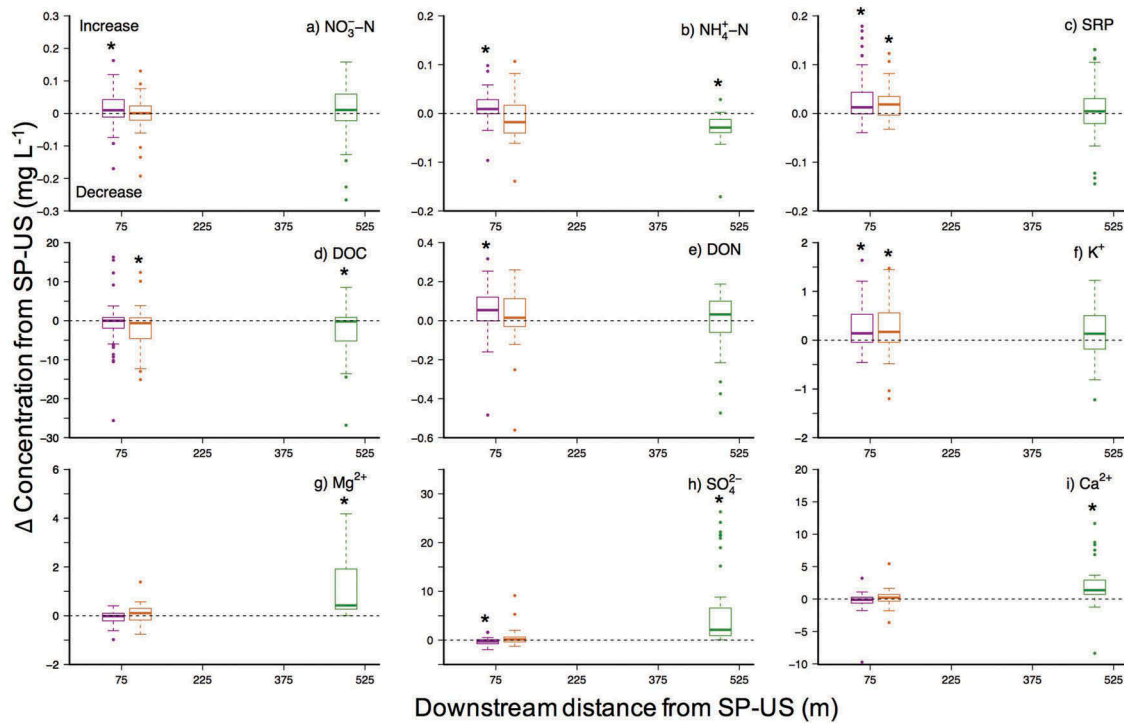
Figure 2. Change in concentration of temporally matched storm samples at SP-US and DS locations – SP-1 (purple), SP-2 (orange) and SP-3 (green) – along the longitudinal gradient. (*) represents a significant difference between SP-US and DS median concentrations with p < 0.05. Number of temporally paired samples ranges from 56–67 at SP-1, 35–44 at SP-2, and 40–51 at SP-3 (See Supplemental Material Table S1 for exact number of samples per solute).

to a total area of 1.0 km^2), the increased development and subsequent input of nutrients via potential sources such as fertilizer application likely led to a disproportionate increase in downstream concentrations below the confluence of the SCM outflow and the stream. SCM mitigation increases in conjunction with impervious surfaces. When SCMs are operating at less than 100% efficiency, they have the potential to increase stream concentrations (Bell et al. 2017).

Beyond the first land cover transition, concentrations of SRP and K$^+$ remained elevated at SP-2, but, by SP-3, all solutes decreased to concentrations similar to or significantly lower than the control (SP-US) (Figure 2). Median concentrations of NO$_3^-$-N, SRP, DON, and K$^+$ matched the upstream control and DOC and NH$_4^+$-N were significantly lower at SP-3 compared to the control. Mean percent decrease in concentration for DOC and NH$_4^+$-N was −9 ± 49% and −43 ± 78%, respectively (Supplemental Material Table S1). While concentrations changed significantly between sites during storms, baseflow

concentrations were not different between the upstream control and the mitigated sites downstream (n = 3–6; Table 2).

