THE EFFECTS OF URBANIZATION ON COASTAL HYDROLOGY AND BIOGEOCHEMISTRY

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ABSTRACT

Adam C. Gold: The effects of urbanization on coastal hydrology and biogeochemistry
(Under the direction of Michael F. Piehler)

The southeastern United States (US) coastal plain is a unique physiographic region with extensive connections between land and water, and these connections fuel transformations and transport of carbon and nutrients to productive coastal ecosystems. Urbanization, or an increase in the extent of urban area, is occurring rapidly in the southeastern US coastal plain, and although stormwater runoff from urban areas can have negative effects on the ecology of downstream waters, research on this topic in the coastal plain is limited. Engineering approaches characterized as stormwater control measures (SCMs) have been widely implemented in the coastal plain to mitigate negative ecological effects of stormwater runoff without information regarding the long-term impact of SCMs or how they process nutrients. This dissertation characterized the effects of urbanization on coastal plain stream nutrient and carbon export and characterized the efficacy and process-level function of SCMs. Chapter 1 is a review and synthesis that highlights critical gaps related to nitrogen cycling within SCMs. Chapter 2 analyzes flow-through sediment core incubations to measure seasonal nitrogen cycling in coastal stormwater ponds. Chapters 3 and 4 use a years-long streamflow and water quality dataset to analyze the impacts of urbanization on coastal plain stream carbon and nitrogen export. Results from this research show that stormwater ponds often act as temporary sinks for stormwater-derived nutrients or as transformers of nitrogen from inorganic to organic forms, especially during periods of high water temperatures. Results indicated that the volume of stormflow and

the amount of nitrogen and carbon exported from coastal streams during storms increased with development. Naturally high concentrations of organic nitrogen and dissolved organic carbon decreased with urbanization, with differences in nitrogen and carbon quality indicating shifts towards more labile anthropogenic sources. This research provides actionable information that managers can use to better mitigate the biogeochemical and ecological effects of urbanization on streams in the southeastern US coastal plain.

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LIST OF ABBREVIATIONS

SCM	Stormwater control measure
ISC	Impervious surface coverage
DNF	Denitrification
DNRA	Dissimilatory nitrate reduction to ammonium
N-fix	Nitrogen fixation
SWP	Stormwater wet pond
DON	Dissolved organic nitrogen
DIN	Dissolved inorganic nitrogen
NO_x	Nitrate + nitrite
NH_4	Ammonium
TN	Total nitrogen
DOM	Dissolved organic matter
PN	Particulate nitrogen
SOM	Sediment organic matter
C:N	Carbon to nitrogen ratio
BFI	Baseflow Index
CV_c/CV_Q	Coefficient of variation in concentration / coefficient of variation in streamflow
C-Q	Log-log relationship between concentration and stream discharge
DOC	Dissolved organic carbon
CDOM	Chromophoric dissolved organic matter

POM	Particulate organic matter
PC	Particulate carbon
DO	Dissolved oxygen
E_2:E_3	Ratio of absorbance at 250 to 365 nm
S_r	Ratio between the linear slope of log-transformed absorbance data between the ranges 275-295 nm and 350-400 nm
$SUVA_{254}$	Specific UV absorbance at 254 nm
$SUVA_{350}$	Specific UV absorbance at 350 nm

CHAPTER 1: NITROGEN CYCLING PROCESSES WITHIN STORMWATER CONTROL MEASURES: A REVIEW AND CALL FOR RESEARCH[1]

Introduction

Stormwater control measures (SCMs) are common across the urban landscape. These structures are primarily used to mitigate the negative effects of watershed development, or increased impervious area, on watershed hydrology and stream water quality. The downstream effects of increasing developed area (without mitigation) include streambed scour (Booth, 1990), increased nutrient loading (Paul and Meyer, 2001; Walsh et al., 2005), loss of stream macroinvertebrate diversity (Stranko et al., 2012), and flashier hydrology (O'Driscoll et al., 2010; Paul and Meyer, 2001; Walsh et al., 2005). Due to these observed consequences of development, most municipalities, counties, or states have permitting requirements for stormwater mitigation and suggested SCM design practices with new development (National Research Council, 2009).

The need to quantify the effectiveness and downstream impacts of SCMs for water quality management has resulted in predominantly concentration- or load-based studies of SCM nitrogen removal (Collins et al., 2010). These studies were typically conducted over short time scales (e.g., hours, days, weeks) and showed that while the average percent removal of different nitrogen species was positive in many different kinds of SCMs, there was large variability in the

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percent nitrogen removed within each kind of SCM (Koch et al., 2014). Also, percent removal of nitrogen calculated using loading measurements can be driven by stormwater volume reduction (e.g., infiltration) rather than actual treatment of nitrogen. Despite this documented variability in percent nitrogen removal and possible confounding effects of volume reduction on load-based measurements, assumptions have been made in policy, management, and research about the internal workings of SCMs based on loading mass-balance studies. The variability in SCM nitrogen removal may be, in part, caused by a lack of studies including direct measurements of nitrogen cycling processes occurring within SCMs. Recent research focuses more on internal SCM processes rather than mass balance between the inflow and outflow, but results range from effective nitrogen removal to results that are counter the stated water quality goals of the SCM (Datry et al., 2003; Duan et al., 2016; Gold et al., 2017a; Song et al., 2017; Williams et al., 2013). The large uncertainty in SCM effectiveness calls for in-depth mass balance and internal nitrogen cycling studies of SCMs.

A common assumption applied to SCM function from mass-balance studies is that denitrification removes a substantial amount of nitrogen in SCMs, especially in retention-based SCMs that never drain fully or drain slowly. Denitrification, the microbially-mediated transformation of nitrate (NO_3^-) to inert N_2 gas, is a removal mechanism for bioavailable nitrate from aquatic ecosystems (Seitzinger et al., 2006). The validity of this assumption has far-reaching implications for the condition of downstream waters because excess nitrogen can cause eutrophication of marine and coastal systems (Howarth and Marino, 2006) and freshwaters (Elser et al., 2007). If denitrification is less prevalent in SCMs than assumed, nitrogen inputs via stormwater could be exported downstream or recycled within SCMs.

If nitrogen in SCMs is not denitrified or exported immediately, it could by recycled internally through temporary uptake and remineralization by primary producers (Williams et al., 2013), buried through sedimentation of particles and organic matter (Passeport et al., 2013; Schroer et al., 2018; Sønderup et al., 2016), transformed via dissimilatory nitrate reduction to ammonium (DNRA) (Scott et al., 2008), or removed through anaerobic ammonium oxidation (anammox) (Burgin and Hamilton, 2007). Various factors could affect the importance of each of these processes within SCMs, as in other aquatic habitats, such as sediment carbon quality, water column N:P ratios, residence time, SCM depth, and SCM length:width ratios. Internal nitrogen processes have yet to be extensively measured in SCMs but they could explain variability in nitrogen removal efficacy observed by previous studies. Understanding the processing of nitrogen in SCMs may improve the ability of stormwater management plans to promote denitrification of nitrogen inputs and improve water quality in developed areas.

The purpose of this review is to present the current understanding of nitrogen cycling within multiple types of SCMs and suggest opportunities for research. The types of SCMs include many that have been promoted as effective sites of nitrogen removal or maintain permanent standing water such as stormwater wet ponds, extended detention dry ponds, stormwater wetlands, and bioretention cells.

The goals of this review article are to:

1. Present examples of the prevailing assumptions about nitrogen cycling in SCMs in the scientific literature and the reasoning behind them
2. Summarize recent studies focusing on nitrogen cycling within SCMs and their assumptions of denitrification

3. Discuss recent advances in nitrogen cycling measurements that can be applied to studies in SCMs
4. Highlight opportunities for future research of nitrogen cycling within SCMs

Methods

This review is based on studies that focused on nitrogen cycling processes within SCMs designed for the main purpose of collecting and treating stormwater derived from urban land uses. Studies were identified by searching various keywords related to stormwater control measures and nitrogen cycling (i.e., denitrification, DNRA, assimilation) in the Web of Science database (Table 1.1), and studies that fell within the scope of the review were summarized and sorted by method in an excel spreadsheet. This review identified a total of twelve studies that reported rates of denitrification (potential or direct measurement)(Table 1.2), two that reported rates or importance of DNRA (Messer et al., 2017; Payne et al., 2014), and three that reported rates or importance of assimilation within stormwater control measures (Messer et al., 2017; Norton et al., 2017; Payne et al., 2014).

Table 1.1. List of keywords used for literature review. The search was conducted by searching the name of each process with additional keywords.

Process	Keywords	# of search results
Denitrification	Stormwater	148
	Retention, basin	144
	Stormwater, nitrogen	132
	Stormwater, wetland	58
	Bioretention	56
	Infiltration, basin	33
	Wet pond	25
	Detention, basin	12
DNRA	Stormwater	3
	Retention, basin	2
	Stormwater, wetland	0
	Bioretention	1

	Infiltration, basin	0
	Wet pond	1
	Detention, basin	0
Nitrogen assimilation	Stormwater,	19
	Retention, basin	16
	Stormwater, wetland	14
	Bioretention	5
	Infiltration, basin	1
	Wet pond	2
	Detention, basin	1

Assumptions of denitrification and measurements within SCMs

Denitrification is an important process for mediating levels of bioavailable nitrogen in aquatic ecosystems (Howarth et al., 1996; Seitzinger et al., 2006). Denitrification occurs under anaerobic or low-oxygen conditions and requires a suiTable 1.carbon source and available nitrate either in the overlying water or produced via nitrification of ammonium from the sediments (Eyre et al., 2013; Kana et al., 1994; Seitzinger et al., 2006; Seitzinger, 1988). Based on these conditions, SCMs appear to be ideal locations for denitrification to occur. Since most SCMs only have inflow during and after storm events, their residence times can range from hours to weeks (Jefferson et al., 2015), and longer residence times are positively correlated with the magnitude of nitrogen removal from overlying waters due mainly to denitrification promoted by increased exposure to the sediment-water interface (Bettez and Groffman, 2012; Klocker et al., 2009; Mallin et al., 2002; Nixon et al., 1996; Passeport et al., 2013). Over time, some SCMs fill in with sediment and organic matter (Gold et al., 2017a; Merriman et al., 2017; Moore and Hunt, 2012; Schroer et al., 2018), which could provide a carbon source for denitrification and increase the incidence of anaerobic conditions due to decomposition. Denitrification can also be promoted in some SCMs through soil amendments and certain design specifications, such as elevating underdrains in bioretention cells to increase low-oxygen conditions (reviewed in Hunt et al., 2012). Many studies have measured low oxygen conditions in the bottom water of stormwater ponds (Duan et al., 2016; Gold et al., 2017a; Newcomer Johnson et al., 2014), further indicating that these SCMs could be important sites for denitrification based on the favorable combination of factors (Bettez and Groffman, 2012; Newcomer Johnson et al., 2014; Zhu et al., 2004).