Generally, dissolved N and P concentrations in urban watersheds are positively correlated with urban land cover and imperviousness (Brett et al. 2005; Hatt et al. 2004; Smucker et al. 2016). The primary source is likely fertilizer application to pervious surfaces, such as lawns, and pervious areas contribute substantially to runoff generation and hence nutrient losses during storms (Soldat and Petrovic 2008). Additionally, impervious surfaces increase the potential that pervious surfaces contribute to runoff and associated loads by saturating adjacent pervious areas (Easton et al. 2007). We hypothesize that the SCMs, as well as riparian and instream ecosystems, play a role in solute retention despite increases in imperviousness. These biologically active areas facilitate N adsorption to sediments and subsequent settling, biological assimilation, and denitrification (Collins et al. 2010). Increased retention time in SCMs promotes N immobilization, via transformation

Table 2. Mean baseflow concentration (mg/L) and 95% confidence intervals. Baseflow samples were collected on the following dates: January 30th, February 1st, July 9th, August 15th, October 31st, and November 11th. SP-1, SP-2, and SP-3 concentrations are bolded if they are significantly different (exceeding the 95% confidence interval) than SP-US.

Solute		SP-US	n	SP-1	n	SP-2	n	SP-3	n
						Site			
Reactive Solutes	NO$_3^-$N	0.09 ± 0.05	6	0.11 ± 0.05	6	0.08 ± 0.04	6	0.11 ± 0.06	6
	NH$_4^+$-N	0.03 ± 0.03	3	0.01 ± 0.01	4	0.02 ± 0.02	3	0.004 ± 0.000	4
	SRP	0.06 ± 0.04	6	0.05 ± 0.03	6	0.01 ± 0.01	6	0.05 ± 0.02	6
	DOC	18.97 ± 10.00	6	18.29 ± 9.71	6	21.25 ± 12.77	6	20.81 ± 11.20	6
	DON	0.30 ± 0.21	6	0.25 ± 0.08	6	0.16 ± 0.07	6	0.20 ± 0.08	6
	K$^+$	4.37 ± 0.39	3	4.18 ± 0.56	4	4.57 ± 0.09	3	4.07 ± 0.45	4
Less Reactive Solutes	Mg^{2+}	9.46 ± 1.48	3	8.26 ± 1.60	4	11.46 ± 1.12	3	10.08 ± 2.43	4
	SO$_4^{2-}$	12.13 ± 3.59	3	13.02 ± 2.19	4	**34.30 ± 3.67**	3	**28.67 ± 9.97**	4
	Ca^{2+}	24.07 ± 4.49	3	19.99 ± 5.08	4	26.53 ± 7.70	3	24.89 ± 6.23	4

of inorganic N to organic N, and subsequent N removal (Collins et al. 2010). Other studies have documented the removal of N in stormwater mitigated watersheds (Newcomer Johnson et al. 2014; Pennino, Mcdonald, and Jaffe 2016). SCMs can act as a sink for P by adsorption of SRP onto sediments and subsequent settling, and uptake of SRP by macrophytes and algae (Reddy et al. 1999). Stormwater control measures have been observed to decrease the instream concentration of SRP during stormflow (Gold, Thompson, and Piehler 2017; Bell et al. 2017).

Unlike NO_3^--N and SRP, median concentrations of DOC and NH_4^+-N cumulatively decreased. We anticipated the stormwater ponds and wetlands to be generators of organic carbon as excess nutrients fuel algal and macrophyte primary production, subsequent senescence or lysis of algal and macrophyte cells, and ultimate DOC release (Bertilsson and Jones 2003). This can result in higher DOC concentrations downstream of SCM effluent (Bell et al. 2017). However, here we saw a decrease in DOC concentrations as SCM-mitigated area increased. The decrease in DOC concentrations at the downstream sites might be a result of a dilution of the DOC-rich streamwater from the control watershed with relatively DOC-poor impervious surface runoff. While our study was not designed to identify biogeochemical processes, longitudinal patterns suggest that a combination of assimilation (instream and in SCMs) and dilution by low-DOC runoff play a role in decreasing DOC concentrations in the stream. The presence and sources of DOC in urban streams can have cascading ecological effects such as increases in microbial activity which promotes assimilatory N demand (Bernhardt and Likens 2002), and increases in instream denitrification rates due to labile urban DOC amendments (Newcomer Johnson et al. 2012). Similarly, SCMs, the riparian zone, and the stream itself act as sinks for NH_4^+-N through assimilative processes that transform inorganic N to organic N, and nitrification.

Whether the decreases in N, P and C concentrations are predominantly hydrologically- or biogeochemically-driven remains to be determined. However, based on our monitoring data, we hypothesize that both are important drivers of instream water quality. Water storage in SCMs likely increases biological and physical transformations of nutrients but also enhances evaporative and infiltrative losses resulting in cumulative reductions in nutrient load exported to the stream (Jefferson et al. 2017).

Longitudinal patterns of less reactive solutes

Our data illustrate that Mg^{2+}, Ca^{2+}, and SO_4^{2-} concentrations during storms cumulatively increased along the longitudinal gradient, suggesting that solute concentrations were coupled with increases in impervious area, but were unaffected by retentive properties of SCM mitigation. Magnesium, calcium, and sulfate exhibited significant and large increases in concentration at SP-3, but not at SP-1 or SP-2 (Figure 2). Mean percent increase in concentration (± standard deviation) of Mg^{2+}, Ca^{2+}, and SO_4^{2-} at SP-3 was 28 ± 22%, 25 ± 24%, and 85 ± 101%, respectively (Supplemental Material Table S1). In general, mean baseflow concentrations at the downstream sites were not different from the control, with the exception of sulfate (n = 3–4; differences determined by exceeding the 95% confidence interval). Mean

baseflow sulfate concentration (± 95% confidence interval) at SP-US, SP-1, SP-2, and SP-3 was 12 ± 4, 13 ± 2, 34 ± 4, and 29 ± 10 mg L^{-1} (Table 2). Baseflow concentrations of SO_4^{2-} and K^+ observed in our study were within the range of observed concentrations in a watershed with similar urban development and Piedmont geology (Miller et al. 1997), although sulfate concentrations were slightly higher at SP-2 and SP-3.

Recent work has documented elevated concentrations of major ions in urban streams and lakes as compared their forested counterparts (Bahar and Yamamuro 2008; Rose 2002; Siver et al. 1996; Wright et al. 2011), however the underlying lithology has frequently been inconsistent across sites. It is difficult to decipher whether changes in major ions are due to anthropogenic or geogenic sources using this approach. A recent study comparing watersheds of the same lithology illustrated that baseflow measurements of pH, Mg^{2+}, Ca^{2+}, SO_4^{2-}, Na^+, Cl^-, specific conductance and alkalinity significantly increased as imperviousness increased from 0–25% (Moore et al. 2017). We build on previous literature by showing that (1) in nested sites of the same underlying lithology, base ion and sulfate concentrations increased as impervious area increased and (2) the positive relationship between imperviousness and base ions was evident under storm conditions and present at relatively low levels of impervious surface coverage (<20%).

While increases in major ion concentrations have been linked to imperviousness, transport pathways to the stream remain uncertain and our work suggests that subsurface macropores could play an important role. Subsurface seeps had the highest source concentration of these ions in the watershed (Figure 3). During the November storm, the wet pond (SCM-A) was depleted of less reactive solutes compared to the stream; in fact, the pond effluent diluted instream concentrations indicating that SCM-A is not a direct source of these solutes to the stream (Figure 4; Supplemental Material Figure S3 for Ca^{2+}). In contrast, the majority of reactive solutes exhibited the highest source concentration in surface flows (SCM-A inflow and outflow), with the exception of DOC, NH_4^+-N, and K^+. Dissolved organic carbon exhibited highly variable seep concentrations, and concentrations were similar across sources for NH_4^+-N and K^+ (Figure 3). The high variability of DOC concentrations in the seep indicates that DOC fluxes from the subsurface are episodic and likely event-based; in comparison, the low variability of seep concentrations for the less reactive solutes suggests the presence of a subsurface plume. Together these results (i.e. low concentrations in SCMs and high concentrations in shallow groundwater) suggest that subsurface flowpaths are predominant vectors of these solutes to the stream. Urban catchments have extensive underground infrastructure that can create preferential flow paths for water and solutes to travel to the stream (Bonneau et al. 2017; Robinson and Hasenmueller 2017). These subsurface flowpaths could potentially mobilize geogenic and/or anthropogenic sources of Mg^{2+}, Ca^{2+}, and SO_4^{2}. Additionally, stormwater ponds themselves have been shown to transport salts to groundwater, and create contaminated plumes (Snodgrass et al. 2017).