A number of published articles that utilized mass-balance experimental designs (i.e., load-based measurements) have suggested that SCMs are important locations for denitrification (summarized in Collins et al., 2010). These load-based studies that have hypothesized about the importance of denitrification in SCMs often attribute reduced loads of nitrogen from SCMs to denitrification, when, in fact, the mechanism for nitrogen removal is unknown. Some studies have measured denitrification within SCMs, and most of these studies have assessed denitrification using various proxy-based or potential-based methods, such as denitrification enzyme assays (DEA; Groffman et al., 1999), acetylene-block intact sediment core incubations (described in Groffman et al., 2006), groundwater "push-pull" ^{15}N tracers (Addy et al., 2002), and N_2O flux measurements that are converted into denitrification rates (Schlesinger, 2009) (Figure 1.1, Table 1.2).

The first investigation of denitrification within SCMs utilized DEA and intact core acetylene-block methods in an infiltration basin and found rates of potential denitrification and *in situ* denitrification that were similar to the highest rates measured in other aquatic environments (Zhu et al., 2004) (Figure 1.1, Table 1.2). This study also found a positive relationship between sediment organic matter (SOM) and potential denitrification, indicating that the settling of sediment and organic matter particles within the SCM may promote denitrification. Later studies found higher rates of potential denitrification in SCMs compared to reference riparian and upland areas and showed positive relationships between potential denitrification and both SOM and inundation time (Bettez and Groffman, 2012; McPhillips and Walter, 2015)(Figure 1.1, Table 1.2). Additionally, these studies concluded that the wetter, retention-based SCMs, for the most part, had higher rates of potential denitrification than other SCMs, possibly due to constant inundation and longer residence times (Bettez and Groffman, 2012; McPhillips and Walter, 2015) (Figure 1.1, Table 1.2). An extensive study of stormwater ponds in 8 US cities found higher rates of potential denitrification than previous studies that used DEA methods, but the influence of environmental and landscape controls were unclear (Blaszczak et al., 2018) (Figure 1.1, Table 1.2). High rates of groundwater denitrification were measured in wet ponds and stormwater wetlands using groundwater "push-pull" ^{15}N tracers, and these rates were comparable to rates in hydrologically-connected floodplains (Harrison et al., 2011; Newcomer Johnson et al., 2014) (Figure 1.1, Table 1.2). Measurements of N_2O fluxes and an SCM nitrogen loading mass-balance determined that a wet detention basin was able to denitrify up to 58% of the dissolved inorganic nitrogen (DIN) that flowed into it, and a dry detention basin was only able to denitrify 1% of incoming DIN (Morse et al., 2017) (Figure 1.1, Table 1.2). Studies utilizing molecular methods have found a positive relationship between inundation time and the abundance of denitrifier functional genes such as *nar* (nitrate reductase), *nirK*, *nirS* (nitrite reductase), *cnor*, *qnor*, *norB* (nitric oxide reductase), and *nosZ* (nitrous oxide reductase) (Chen et al., 2013; Morse et al., 2017). Aligning with the prevailing knowledge about SCM nitrogen removal, these studies suggest that SCMs, especially SCMs with long residence times, are important sites of denitrification and could help reduce nitrogen export from urban watersheds.

A growing number of studies have directly measured denitrification in SCMs, utilizing either the N_2:Ar method to measure net N_2 fluxes (described in Kana et al., 1994) or lab-based, mass-balance ^{15}N tracers (described in Payne et al., 2014). Direct methods, in this review, are defined as methods that measure the end-product of a microbial process or net production of opposite processes over time (e.g., denitrification vs. nitrogen fixation) rather than proxies or potential measurements. Direct methods are key to understanding the importance of denitrification and other nitrogen removal pathways within SCMs. Recent work utilizing ^{15}N mass-balance methods found that assimilation in plants and soils was the dominant nitrate removal pathway in bioretention and stormwater wetland mesocosms (Messer et al., 2017; Morse et al., 2018; Payne et al., 2014). Another study measured rates of net N_2 flux ranging from -63 (net nitrogen fixation) to 520 (net denitrification) µmol N m^{-2} h^{-1} in bioretention mesocosms (Figure 1.1, Table 1.2), and denitrification accounted for a maximum of 23% of dissolved inorganic nitrogen removal (Norton et al., 2017). This study also concluded through concurrent measurements of DEA and simple nitrogen mass balances that these latter methods might vastly overestimate the net rate and importance of denitrification (Norton et al., 2017). The only published study to measure net N_2 fluxes from SCMs in the field (rather than mesocosms) reported substantial rates of net nitrogen fixation in unamended sediments of wet ponds during the summer (Gold et al., 2017a), with net N_2 fluxes ranging from -206 and 14.8 µmol N m^{-2} h^{-1} (Figure 1.1, Table 1.2). Further, in this study the response of sediments to a nitrate addition varied based on wet pond age, where younger ponds took up nitrate and switched to net denitrification while older ponds also took up nitrate but did not utilize it for denitrification (Gold et al., 2017a). The measured rates of net nitrogen fixation coincident with uptake of nitrate in older ponds supports conclusions of other recent studies that alternative nitrogen pathways, such as DNRA or assimilation in plants and soils, could be more important than denitrification in SCMs.

This new body of evidence utilizing direct methods such as N_2:Ar and mass-balance ^{15}N methods provides context for previous work in SCMs and raises questions about the importance assigned to denitrification in SCMs based on DEA and field-based ^{15}N tracers. While DEA does, indeed, measure the ability of the microbial community to denitrify given ideal conditions, it is a measure of potential rates of denitrification without a concurrent measure of nitrogen fixation, which could be occurring at a higher rate than denitrification (Foster and Fulweiler, 2014; Fulweiler et al., 2007, 2013; Gold et al., 2017a; Newell et al., 2016a). Regardless of the absolute value of denitrification, if the process of nitrogen fixation is occurring at a higher rate than denitrification, nitrogen is being created faster than it is being removed and there is a net addition of nitrogen to the system. Furthermore, bottle effects from the DEA methodology can change the microbial community (Hartzog et al., 2017), and the method underestimates coupled nitrification-denitrification (Seitzinger et al., 1993) due to the inhibition of nitrification by acetylene (Hynes and Knowles, 1982, 1978; Mosier, 1980; Walter et al., 1979). Potential denitrification is reported as a sediment mass-based rate, which increases the complexity of scaling up field measurements and comparing results to area-based rates measured with other methods. Field-based measurements of denitrification with ^{15}N tracers are an effective way to measure denitrification (Groffman et al., 2006), but they also do not assess nitrogen fixation and have some limitations due to underestimates of denitrification from water column nitrate (Seitzinger et al., 1993). Conversions of N_2O fluxes to denitrification rates introduce large amounts of variability because these ratios vary greatly within aquatic (Seitzinger, 1988) and terrestrial ecosystems (Schlesinger, 2009). N_2:Ar methods and mass-balance ^{15}N tracers have some drawbacks as well because, as stated in Groffman et al., 2006, denitrification "is a miserable process to measure". Mass-balance ^{15}N tracers may underestimate nitrogen fixation by almost half (Newell et al., 2016a) and are typically limited to mesocosm experiments. N_2:Ar methods are also typically constrained to mesocosm experiments, and they can also take longer to conduct and may not capture heterogeneity within the sampled ecosystem (Groffman et al., 2006).

In light of recent research that questions the relative importance of denitrification to SCM nitrogen removal, N_2:Ar methods or mass balance ^{15}N tracers should be used to determine the balance of nitrogen fluxes in SCM sediments and distinguish between temporary nitrate removal (e.g., assimilation, DNRA) and permanent nitrogen removal (e.g., denitrification, anammox). Nitrogen fixation and denitrification co-occur (Fulweiler et al., 2013), so measuring the net effects of these processes and the rates of other nitrogen cycling processes is key to understanding if SCMs are sources or sinks for nitrogen.

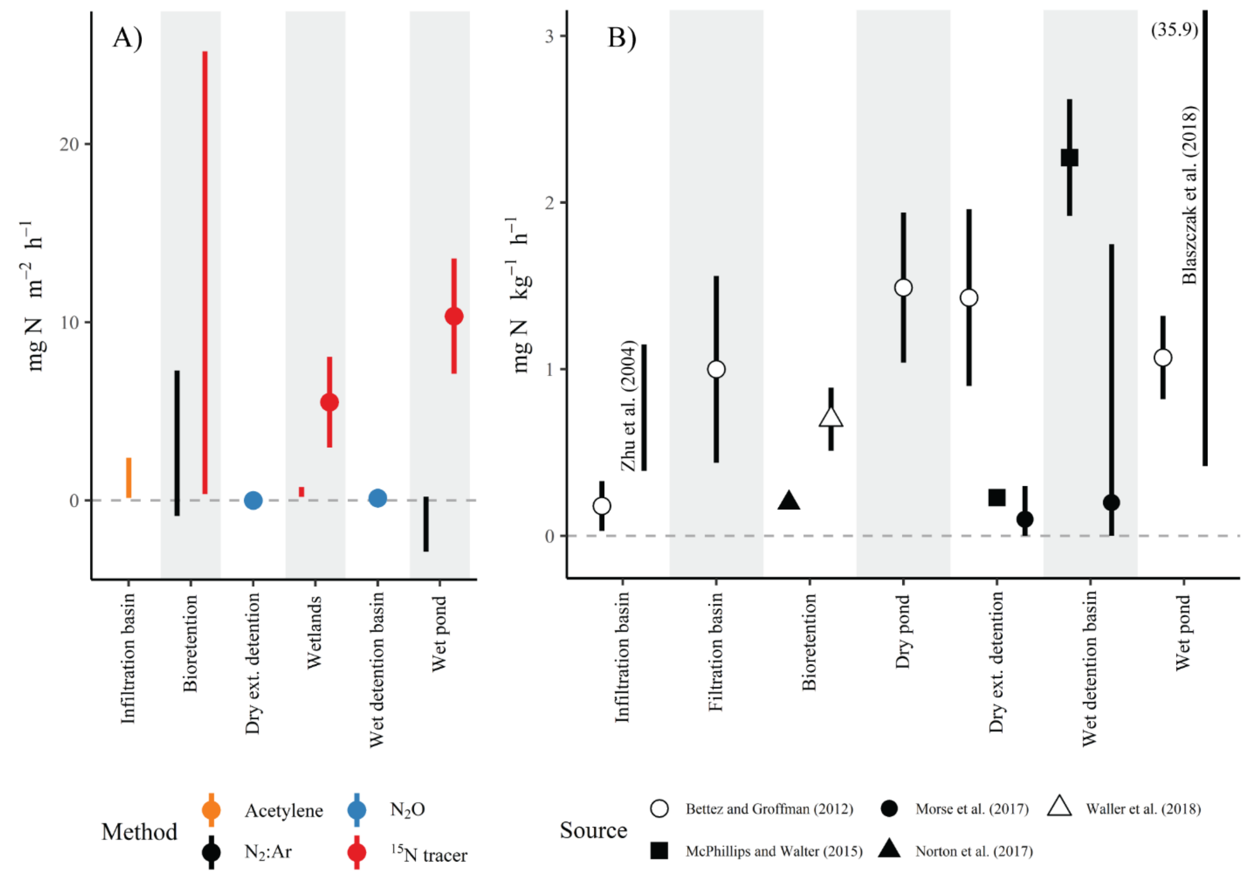

Figure 1.1. A) Areal rates of denitrification or net N_2 flux (N_2:Ar) and **B)** rates of denitrification based on denitrification enzyme assay (DEA) from SCM nitrogen cycling studies (Table 1.2). SCM types for each panel are ordered from less frequently inundated (left) to more frequently inundated (right). Some rates were converted from published units to above units reported in the majority of studies. ^{15}N tracer studies that reported only mass-based rates of denitrification are not shown (n=1).