Influence of storage on nutrient response

To examine changes in solute regime with respect to water storage, we plotted CV_C:CV_Q versus antecedent precipitation
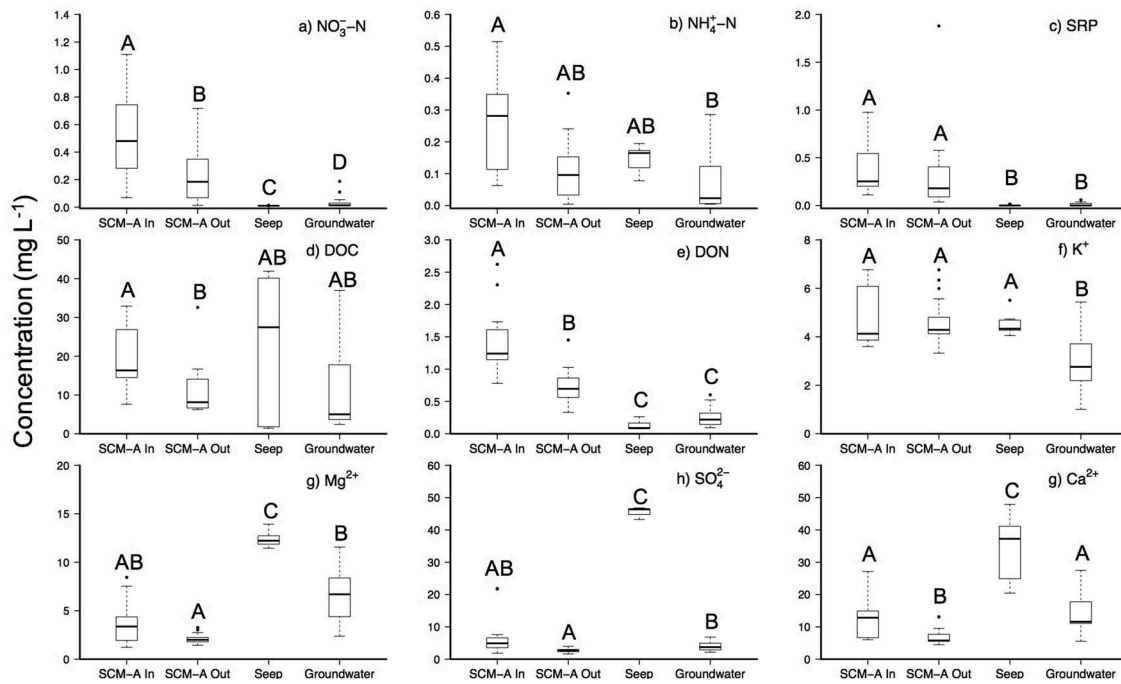
Figure 3. Concentrations of groundwater (n = 20 for reactive solutes; n = 16 for less reactive solutes), seep water (n = 11 for reactive solutes; n = 8 for less reactive solutes), SCM-A inflow (n = 13 for reactive solutes; n = 11 for less reactive solutes) and SCM-A outflow (n = 37 for reactive solutes; n = 29 for less reactive solutes) during storms distributed seasonally. A Mood's Median Test was used to determine significant differences between sites. Significant differences are indicated with different letters.
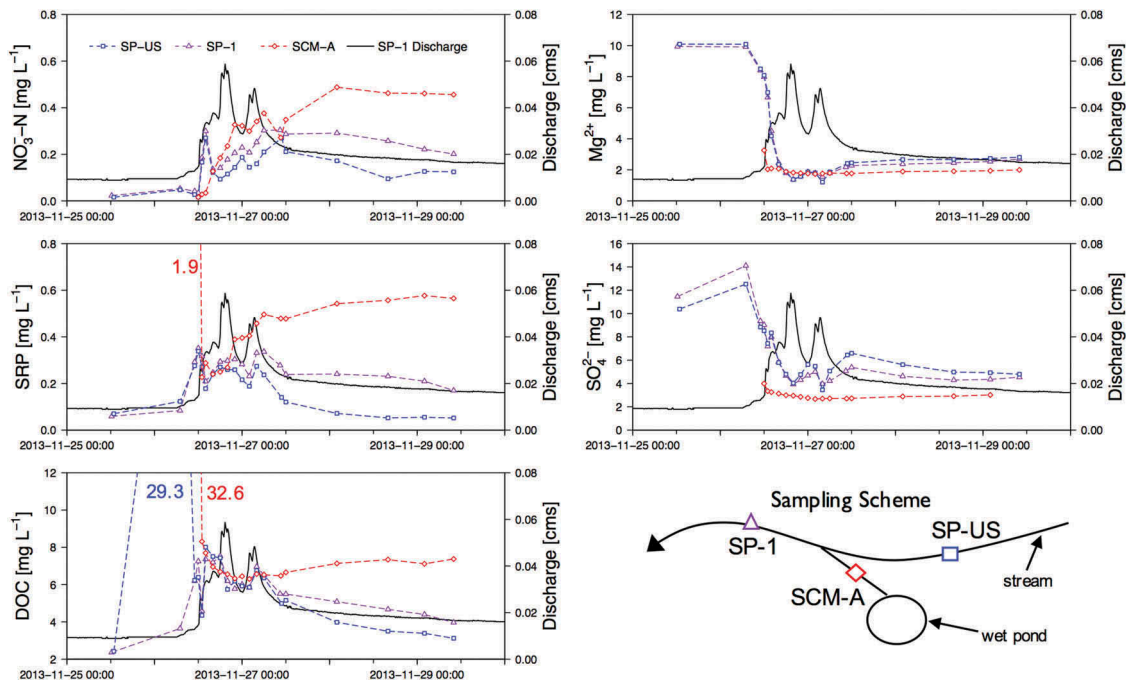

Figure 4. Concentrations at SP-US, SP-1, and SCM-A during the November storms. SP-1 represents the confluence of SCM-A outflow and instream flow at SP-US. Concentrations that are higher than the maximum value of the graph space are noted within the figure and color coded by site.

(Figure 5). Each point in the figure represents one storm event at SP-1, SP-2, or SP-3 and events are coded by precipitation depth. Our results show that stream concentration variability was correlated with watershed storage conditions (as represented by 2-day antecedent precipitation depth) (Figure 5). In general, solute regimes were chemodynamic

during small storms and those with low antecedent moisture and chemostatic during large storms and those with high antecedent moisture (Figure 5). Sulfate exhibited the strongest significant negative correlation between antecedent precipitation depth and $CV_C:CV_Q$, while NO_3^--N, DOC, and DON exhibited moderately weaker yet significant
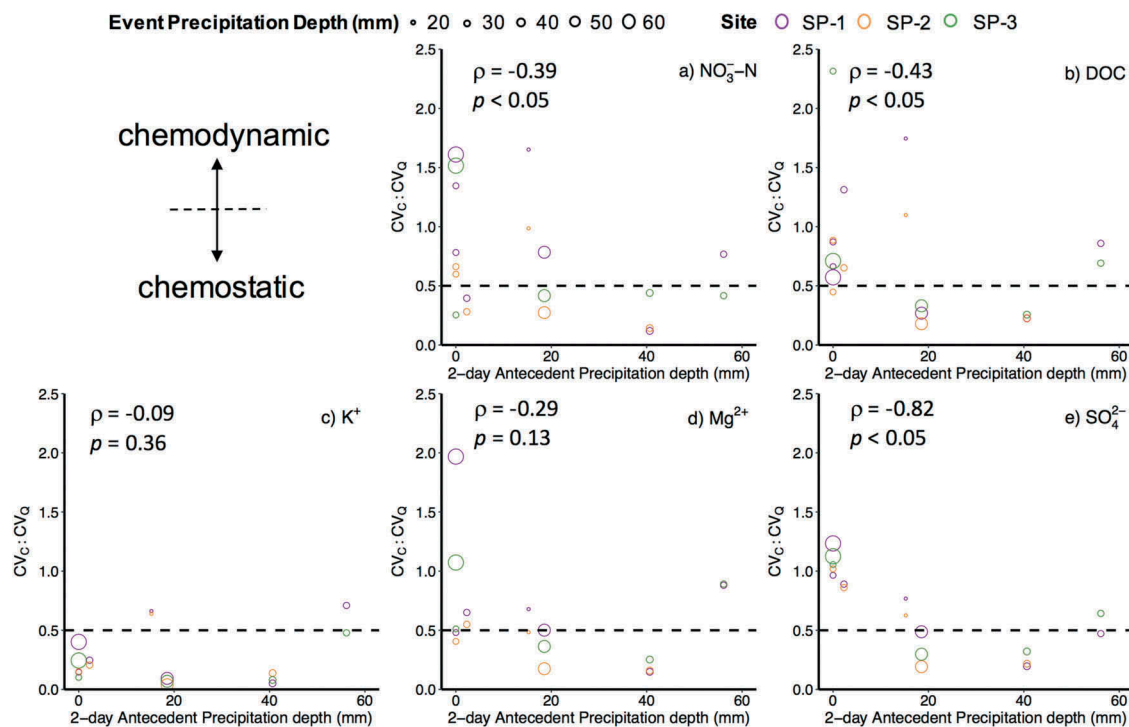
Figure 5. CV_C:CV_Q vs. 2- day antecedent precipitation depth, coded by size to indicate event precipitation depth and by color to indicate site. Sites included SP-1, SP-2, and SP-3, and all sites are aggregated to a single plot. CV_C:CV_Q values below 0.5 are considered chemostatic, and values above 0.5 are considered chemodynamic (Musolff et al. 2017; Thompson et al. 2011). At each site, we collected between 6– 15 samples during a storm event.

correlations (See Figure 5; Spearman's $\rho = -0.60$, $p < 0.05$ for DON (Supplemental Material Figure S4(c))). Although statistically insignificant (at $p > 0.05$), suggestive associations between antecedent precipitation and CV_C:CV_Q were observed for NH_4^+-N, SRP, Mg^{2+}, and Ca^{2+} (Spearman's $\rho = -0.19$, $p = 0.23$; $\rho = -0.32$, $p = 0.09$; $\rho = -0.29$, $p = 0.13$; $\rho = -0.31$, $p = 0.11$, respectively; see Supplemental Material Figure S4). While the general responses to storms are similar for both reactive and less reactive solutes, K^+ demonstrates lower sensitivity to both storm size and antecedent conditions. Figure 5(c) demonstrates that K^+ has a lower variability in CV_C:CV_Q than the other solutes, and the solute regime is consistently chemostatic.