Table 1.2. SCM studies that have measured denitrification (Adapted from Norton et al., 2017)

Area-based rates						
Source	**SCM Type**	**Location**	**Time** (frequency)	**Method**	**Rate** (Published units)	**Rate** (mg N m^{-2} h^{-1})
Norton et al. (2017)	Bioretention	Portland, OR, USA	October (1)	N_2:Ar	-63 to 520 µmol N m^{-2} h^{-1}	-0.88 to 7.28
Payne et al. (2014)	Bioretention	Victoria, Australia	July (1), August (1), October (1)	^{15}N tracer	25 – 1800 µmol N m^{-2} h^{-1}	0.35 – 25.2
Morse et al. (2017)	Dry ext. detention basin	Ithaca, NY, USA	April - October	N_2O	0.03 ± 0.0006 g N m^{-2} yr^{-1}	$3.36 \times 10^{-3} \pm 5.6 \times 10^{-5}$
Zhu et al. (2004)	Infiltration basin	Phoenix, AZ, USA	July (1)	Soil core/C_2H_2	3.3 – 57.6 mg N m^{-2} d^{-1}	0.137 – 2.39
Newcomer Johnson et al. (2014)	Wetlands (inline)	Baltimore County, MD, USA	Summer (2), Winter (1)	"push-pull" ^{15}N tracer	132.3 ± 61.1 mg N m^{-2} d^{-1}	5.513 ± 2.55

Lancaster et al. (2016)	Wetlands	Yale Myers Experimental Forest, CT	November (1) January (1)	^{15}N tracer	14 – 53 μmol N m^{-2} h^{-1}	0.19 – 0.74
Morse et al. (2017)	Wet detention basin	Ithaca, New York, USA	April - October	N_2O	1.09 ± .02 g N m^{-2} yr^{-1}	0.124 ± .0025
Gold et al. (2017a)	Wet pond	Jacksonville, NC	June (1), September (1)	N_2:Ar	-206 to 14.8 μmol N m^{-2} h^{-1}	-2.88 to 0.207
Newcomer Johnson et al. (2014)	Wet pond	Baltimore County, MD, USA	Summer (2), Winter (1)	"Push-pull" ^{15}N tracer	248.2 ± 77.4 mg N m^{-2} d^{-1}	10.34 ± 3.23
Mass-based rates						
Source	**SCM Type**	**Location**	**Time (**frequency**)**	**Method**	**Rate (**Published units**)**	**Rate (**mg N kg^{-1} h^{-1}**)**
Norton et al. (2017**)**	Bioretention	Portland, OR, USA	October (1)	DEA	0.20 mg N kg^{-1} h^{-1}	0.20
Waller et al. (2018)	Bioretention	MD, VA, NC	November/December (1)	DEA	0.7 ± 0.19 mg N kg^{-1} h^{-1}	0.7 ± 0.19
McPhillips and Walter (2015)	Dry detention basin	Ithaca, NY, USA	October (1)	DEA	0.23 mg N kg^{-1} h^{-1}	0.23
Morse et al. (2017)	Dry detention basin	Ithaca, NY, USA	June (1)	DEA	0 – 0.3 mg N kg^{-1} h^{-1}	0 – 0.3
Bettez and Groffman (2012)	Dry extended detention	Baltimore County, MD, USA	September (1)	DEA	1.43 mg N kg^{-1} h^{-1}	1.43
Bettez and Groffman (2012)	Dry pond	Baltimore County, MD, USA	September (1)	DEA	1.49 mg N kg^{-1} h^{-1}	1.49
Bettez and Groffman (2012)	Filtration basin	Baltimore County, MD, USA	September (1)	DEA	1.00 mg N kg^{-1} h^{-1}	1.00
Bettez and Groffman (2012)	Infiltration basin	Baltimore County, MD, USA	September (1)	DEA	0.18 mg N kg^{-1} h^{-1}	0.18
Zhu et al. (2004)	Infiltration basin	Phoenix, AZ, USA	July (1)	DEA	390 – 1151 ng N g^{-1} h^{-1}	0.39 – 1.15
Harrison et al. (2011)	Wetlands	Baltimore County, MD, USA	June – August & November - December	"Push-pull" ^{15}N tracer	147 ± 29 μg N kg^{-1} d^{-1}	0.00613 ± 0.0012
McPhillips and Walter (2015)	Wet detention basin	Ithaca, NY, USA	October (1)	DEA	2.27 mg N kg^{-1} h^{-1}	2.27
Morse et al. (2017)	Wet detention basin	Ithaca, NY, USA	June (1)	DEA	0 – 1.75 mg N kg^{-1} h^{-1}	0 – 1.75
Blaszczak et al. (2018)	Wet pond	Baltimore, MD	June (1)	N_2:Ar (Potential)	0.42 – 35.9 mg N kg^{-1} h^{-1}	0.42 – 35.9
Blaszczak et al. (2018)	Wet pond	Boston, MA	June (1)	N_2:Ar (Potential)	0.42 – 35.9 mg N kg^{-1} h^{-1}	0.42 – 35.9
Blaszczak et al. (2018)	Wet pond	Durham, NC	June (1)	N_2:Ar (Potential)	0.42 – 35.9 mg N kg^{-1} h^{-1}	0.42 – 35.9
Blaszczak et al. (2018)	Wet pond	Miami, FL	August (1)	N_2:Ar (Potential)	0.42 – 35.9 mg N kg^{-1} h^{-1}	0.42 – 35.9
Blaszczak et al. (2018)	Wet pond	Minneapolis-St.Paul, MN	August (1)	N_2:Ar (Potential)	0.42 – 35.9 mg N kg^{-1} h^{-1}	0.42 – 35.9

Blaszczak et al. (2018)	Wet pond	Phoenix-Scottsdale, AZ	August (1)	N_2:Ar (Potential)	0.42 – 35.9 mg N kg^{-1} h^{-1}	0.42 – 35.9
Blaszczak et al. (2018)	Wet pond	Portland, OR	August (1)	N_2:Ar (Potential)	0.42 – 35.9 mg N kg^{-1} h^{-1}	0.42 – 35.9
Blaszczak et al. (2018)	Wet pond	Salt Lake City, UT	July (1)	N_2:Ar (Potential)	0.42 – 35.9 mg N kg^{-1} h^{-1}	0.42 – 35.9
Bettez and Groffman (2012)	Wet pond	Baltimore County, MD, USA	September (1)	DEA	1.07 mg N kg^{-1} h^{-1}	1.07

Note: DEA = denitrification enzyme assay, Wetlands (inline) = constructed wetlands that replaced a stream channel, N_2:Ar (Potential) = potential denitrification assays that used N_2:Ar rather than acetylene reduction.

Heterotrophic nitrogen fixation in nitrogen cycling studies

Nitrogen fixation, the conversion of N_2 gas to NH_4^+ by heterotrophic bacteria, has been measured using acetylene reduction assays (Hardy et al., 1968) for almost fifty years, and these measurements informed thinking that nitrogen fixation was not an important nitrogen input in most aquatic environments. We now know that these acetylene reduction assays can significantly alter the sediment microbial community (Fulweiler et al., 2015), renewing questions about the importance of nitrogen fixation in aquatic ecosystems. Recent studies have measured large rates of net nitrogen fixation in estuarine environments using N_2:Ar measurements, indicating that heterotrophic nitrogen fixation may play a larger role in aquatic nitrogen cycling than previously thought (Foster and Fulweiler, 2014; Fulweiler et al., 2013, 2007; Newell et al., 2016a, 2016b; Rao and Charette, 2012).

The rapidly increasing use of microbial methods for identifying active microbial communities and quantifying functional gene expression through quantitative PCR (qPCR) and metagenomics testing has allowed for more precise measurements of bacteria and archaea community structure. This methodology is especially useful for studying the nitrogen cycle because these microbial organisms are responsible for modulating each step of the nitrogen cycle. Recent genetic work measuring potential nitrogen fixation by targeting *nifH* gene expression or measuring total abundance of *nifH* has provided evidence of the importance of nitrogen fixation in certain areas of the estuarine environment (Andersson et al., 2014; Fulweiler et al., 2013; Newell et al., 2016b), and these genetic results have been corroborated with direct measurements of net N_2 fluxes from sediment cores (Fulweiler et al., 2013; Newell et al., 2016b). These studies have determined that a small number of heterotrophic nitrogen fixing bacteria can dominate and outcompete denitrifiers in organic-rich sediments (Newell et al., 2016b). Poor carbon quality and low-oxygen conditions may also allow heterotrophic nitrogen fixers to outcompete denitrifiers in aquatic sediments (Eyre et al., 2013; Fulweiler et al., 2013, 2007). The dominance of heterotrophic nitrogen fixers over denitrifiers in SCM sediments would lead to more nitrogen fixation than denitrification, essentially flipping sediments from nitrogen sinks to sources. The techniques for measuring denitrifier and nitrogen-fixer genes have not yet been applied together to study SCM nitrogen cycling but could be utilized together in the future. Functional genes and molecular metrics associated with parts of the nitrogen cycle (e.g., denitrification, nitrification) have been studied in SCMs (Chen et al., 2013; Morse et al., 2018, 2017; Waller et al., 2018), but none have measured the nitrogen fixing community. Along with measurements of net N_2 fluxes and mass-balance ^{15}N tracers, microbial methods should be used to better understand the balance of nitrogen cycling processes in SCMs. Without the measurement of nitrogen fixation or the heterotrophic nitrogen-fixing community that can add new nitrogen to the system, studies are likely capturing only part of the picture, possibly inflating the importance of SCMs as hot spots of net nitrogen removal via denitrification.

Dissimilatory nitrate reduction to ammonium (DNRA)

Dissimilatory nitrate reduction to ammonium (DNRA) is often overlooked as a fate of nitrate in SCMs, but some types of SCMs may have conditions favorable for DNRA - low nitrate concentrations, organic-rich sediments, low-oxygen conditions, and high iron concentrations (Burgin and Hamilton, 2007; Kessler et al., 2018). The conditions that support DNRA are similar to those which are needed for denitrification, and the ratio of nitrate to carbon seems to determine which pathway reduces nitrate (Burgin and Hamilton, 2007; Kessler et al., 2018; Morrissey et al., 2013). There is some indirect evidence for DNRA in SCMs from nitrogen loading mass-balance studies. For example, some SCMs, especially deeper ponds that are designed to settle suspended particles and enhance denitrification, have been shown to increase ammonium concentrations based on short-term loading studies (Koch et al., 2014). However, this could also be due to decreased nitrification in low-oxygen conditions (Koch et al., 2014). Also, nitrate uptake in sediments of older ponds that also exhibited net nitrogen fixation suggests that DNRA could have occurred (Gold et al., 2017a). Of the few studies that have directly measured rates and the relative importance of DNRA in SCMs or man-made aquatic ecosystems, DNRA can range from constituting a relatively minor nitrate reduction pathway in wetlands and ponds (Messer et al., 2017; Nogaro and Burgin, 2014; Scott et al., 2008) to exceeding rates of denitrification in urbanized tidal creeks (Dunn et al., 2013), groundwater of constructed wetlands treating wastewater (Jahangir et al., 2017), and other freshwater ecosystems (Burgin and Hamilton, 2007).

Rates of DNRA have typically been measured using ^{15}N tracers, but similar to techniques described for denitrification and nitrogen fixation, genetic methods can be used to measure the prevalence of genes that encode the enzyme responsible for DNRA, *nrfA*. The abundance of DNRA communities, as measured by *nrfA* abundance via qPCR, correlates with rates of DNRA (Smith et al., 2015; Song et al., 2014). Future research should attempt to quantify DNRA in SCMs through the use of ^{15}N mass balances and genetic measurements. This future research should also examine the relationships between DNRA and environmental controls on DNRA found in other aquatic ecosystems (e.g., carbon quality, oxygen concentrations, nitrate concentrations) so that management actions can be directed to promote denitrification over DNRA.

Biotic assimilation and remineralization

Transformations of nitrogen in SCMs can be biological rather than chemical, with nitrogen in SCMs being assimilated by soil microbes (Messer et al., 2017; Payne et al., 2014), algae (DeLorenzo et al., 2012; Gold et al., 2017b; Lewitus et al., 2008; Reed et al., 2016), and vegetation (Lenhart et al., 2012; Messer et al., 2017; Payne et al., 2014). Plant, algal, and microbial uptake of nitrogen can be important sinks of nitrogen in SCMs (Lenhart et al., 2012; Messer et al., 2017; Morse et al., 2018; Payne et al., 2014) and can supply organic matter to the sediments of SCMs (Merriman et al., 2017). Organic matter accumulation in SCMs could have an equivocal effect on denitrification rates in SCMs depending on the depth. In shallower or intermittently inundated SCMs, denitrifying bacteria could utilize accumulated organic matter as a substrate and the concurrent remineralization of organic matter could produce microsites for coupled nitrification-denitrification to occur. Denitrification of nitrate from the water column, however, may be lower in shallower SCMs that are densely vegetated because of competition for nitrate with plants (Morse et al., 2018). In deeper SCMs that have longer residence times, high levels of organic matter could produce extended anoxic conditions in the bottom water. Stratification can occur during warm temperatures in deep SCMs (Song et al., 2013) and can contribute to phosphorus release (Duan et al., 2016; Gold et al., 2017a; Song et al., 2013), driving down N:P ratios in the water column and promoting nitrogen limitation observed in deep

SCMs (Gold et al., 2017a; Reed et al., 2016). In some deep SCMs, high rates of remineralization promoted by alternating low and high-oxygen conditions caused by seasonal or storm-based mixing are likely to result in more recalcitrant (i.e., High C:N) carbon pool, which could favor nitrogen fixers over denitrifiers (Eyre et al., 2013; Fulweiler et al., 2013, 2007). Low quality carbon in SCMs could also originate from terrestrial sources (Schroer et al., 2018), and help promote the dominance of nitrogen fixers over denitrifiers. Low-nitrogen and low-oxygen water columns and organic-rich sediments from intense remineralization also could promote DNRA (Burgin and Hamilton, 2007; Kessler et al., 2018), leading to increased internal loading of nitrogen.

Unless plant or algal material is buried, biotic assimilation is only a temporary sink of nitrogen because of the potential for remineralization of nitrogen contained in organic matter. Assimilated nitrogen in SCMs is eventually either buried in sediments, exported downstream, or remineralized and transformed through further biological or chemical transformations. For this reason, traditional studies of SCM nitrogen removal that utilize load-based measurements should aim for sampling periods that span periodicity of both plant and algae growth and senescence and also aim to measure sediment properties (e.g., C:N, organic matter %, etc.). Studies that utilize isotopic tracer methods to partition assimilation between soils, algae, and plants will be especially helpful in better understanding the role of biotic assimilation and remineralization. The process of organic matter accumulation and remineralization should continue to be characterized in SCMs due to its role in internal nutrient loading and nitrogen cycling.

Opportunities for research

There is ample opportunity for research on nitrogen cycling within SCMs. This review identified a total of twelve studies that reported rates of denitrification within stormwater control measures, of which only four utilized direct measurements (Table 1.2). This review also found two studies that reported rates or relative importance of DNRA and three that reported rates or relative importance of biotic assimilation. There exists an opportunity to characterize nitrogen cycling processes over all seasons and locations.

The effectiveness of nitrogen removal from stormwater ponds (via loading measurements) can vary seasonally (Rosenzweig et al., 2011), so seasonal investigations of nitrogen cycling within SCMs are critical for characterizing nitrogen cycling processes and understanding controlling mechanisms. This information is also important for predicting how SCMs will function in the future with increasing effects from climate change. Most studies of nitrogen cycling within SCMs have been conducted during the summer and early fall (Figure 1.2), leaving the late fall, winter, and spring months relatively understudied. It should be noted, however, that three ^{15}N sampling events (Payne et al., 2014) (July, August, and October) were conducted in the southern hemisphere, so this experiment adds resolution to “winter” months (cross-hatched in Figure 1.2). Future research should address this gap in knowledge by conducting seasonal or monthly experiments to characterize nitrogen cycling in SCMs throughout the year.

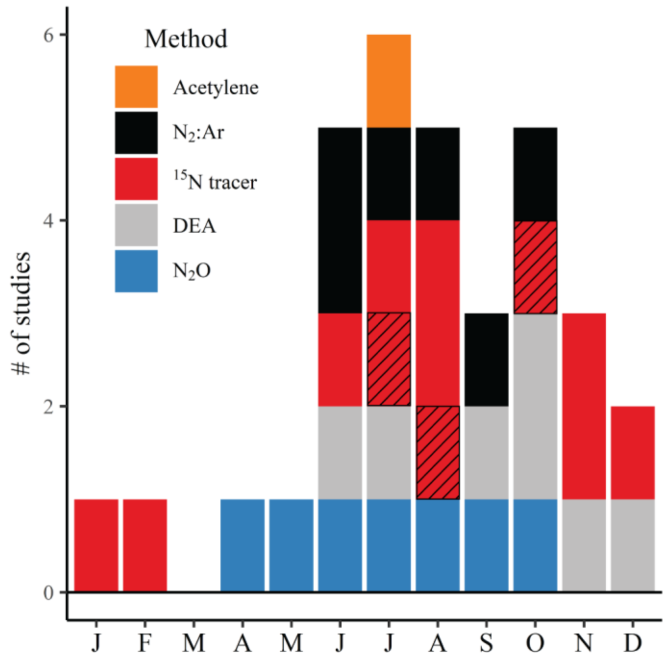

Figure 1.2. Histogram of sampling dates from SCM nitrogen cycling studies by month. Cross-hatched bars indicate studies conducted in the southern hemisphere.

Most of the studies investigating nitrogen cycling in SCMs have taken place in the eastern US (n=8) (Figure 1.3). Two studies were located in the western US in varying climatic regions (Portland, OR & Phoenix, AZ), one study spanned 8 cities across the US, and one study took place in southeastern Australia (Victoria) (Figure 1.3). Due to the varying climatic regions of the study sites and differences in SCM types, seasonal dynamics of nitrogen cycling in SCMs remain unclear at any single site. The types of SCMs that are implemented in different climatic regions can differ drastically (McPhillips and Matsler, 2018), so studies on SCM nitrogen cycling in under-sampled or un-sampled locations (Figure 1.3) will be important for characterizing nitrogen cycling for the entire range of SCM types. It is important to note that the studies reviewed and topics discussed in this article may be inherently biased towards SCMs that are more prevalent in the eastern US due to the locations of existing SCM nitrogen cycling studies. The in-depth characterization of nitrogen cycling within SCMs at any location, even in systems where nitrogen is not limiting (higher N:P ratio), would be a worthwhile endeavor due to the scarcity of studies on the topic.

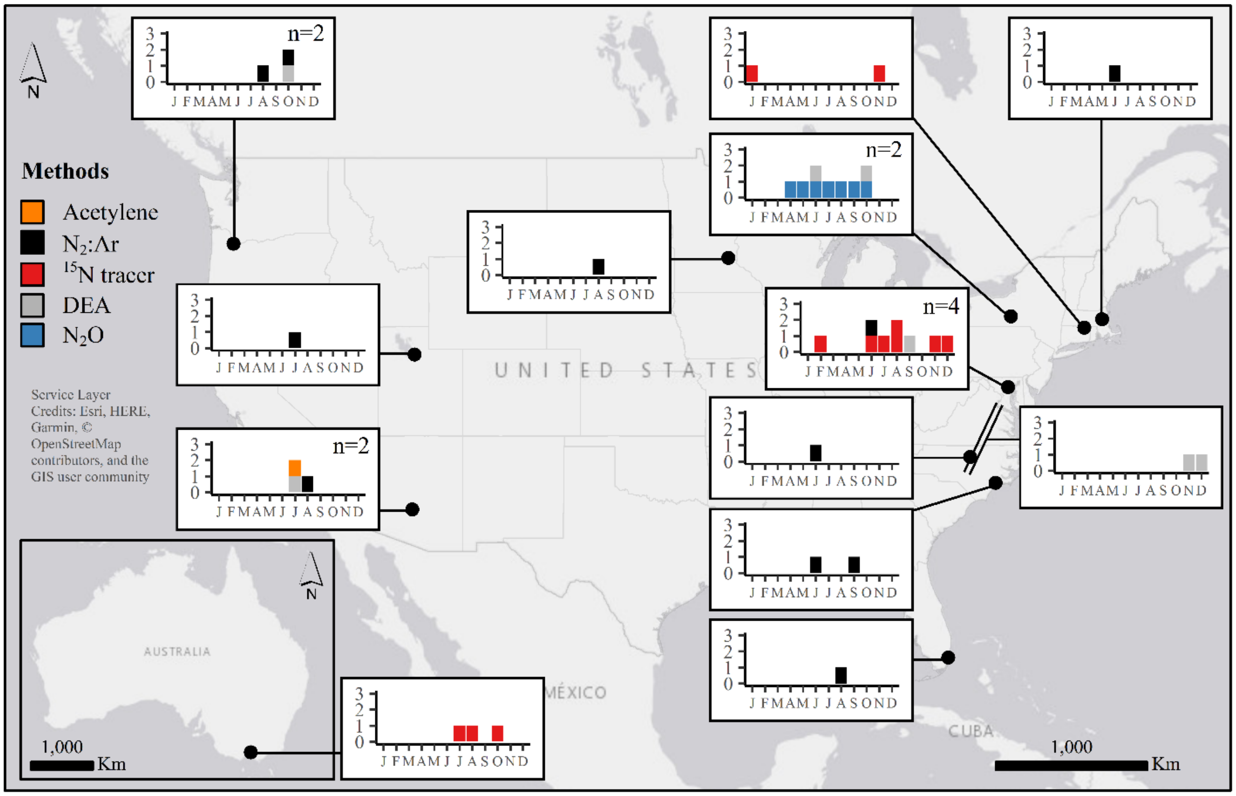

Figure 1.3. Study sites of SCM nitrogen cycling studies and histograms of sampling event timing by month.