To our knowledge, the CV_C:CV_Q metric has not been utilized in urban catchments on the storm event scale, with most empirical and modeling studies conducted in agricultural watersheds dominated by subsurface flowpaths (Thompson et al. 2011; Musolff et al. 2017). A substantive body of research shows that the driving factors of solute export are the spatial distribution of solute sources across the landscape (Musolff et al. 2017; Thompson et al. 2011) and through the soil profile (Inamdar, Christopher, and Mitchell 2004), and mechanisms of solute attenuation along flow paths (Creed and Band 1998; McGlynn and McDonnell 2003; Musolff et al. 2017; Pacific, Jencso, and McGlynn 2010). We suggest that chemodynamic export regimes are a result of diverse solute source zones, and short-term attenuation of runoff and solutes from paved surfaces. During dry conditions, storage availability is high and there is potential for biogeochemical and hydrologic controls on solute mobility. Solute load is mobilized from multiple

sources such as groundwater (Rose 2002), directly connected impervious surfaces (Lee et al. 2004; Rose 2002), and overflow of storage zones (Lawler et al. 2006). These sources deliver solutes to the stream at different times – directly connected paved surfaces contribute to 'first flush' in the beginning of a storm, while overflow of storage occurs later in the storm. Furthermore, solute retention within storage zones could decouple runoff from solute export – for example SRP sorption to sediment and settling in SCMs could delay its export to larger discharge events. Hence, the high variability in concentration relative to discharge is reflective of pulses of solute export when sources are temporarily hydrologically connected to the stream.