Another opportunity for research is the possible tradeoff between the management of nitrogen and phosphorus using SCMs and the interactions between nitrogen and phosphorus cycling in SCMs. The conditions that may promote denitrification in SCMs, such as low-oxygen conditions and a suitable carbon source, can promote the release of inorganic phosphorus from SCM sediments and its export downstream (Collins et al., 2010; Duan et al., 2016; Gold et al., 2017a; Song et al., 2017, 2013). On the other hand, aerobic conditions would decrease phosphorus release from sediments but would discourage denitrification and promote mineralization and nitrification. Rooted vegetation can oxygenate soils and prevent the release of sediment-bound phosphorus, and some studies have recommended that more rooted vegetation can be used to promote phosphorus retention in SCMs (Duan et al., 2016; Mallin et al., 2002). With regard to nitrogen, rooted vegetation in SCMs can increase nitrogen retention within SCMs due to plant assimilation (Messer et al., 2017; Morse et al., 2018; Payne et al., 2014), but the effects on denitrification can vary greatly in aquatic environments from decreased denitrification caused by competition for nitrate with plants (Morse et al., 2018) to increased denitrification due to the stimulation of nitrification-denitrification by plant roots (Kreiling et al., 2011). Also, as noted in section 6, the release of inorganic phosphorus from SCM sediments could promote nitrogen limitation by increasing the N:P ratio, possibly increasing rates of nitrogen fixation or DNRA. Measuring phosphorus cycling in SCMs along with the nitrogen cycling measurements suggested in this review would provide a more complete understanding of how SCMs function and how they can affect downstream water quality.

Conclusions

Denitrification is assumed to be an important process of nitrogen removal within SCMs, but very few studies have directly measured this process. Recent studies that utilized direct measurements in SCMs showed that denitrification was less important than previously assumed, and research from other aquatic environments suggests that other nitrogen cycling processes may be important in SCMs.

Nitrogen fixation can exceed denitrification in some open-water SCM sediments. A working hypothesis is that conditions within some open-water SCMs, such as stormwater ponds, could promote the dominance of heterotrophic nitrogen-fixing bacteria over denitrifiers because of the presence of extended anoxic conditions, extreme nitrogen limitation, and poor sediment carbon quality (Figure 1.4). Research from estuarine environments has observed the same phenomenon of net sediment nitrogen fixation. Conditions within deeper open-water SCMs, such as organic matter amount and quality, could also promote DNRA or assimilation over denitrification when nitrate is available (Figure 1.4), but this area requires additional research. Nitrate uptake in shallow or intermittently inundated SCMs can be dominated by assimilation by plants and soils rather than by denitrification, but assimilation is likely more dominant when DIN is low (Figure 1.4). Microbial studies within SCMs have determined that organic matter quality may also play a part in determining the pathway of nitrate reduction (i.e., denitrification vs. DNRA) (Figure 1.4). Large amounts of algae reported in open-water SCMs suggests that algal uptake could be an important pathway of temporary nitrogen removal that can be exported, buried, internally recycled, or denitrified (Figure 1.4).

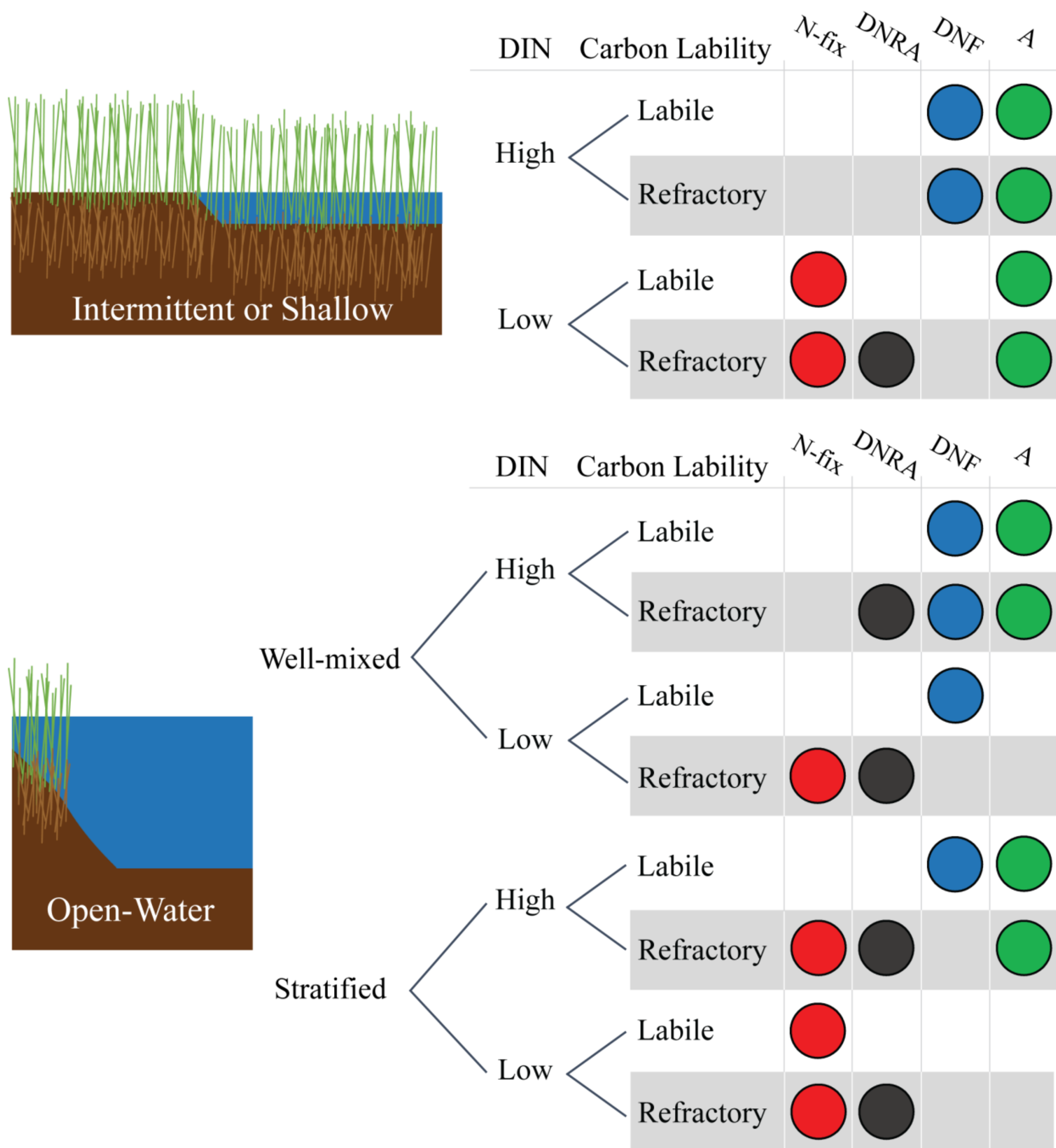

Figure 1.4. Conceptual diagram showing nitrogen cycling processes that are hypothesized to be important in different types of SCMs. This diagram does not show hypothesized fate of nitrogen as nitrogen fixation adds nitrogen to the system and both DNRA and assimilation are temporary transformations of nitrogen that can then lead to remineralization, denitrification, burial, or export from the SCM. Note: DIN = Dissolved inorganic nitrogen, N-fix = Nitrogen fixation, DNF = Denitrification, A= Plant, algal, and soil assimilation.

The scarcity of nitrogen cycling measurements within SCMs means that there is abundant opportunity for research. Seasonal variation in SCM function has been poorly characterized in any single location, and the eastern US by far has had the most studies. Seasonal studies of various types of SCMs will be essential for effective stormwater management and water quality improvement in urban areas, especially to plan for the effects of climate change. The connection between nitrogen cycling and phosphorus cycling has not been characterized in SCMs, but future work on this topic is necessary to understand the impacts of nitrogen removal on phosphorus removal and vice versa. Nitrogen cycling in SCMs should be measured by utilizing direct measurements of N_2:Ar, mass-balance ^{15}N tracer experiments that capture both nitrogen removal and addition, or microbial methods that include a measure of *nifH* expression with the more commonly measured denitrification genes. The process of nitrogen fixation must be accounted for in future studies because it produces new bioavailable nitrogen to the system. Ideally, a combination of these methods would be used to examine specific nitrogen removal pathways as well as the balance between them. DNRA, assimilation, remineralization (or sediment carbon quantity and quality), and the controlling factors for these processes should also be analyzed so that managers can promote denitrification in SCMs.

SCMs have shown potential to mitigate negative effects of urbanization on hydrology and water quality, but their ability to remove nitrogen has been extremely variable. The internal nitrogen cycling processes that occur in SCMs should be characterized so that managers can implement efficient management strategies that improve SCM function and downstream water quality.

CHAPTER 2: SEASONALITY OF NITROGEN CYCLING IN COASTAL STORMWATER PONDS

Introduction

Stormwater runoff from urban areas can have negative ecological consequences for downstream waters (Paul and Meyer, 2001; Walsh et al., 2005), but structural stormwater control measures (SCMs) aim to mitigate the negative effects of stormwater runoff (Burns et al., 2012) . One of the most common types of SCMs in place today are stormwater wet ponds (SWPs) which collect fast-moving stormwater during storm events, slowly release stormwater over the days following a storm, and maintain a permanent water level (National Research Council, 2009). Stormwater runoff from urban areas is often high in nutrient concentrations, such nitrogen (N) and phosphorus (P) (Sarah E. Hobbie et al., 2017; Kaushal et al., 2011), and SWPs are designed to promote treatment of stormwater runoff through the settling of particulates and extended periods of contact with carbon-rich sediments and plants (Collins et al., 2010; Mallin et al., 2002).