In contrast to chemodynamic regimes, chemostatic export regimes are reflective of homogenization of solute sources and low residence time of runoff in storage zones. Under wet antecedent conditions, the watershed is saturated and storage zones are hydrologically connected to the stream, leading runoff and solutes to quickly bypass storage and travel to the stream (Pacific, Jencso, and McGlynn 2010). Quick flow paths, such as directly connected paved surfaces, continue to contribute runoff; however, these surfaces are less likely to contribute large loads of solutes due to wash-off during previous storms which produced the wet antecedent conditions (Deletic 1998). Hence, there is a lower percent contribution of solutes from directly connected surfaces, and continuous export of solutes from storage zones, such as the riparian zone and SCMs, throughout the storm. We suggest that continuous solute export from storage zones and low attenuation times contribute to chemostatic behavior.

While our results are inconclusive with regards to the underlying mechanism of potassium's consistent chemostatic behavior, major ions demonstrate chemostatic relationships with discharge across a wide range of catchments (Godsey, Kirchner, and Clow 2009). Chemostatic behavior develops from hydrologically-driven solute export. One possible explanation is that potassium originates from soil minerals, and as discharge increases there is a proportional increase in mineral dissolution rates – due to an increase in mineral wetted surface area as soil saturation increases – and flushing from soil pore space (Godsey, Kirchner, and Clow 2009). This mechanism is plausible in Beaverdam Creek watershed because the mineral composition of gabbro and grandiorite contains potassium. However, mechanisms of chemostasis can also be site-specific. Herndon et al. (2015) suggest that connectivity of the exchangeable ion pool increases as soil saturation increases leading to proportional solute mobilization with soil saturation. The Beaverdam Creek watershed is more impervious relative to the aforementioned studies, but both mechanisms are plausible in the wide forested riparian zone and pervious areas, such as lawns and parks. We speculate that magnesium, calcium, and sulfate would demonstrate chemostasis if soil minerals were the primary source.

SCMs are designed to buffer large pulses of solutes during stormflows and assumed to function similarly over time. Our results show that SCMs have the potential to buffer solute export when available storage is high (i.e. dry antecedent conditions) but they are continuously delivering solutes to the stream during wet antecedent conditions. The transient nature of storage suggests that hydrologic regimes of water storage zones are a major driver of nutrient export regimes. It is likely that both natural storage (e.g. riparian zones) and SCMs play a role in solute attenuation/export, however the effects of each were not isolated in our analysis. Our results show that biogeochemically active storage zones, whether constructed or natural, have a real water quality impact, but mitigation potential is temporally dynamic.

SCMs significantly contribute to watershed storage capacity

Chemographs of SCM-A outflow, SP-US, and SP-1 demonstrate mixing of SCM outflow and streamwater during the intensively sampled November storms (Figure 4). These results illustrate that water stored in SCMs has a significant impact on the timing of solute delivery to the stream. Furthermore, these storms exemplify the potential for SCMs to store solutes when water storage availability is high, and flush solutes when storage availability is low. The first November storm was the largest precipitation event (65.3 mm) that we sampled, and it was preceded by dry antecedent conditions (25 days) that likely contributed pollutant build up prior to the storm (Supplemental Material Figure S2).

Nutrient pulses during these storms indicate that multiple flowpaths contribute to solute export. Our results clearly showed an initial 'first flush' – evidenced by rapidly increasing concentrations – followed by a dilution of stream concentrations. As SCM-A outflow concentrations increase, we observed a delayed and extended solute pulse elevating concentrations at SP-1 compared to the control (Figure 4). The difference between SP-US and SP-1

concentration was most pronounced during the hydrograph recession of the second November storm with mean concentrations of reactive solutes higher at SP-1 than SP-US and the highest concentrations were found in SCM-A outflow (Figure 4; see Supplemental Material Figure S3 for NH_4^+-N, DON, and K^+; see Supplemental Material Table S2 for summary of concentration during hydrograph recession).