Stormwater ponds are often regarded as net N sinks and hotspots for permanent N removal (Bettez and Groffman, 2012; Collins et al., 2010), but recent research shows that this prevailing assumption has been informed mostly by indirect or proxy measurements of SCM N cycling (Gold et al., 2019a). Denitrification is the microbially-mediated process that permanently removes bioavailable nitrate (NO_3^-) from aquatic ecosystems by converting it to inert dinitrogen gas (N_2)(Seitzinger et al., 2006). Denitrification generally requires a suitable carbon source, low-oxygen conditions, and NO_x (Eyre et al., 2013; Seitzinger et al., 2006), and SWPs generally fit the bill for all of these requirements (Bettez and Groffman, 2012; Duan et al., 2016; Moore and Hunt, 2012). Until recently, most studies of SWP N cycling have either utilized a mass-balance loading approach to determine the percent of nitrogen retained by an SWP or used indirect or proxy measurements to characterize certain nitrogen cycling processes (Gold et al., 2019a). In the case of mass-balance calculations, a portion of the nitrogen retained by a SWP is often attributed to denitrification even though the process of denitrification was not measured (Collins et al., 2010). Indirect or proxy measurements, such as denitrification enzyme assays (DEA)(Groffman et al., 2006), often measure potential rates of denitrification after additions of carbon and nitrate but do not account for relevant alternative processes of N cycling such as biotic NO_x uptake (plants, algae, or heterotrophic bacteria), dissimilatory nitrate reduction to ammonium (DNRA), or nitrogen fixation (Gold et al., 2019a).

Alternative nitrate removal pathways other than denitrification (Burgin and Hamilton, 2007) could play an important role in SCM nitrogen cycling (Gold et al., 2019a), and measurements of water quality in SWPs supports this idea. SWPs have been found to harbor high levels of algal biomass (DeLorenzo et al., 2012; Lewitus et al., 2008) and DOC derived from autochthonous sources (Kalev et al., 2020; Williams et al., 2016), indicating that some nutrients retained in SWPs can be transformed to organic forms. Direct measurements of nitrogen cycling show that biotic assimilation of NO_x and DNRA can be major pathways of nitrate removal during certain conditions in bioretention cells (Burgis et al., 2020; Norton et al., 2017; Payne et al., 2014) and stormwater wetlands (Messer et al., 2017; Rahman et al., 2019). Additionally, measurements of net N_2 fluxes from stormwater pond sediments showed that sediment nitrogen fixation can exceed rates of sediment denitrification, and both sediment and water column biotic assimilation can play a critical role in nitrate removal (Gold et al., 2017a). Results from this recent research suggests that SCMs can often function as transformers of nitrogen and may alternate between functioning as net sinks and net sources of nitrogen to downstream waters.

The seasonality of nitrogen cycling within SWPs has not been broadly characterized (Gold et al., 2019a; Rosenzweig et al., 2011), but seasonal measurements of SWP nitrogen cycling are key for understanding the effectiveness of SWPs as N sinks or transformers. Though the factors controlling SWP nitrogen cycling have not been characterized, factors that vary seasonally are likely important drivers of SWP nitrogen cycling (Rosenzweig et al., 2011). Temperature strongly influences the fate of nitrate in aquatic environments (Gardner and McCarthy, 2009), and higher temperatures in stormwater wetlands can promote denitrification (Rahman et al., 2019). Seasonal vegetation growth and senescence in stormwater wetlands can alter nutrient cycling (Macek et al., 2019), and sediment microbial community structure and function can change seasonally (Bledsoe et al., 2020). SWPs differ from stormwater wetlands by having less vegetation and much deeper water columns, but temperature drives seasonal water column stratification within SWPs that can decrease oxygen concentrations at the sediment-water interface (Gao et al., 2016; McEnroe et al., 2013; Song et al., 2013). Despite evidence of seasonal variation in factors relevant to SWP N cycling, no studies have characterized seasonal variation in SWP nitrogen cycling in any single location (Gold et al., 2019a).

To better understand the effectiveness of SWPs at removing stormwater N, this study aimed to characterize seasonal rates of sediment nitrogen cycling in SWPs in the southeastern US coastal plain. We selected three stormwater ponds and sampled them across a seasonal temperature gradient, excluding winter (n = 7). For each sampling event, we collected intact sediment cores and water from each site and conducted flow-through incubations to measure gas and nutrient fluxes from the sediment-water interface. During each flow-through incubation, we measured fluxes before and after a nitrate-amendment to simulate “ambient” and “storm” conditions.

Methods

Site Description

Three SWPs located in Beaufort, NC were selected for sampling (Figure 2.1). The ponds spanned an age gradient from less than 1 to 8 years old at the time of initial sampling in June 2017, and the ponds drained similar land uses (i.e., residential & light commercial)(Table 2.1). Pond size and depth ranged from Pond 1, the newest, largest, and deepest pond, to Pond 3, the oldest, smallest, and shallowest pond, with Pond 2 having an intermediate age and depth (Table 2.1). Our aim for this sampling design was to capture seasonal patterns across a range of SWP characteristics rather than to focus on how specific physical attributes (e.g., age, size, depth) affect SWP nitrogen cycling.

Study SWPs were sampled seven times, and for each sampling event, three replicate sediment cores were extracted from the middle of each SWP using a PVC coring apparatus while aboard a small boat. Sediment core tubes were 6.4 cm in diameter and 30 cm long, and the tubes were filled with approximately 17 cm of sediment and site-specific water overlying the sediment (approximately 400 ml). Once collected from the study SWP, cores were sealed on the top and bottom of the core tube using rubber stoppers, briefly stored in a cooler (maximum 3 hours), and transported to the UNC Institute of Marine Sciences (IMS) in Morehead City, NC. Water from each study SWP (60 L) was collected from depth using a bilge pump on the end of a PVC pipe and transported with the sediment cores.

Table 2.1. Study SWP information

Name	Surface area (m^2)	Perimeter (m)	Surface area/perimeter	Sample depth range (m)	Date built	n
Pond 1 (P1)	7258.2	555.2	13.1	2 – 2.9	4/2017	7
Pond 2 (P2)	1157.7	169.7	6.8	1.9 – 2.5	12/2014	6
Pond 3 (P3)	2235.4	298.6	7.5	1.1 - 2	1/2010	7

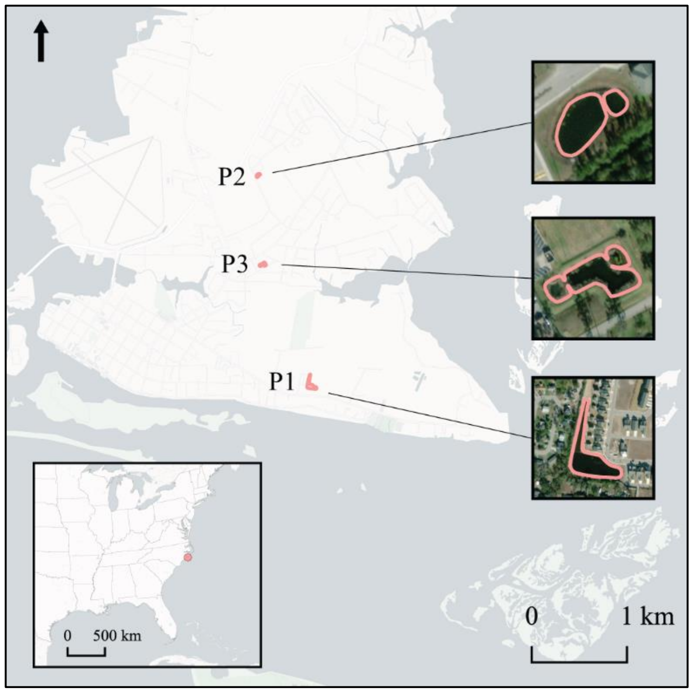

Figure 2.1. Overview map of the study area.

Water and sediment properties

The temperature and dissolved oxygen content of surface and bottom water was measured at each study pond during sampling events using a YSI 6600EDS-S water quality sonde. The relative thermal resistance to mixing (RTRM) was calculated following established methods (Wetzel, 2001), and values greater than 50 were considered to be indicative of stratification (Chimney et al., 2006; Song et al., 2013). Surface water samples from all SWPs were collected, filtered through Whatman GF/F filters (25 mm diameter, 0.7 µm nominal pore size), and analyzed for nitrate + nitrite (NO_x^-), ammonium (NH_4^+), orthophosphate (PO_4^{3-}), and total nitrogen (TN) with a Lachat Quick-Chem 8000 automated ion analyzer. Dissolved organic nitrogen (DON) was calculated by subtracting inorganic nitrogen concentrations from total nitrogen concentrations. Concentrations of chlorophyll-*a* in surface water samples were measured by filtering water samples (Whatman GF/F), sonicating and extracting frozen filters for 24 hours in a 90% acetone solution, and measuring the fluorescence of the solution with a Turner Designs Trilogy fluorometer (Welschmeyer, 1994).

Sediment cores were subsampled for sediment organic matter content (SOM) and carbon to nitrogen ratios (C:N) immediately after the flow-through core incubation experiment. SOM was measured by loss on ignition. Carbon and nitrogen content was measured in dried sediment samples using a Costech Elemental Combustion System with Elemental Analysis software and used to compute molar carbon to nitrogen ratios.

Sediment N fluxes

Dissolved gas and nutrient fluxes were measured from the sediment-water interface of intact sediment cores for ambient and NO_x-enriched conditions using flow-through incubation experiments (Gold et al., 2017a; Piehler and Smyth, 2011). SCM core incubation experiments took place over the span of two years (June 2017 – October 2019). The incubation experiments were conducted at *in situ* temperatures (determined in the field from YSI readings) and in the dark within an environmental chamber (Bally, Inc.). After sediment cores and water were brought to IMS, sediment cores and water were immediately placed within the environmental chamber at *in situ* temperature. The top stopper of each sediment core was then removed, and cores were submerged in site-specific water for approximately two hours. After two hours, the tops of cores were capped with water-tight plexiglass tops containing ports for Tygon tubing, and the ports were connected to the flow-through system. The flow-through system consisted of a peristaltic pump and Tygon tubing that pulls site-specific water into the core at the top of the core tube and out of the core from 2 cm above the sediment-water interface at a rate of 1 ml/min.

Cores were left overnight to equilibrate for 17 hours, which was slightly more than two residence times of the overlying water within the sediment core tubes. The following day, 5 ml water samples were collected from the inflow and outflow each core at hours 17 and 22 of the incubation, and dissolved N_2, O_2, and Ar concentrations were measured using a membrane inlet mass spectrometer (MIMS)(Kana et al., 1998). Inflow water samples were obtained for each study SWP (i.e., each set of three cores) using two bypass lines tubing that flowed through the entire flow-through system but did not flow over cores. Water was also collected for nutrient analysis at 20 hours, filtered, and analyzed using methods described above. After 24 hours in the flow-through system, the source water for the flow-through system was enriched with $NaNO_3$ so the concentration of nitrate (NO_3^-) was raised by 30 µM. Water samples were taken from the source water bins 10 minutes after NO_x addition and analyzed for nutrient concentrations to verify correct nutrient amounts were added. After 17 hours of nitrate-enriched conditions, water samples were again collected and measured for gas and nutrient concentrations.

Net N_2 and O_2 fluxes were calculated using N_2 to Ar ratios (N_2:Ar), O_2:Ar ratios (O_2:Ar), and the following equation:

$$flux = (C_{out} - C_{in}) \times \frac{flow\ (ml\ \cdot\ min^{-1})}{area\ (m^2)}$$

where C represents N_2:Ar or O_2:Ar, flow is the pumping rate of 1 ml/min, and area is the surface area of the sediment-water interface in the sediment core tube (0.0032 m^2). The two measurement events before the nitrate-enrichment represent “ambient” or *in situ* conditions, and values from both measurement events were averaged. The two measurement events after the nitrate enrichment were averaged and represent "nitrate-enriched" conditions that aim to simulate increased nitrate concentrations following a storm event. A nitrate-enriched concentration of 30 µM was chosen because this concentration of nitrate was typical in stormwater ponds in this region measured previously (Gold et al., 2019b, 2017b).

Data analysis

To compare measurements by temperature, all sampling events were classified as "cool" or "hot" based on the incubation temperature used in the flow-through core experiment. Sampling events classified as "cool" had incubation temperatures ranging from 19 - 22 ˚C (n = 3), and "hot" sampling events had incubation temperatures ranging from 26 – 31 ˚C (n = 4). Sediment core gas and nutrient fluxes were separated into ambient and NO_x-enriched conditions for each temperature class, and gas and nutrient fluxes from all four groups ("cool" and "hot" x "ambient" and "NO_x-enriched") were tested for significant differences using Kruskal-Wallis and Dunn's tests ("cool" n = 27, "hot" n = 31, $\alpha = 0.05$).

An estimate of the percent of NO_x uptake that was permanently removed via denitrification after NO_x-enrichment was calculated using the following formula:

$$\%\ NO_x\ denitrified = -100 \cdot \frac{Net\ N_2\ Flux}{NO_x\ Flux}$$

This estimate compares the amount of denitrification to the amount of NO_x taken up by sediments, where a value of 100% would mean that the amount of NO_x-N taken up by the sediments was equal to the amount of N released from the sediments via denitrification (as N_2-N). A value greater than 100%, where denitrification exceeds NO_x uptake, would suggest that in addition to denitrification of water column NO_x, coupled nitrification-denitrification was occurring (Von Korff et al., 2014). Cores that had positive NO_x fluxes, indicating that the sediments were releasing NO_x after NO_x additions were removed for this analysis (“cool” n = 4, “hot” n = 2). This metric was used to estimate the fate of NO_x taken up by sediments, with high values indicating that denitrification was an important mechanism for NO_x removal and low values indicating that NO_x uptake was removed via temporary processes (i.e., assimilation or DNRA) and temporarily retained in the sediments. Significant differences in % NO_x denitrified between “cool” and “hot” conditions were calculated using a Kruskal-Wallis test ($\alpha = 0.05$).

All analyses were completed using R version 4.0.2 (R Core Team, 2020)

Results

Water and sediment properties

Dissolved organic nitrogen was the dominant form of dissolved nitrogen in the water column of all sampled SWPs during all sampling events (Table 2.2). Ammonium was the second most prevalent form of dissolved nitrogen, while NO_x concentrations were almost always below the detection limit (Table 2.2). The sampled SWPs varied in their sediment organic matter content and sediment C:N ratios with pond age and depth, with the newest and deepest pond having the highest SOM and C:N (P1) and the oldest and shallowest pond having the lowest SOM and C:N (P3) (Table 2.2).

Ambient DON concentrations were significantly positively correlated with SWP surface water temperature at the time of sampling, but temperature was not significantly correlated with any other water quality variables or sediment properties (Table A.1). Both RTRM and chl-a concentrations were positively correlated with SOM and C:N, driven primarily by differences between sample SWP depth where the deeper ponds had higher values of all four variables (Table 2.2, Table A.1).

After characterizing sampling events as either "hot" or "cool", the main differences in ambient SWP water quality between temperature classes were driven by DON and chl-a (Figure A.1). For all SWPs, median DON and chl-a concentrations were elevated during "hot" conditions, although these differences were only significant for P2 (Figure A.1). Other differences in ambient water quality were elevated median PO_4 concentrations and RTRM, although these differences were not significant (Figure A.1).

Table 2.2. Ambient water quality and sediment characteristics from sampled ponds (P1 & P3 n = 7, P2 n = 6). Concentrations of ON, NH_4, NO_x, and PO_4 are in µM.

Site	Date	Incubation Temp (C)	RTRM	[ON]	[NH_4]	[NO_x]	[PO_4]	OM (%)	C:N
P1	6/27/2017	28	196.5	29.18	1.65	0.05	0.18	-	-
	8/1/2017	26	36.4	37.94	0.88	0.04	0.35	24.01	-
	10/23/2017	22	32.3	27.29	2.14	0.00	0.18	34.02	36.35
	5/8/2018	19	129.4	17.75	0.40	0.00	0.04	18.41	34.15
	7/10/2018	28	201.1	28.11	0.96	0.00	0.20	26.45	30.47
	7/15/2019	31	165.3	27.22	0.57	0.00	0.20	23.77	46.35
	10/21/2019	20	9.1	20.99	1.67	0.27	0.22	18.86	42.78
	Mean		**110.0**	**26.92**	**1.18**	**0.05**	**0.20**	**24.25**	**38.02**
P2	8/1/2017	26	35.6	31.73	0.61	0.16	0.13	11.66	21.26
	10/23/2017	22	34.1	26.16	0.41	0.00	0.18	16.28	17.19
	5/8/2018	19	2.1	18.73	0.20	0.00	0.06	12.76	17.75
	7/10/2018	28	11.9	29.21	0.29	0.00	0.26	12.85	19.14
	7/15/2019	31	90.0	29.63	0.16	0.00	0.35	9.81	20.23
	10/21/2019	20	14.3	15.36	0.86	0.00	0.24	14.74	20.05
	Mean		**31.3**	**25.14**	**0.42**	**0.03**	**0.20**	**13.02**	**19.27**
P3	6/27/2017	28	4.4	30.98	0.67	0.23	0.13	-	-
	8/1/2017	26	10.4	39.82	0.60	0.15	0.13	2.72	11.21
	10/23/2017	22	21.6	37.84	0.45	0.00	0.14	5.67	10.56
	5/8/2018	19	2.8	14.68	0.32	0.00	0.09	8.45	12.26
	7/10/2018	28	4.1	21.36	0.57	0.00	0.16	4.85	11.70
	7/15/2019	31	24.2	26.18	0.32	0.00	0.14	3.12	11.87
	10/21/2019	20	-0.1	9.60	0.33	0.00	0.55	4.06	12.93
	Mean		**9.6**	**25.78**	**0.47**	**0.05**	**0.19**	**4.81**	**11.75**

Sediment N fluxes

Sediment TN fluxes during ambient conditions were significantly correlated with SWP sediment C:N and SOM (Table A.2), but there were no significant differences in sediment TN fluxes between "cool" and "hot" conditions (Figures 2.2, 2.3). Ambient TN fluxes were almost completely comprised of DON fluxes ($\rho = 0.96$, $p < 0.05$, Table A.2), and DON fluxes were significantly positively correlated with sediment C:N and SOM (Table A.2). NH_4 fluxes were small (<10 µmol NH_4-N m^{-2} hr^{-1}) and NO_x fluxes were often below detection (Figure 2.2). Median DON fluxes during "hot" conditions were slightly larger than during "cool" conditions, although this difference was not significant (Figure 2.2c). Net N_2 fluxes were generally small (-20 – 20 µmol N_2-N m^{-2} hr^{-1}) and alternated between net denitrification and net nitrogen fixation with no significant correlations with other measured variables (Figure 2.3).

Sediments had significantly lower TN fluxes after NO_x-enrichment, and compared to "cool" conditions, sediments during "hot" conditions had significantly more NO_x uptake and significantly lower net N_2 and O_2 fluxes (Figures 2.2, 2.3). NO_x fluxes were generally the largest sediment nutrient fluxes during NO_x-enriched conditions (Figure 2.2), and NO_x fluxes were significantly positively correlated with O_2 fluxes ($\rho = 0.73$, $p < 0.05$, Figure 2.4). Although not as strong as the correlation between O_2 and NO_x fluxes, O_2 fluxes were also positively correlated with net N_2 fluxes ($\rho = 0.30$, $p < 0.05$, Table A.2) and negatively correlated with DON fluxes ($\rho = -0.35$, $p < 0.05$, Table A.2).

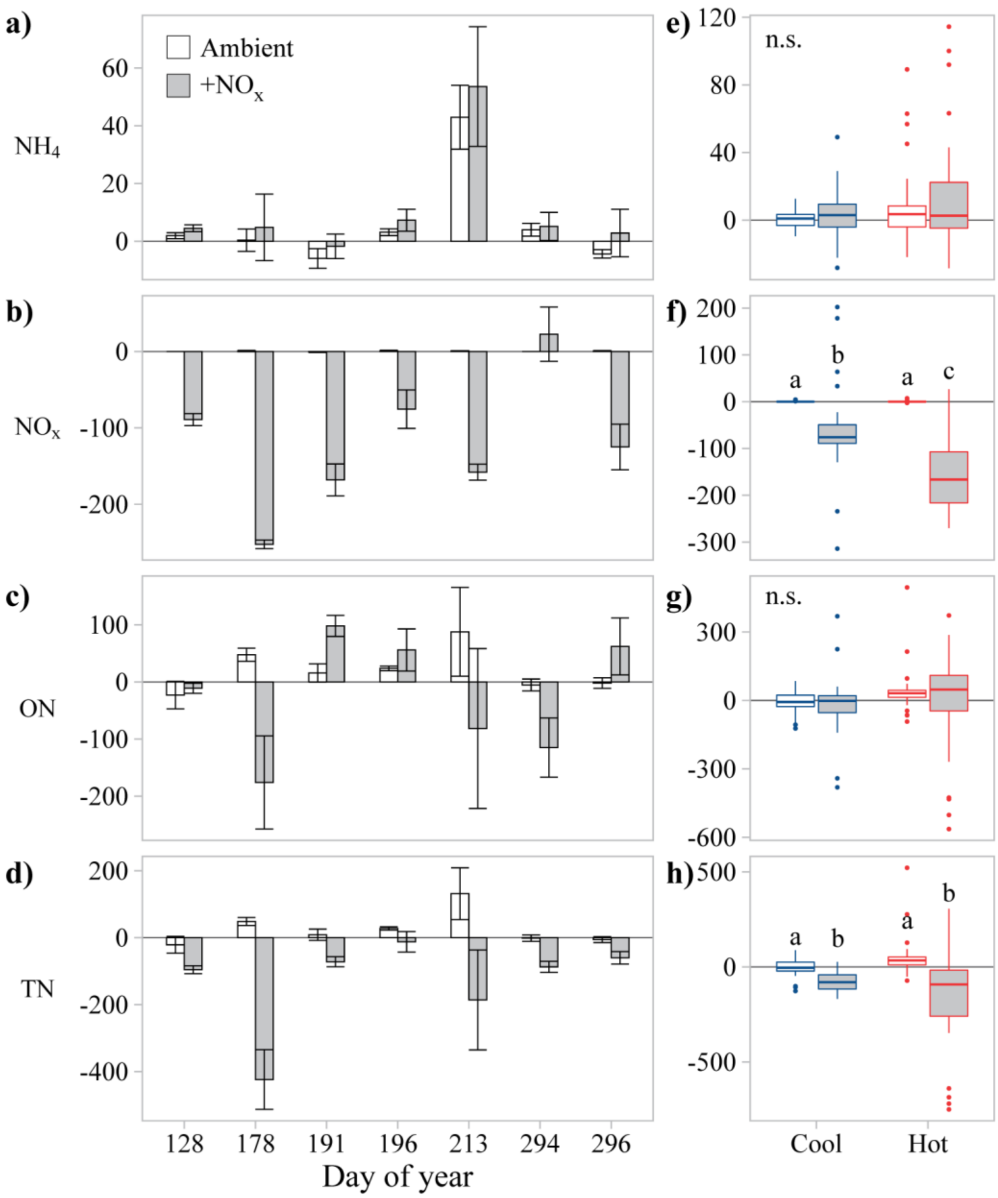

Figure 2.2. a – d) Dissolved nutrient fluxes (μmol N m^{-2} yr^{-1}) during ambient and NO_x-enriched conditions, and **e – h)** ambient and NO_x-enriched dissolved nutrient fluxes separated by "cool" and "hot" conditions. Note the different y-axes between plots.