The first pulse of solutes, the first flush, is indicative of quick transport of accumulated solutes from untreated directly connected impervious surfaces to the stream at SP-US and SP-1 (Lee and Bang 2000). Next, we observed an immediate dilution of reactive solute concentrations at SP-US and SP-1, which implies that dissolved solutes were diluted by surface runoff from upstream sources. A potential source of these solutes is the untreated highway that crosses Beaverdam Creek in the control watershed (Figure 1). During the 25-day antecedent period, solute build-up and wash-off from highway surfaces could drive first flush behavior. Additionally, the synchronicity between SP-US and SP-1 implies that SCM-A outflows are not significantly influencing solute concentration at SP-1 during the rise of the storm hydrograph. By design, SCMs store stormwater runoff, delay solute delivery to the stream during peak flow periods, and slowly release runoff 24–48 hours later (CMSWS 2013). Increases in runoff and solute residence time provide opportunities for assimilative, transformative, and adsorptive processes.

Observed wet pond effluent concentrations suggest that assimilation was occurring during these periods of storage between storm events, which was shown in a modeling study (Bell, Tague, and McMillan 2017). Temporal patterns over the course of the storm showed that concentrations of NO_3^--N and SRP increased in the wet pond effluent (SCM-A) indicating N and P-rich runoff, while concentration of DOC decreased due to dilution of pond water from DOC-poor impervious surface runoff (Figure 4). This pattern suggests that solute sources differed: sources of DOC were near or autochthonously produced within SCM-A, while NO_3^- and SRP were allochthonous and concentrated in runoff that passed through the wet pond. Within stormwater ponds, ample sunlight and nutrient amendments from urban runoff can fuel algal and macrophyte primary production. During growth, primary producers consume inorganic N and P, leading to transformation of inorganic species (NH_4^+-N and NO_3^-N) to organic species (DON). Subsequent senescence or lysis of algal and macrophyte cells and extracellular release of DOC contribute to a standing stock of labile DOC in these lotic systems (Bertilsson and Jones 2003).

Following the period of delayed solute export, we observed an extended pulse of reactive solutes to the stream during the hydrograph recession. Elevated concentrations at SP-1 appear to be sustained by wet pond effluent for two days after the storm subsided (Figure 4). We attribute this pulse to the release of stored water from the wet pond. This phenomenon confirms that the wet pond is functioning as it was designed by retaining peak flows until hydrograph recession. In a study of the same system, researchers used an end member mixing analysis approach with stable water isotopes as tracers of SCM stored water and showed that SCMs contributed water throughout the event but disproportionately higher on the

receding limb (Jefferson et al. 2015). Our results show that the chemistry of SCMs – which is distinctly different from other water sources in the watershed – influences stream chemistry and persists for several days after an event.

Conclusions

Reactive solute concentrations were cumulatively decreased or stabilized by SCM mitigation in our study watershed. As mitigation increased, the subsequent decrease of instream concentration can be explained by the combined effects of solute retention and transformation processes within SCMs, the riparian zone and stream. Furthermore, less biologically reactive solute concentrations increase with impervious cover, likely due to weathering of concrete surfaces. These findings can have implications for management of benthic organisms; elevated concentrations of Mg^{2+}, SO_4^{2-}, and Ca^{2+} are potentially toxic to sensitive benthic species (Clements and Kotalik 2016). While our site is only one example, our nested approach isolated the effects of imperviousness and SCM mitigation by controlling for differences in climate, land use, and lithology among sites.

We also observe a delayed pulse of nutrients from the SCM to the receiving stream during hydrograph recession. This finding implies that hydrologic regimes within SCMs have a significant effect on essential nutrient availability in the stream and likely on stream ecological processes. It is suggested, yet seldom observed, that the redistribution of stormflows to baseflows and control of peak flows through stormwater mitigation can aid in ecological recovery of urban streams by protecting instream ecosystems from disturbances such as scour (Palmer, Hondula, and Koch 2014; Konrad and Booth 2005). We show that hydrologic regimes also alter nutrient availability in the stream during low flow periods, which may be a key limitation to or aid in mediating ecological recovery after a hydrologic disturbance.

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