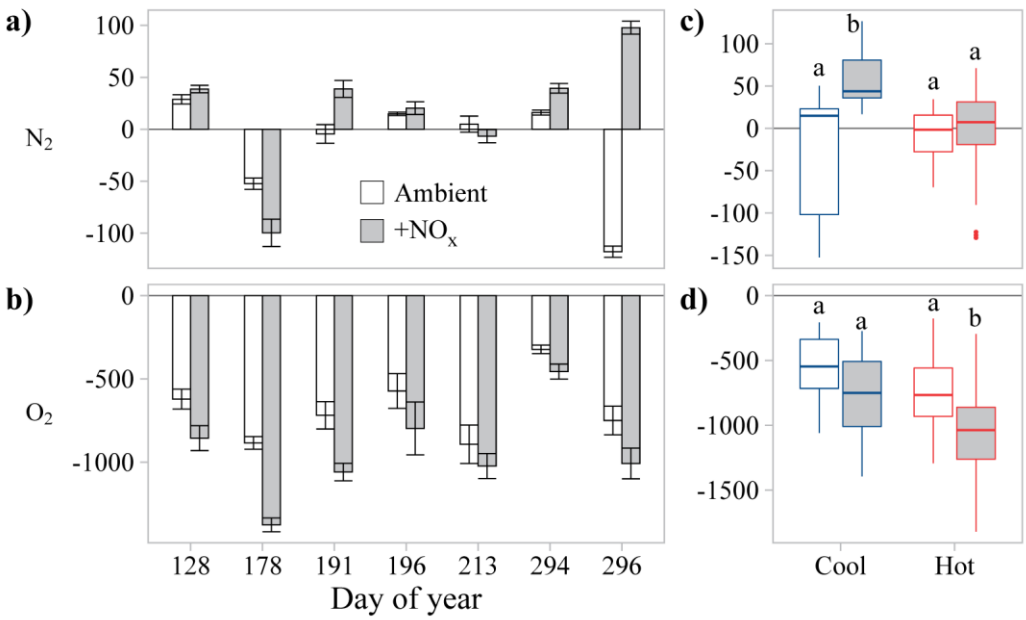

Figure 2.3. a, b) Dissolved gas fluxes (µmol N m^{-2} yr^{-1} and µmol O_2 m^{-2} yr^{-1}) during ambient and NO_x-enriched conditions, and **c, d)** ambient and NO_x-enriched dissolved gas fluxes separated by "cool" and "hot" conditions. Note the different y-axes between plots.

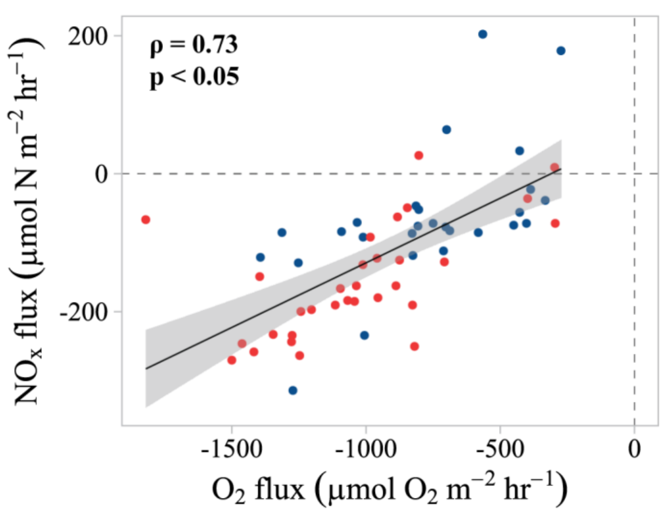

Figure 2.4. NO_x flux versus O_2 flux separated by temperature class (red = "hot", blue = "cool")

The estimated percent of NO_x denitrified during NO_x-enriched conditions was significantly lower during "hot" conditions compared to "cool" conditions (Figure 2.5), and the percent of NO_x denitrified was significantly positively correlated with O_2 fluxes ($\rho = 0.39$, $p < 0.05$, Figure 2.5). During "cool" conditions, there was evidence of coupled denitrification during "cool" conditions, where the rate of denitrification was higher than the rate of NO_x uptake, resulting in a value of % NO_x denitrified that was greater than 100% (Figure 2.5). During "hot" conditions, some values of percent NO_x denitrified were less than zero, indicating net nitrogen fixation (negative net N_2 fluxes) combined with NO_x uptake (Figure 2.5).

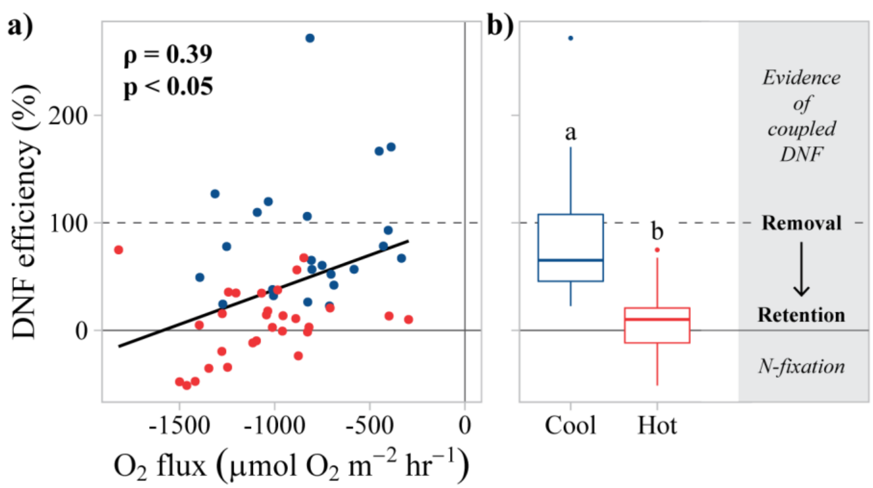

Figure 2.5. a) Percent of NO_x denitrified (N_2:NO_x uptake) versus O_2 flux separated by temperature, and **b)** boxplots of percent of NO_x denitrified separated by temperature. Letters indicate a significant difference between temperature bins based on a Kruskal-Wallis test (α = 0.05). Percent of NO_x denitrified calculated using sediment cores with negative NO_x fluxes (indicating uptake by sediments).

Discussion

SWPs are often considered important nutrient sinks and denitrification hotspots in urban areas (Bettez and Groffman, 2012; Collins et al., 2010), but seasonal variation of N cycling processes within SWPs has not been investigated (Gold et al., 2019a). Our results show that the study SWP sediments were strong N sinks when NO_x was added, but hotter conditions led to larger amounts of sediment NO_x uptake driven by temporary NO_x retention rather than permanent removal via denitrification. This study suggests that elevated seasonal temperatures can push stormwater pond sediments from acting as net N sinks to N transformers, which could have negative impacts on downstream water quality. Based on these findings and other recent research, we hypothesize that the design of SWPs can cause persistent reduced and low-NO_x conditions that promote N recycling and reduce permanent N removal.

Influence of sediment characteristics on N cycling

Differences in morphologies and sediment characteristics generally did not correspond with notable differences in sediment N cycling across sampling events (Figure 2.2). Sediment C:N and SOM were both significantly correlated with TN fluxes during ambient conditions (Table A.2), but TN fluxes during ambient conditions were relatively small when compared to TN fluxes during NO_x-enriched conditions. There were fairly large differences in RTRM and sediment properties between study SWPs (Table 2.2), but these variables were only significantly correlated with ambient NH_4 and chl-a concentrations (Table A.1). Although these results do not provide a definitive assessment of SCM morphology, the minimal influence of sediment characteristics on sediment N cycling during NO_x-enriched conditions suggests that SWP sediment N removal may be less influenced by morphology than broader environmental variables such as temperature or antecedent weather. A survey of stormwater ponds across the US found, similarly, that potential denitrification rates were likely controlled by environmental variables that varied by place rather than surrounding land cover or sediment properties (Blaszczak et al., 2018). Our past study showing that pond age was negatively related to net N_2

fluxes suggests that physical pond properties play some role in controlling N cycling (Gold et al., 2017a), but as shown in this study, the seasonal variability in N cycling caused by temperature and weather patterns is likely much greater.

Seasonality of SWP N cycling

A temperature-related effect on N cycling was evident for the study SWPs, with SWP sediments shifting from net N sinks to N transformers with elevated temperatures and sediment oxygen demand. SWP sediment N cycling during cool conditions generally matched the assumptions often made regarding SWP function: SWPs are N sinks and are important sites for permanent N removal via denitrification (Bettez and Groffman, 2012; Collins et al., 2010)(Figure 2.3). In this "cool" state, the sediment microbial community responsible for N cycling is efficiently taking up smaller amounts of NO_x from the water column and converting it to N_2 gas through denitrification (Figures 2.2, 2.5). This state of N cycling was typified by lower ambient DON concentrations in the water column, less NO_x uptake, and less sediment oxygen demand from the sediments, which is a proxy for the rate of organic matter oxidation (Eyre et al., 2013)(Figures A.1, 2.2, 2.3). SWPs that were acting as sites for permanent N removal during cool conditions became sites of N transformation during hot conditions when median DON concentrations in the water were elevated (Figure A.1). After NO_x-enrichment during "hot" conditions, SWP sediments had more sediment oxygen demand and temporary uptake of NO_x (i.e., lower % NO_x denitrified) compared to "cool" conditions (Figures 2.3, 2.5). This temporary uptake could either be assimilative uptake or DNRA, but a lack of nitrate induced ammonium flux (NIAF) in our sediment cores suggests (Figure 2.2) that assimilation was the dominant process (Hoffman et al., 2019; Slone et al., 2018). Net N_2 fluxes during "hot" conditions were frequently negative under both ambient and NO_x-enriched conditions, which indicates that the sediment microbial community was adding N to the SWP by performing net nitrogen fixation (Figure 2.3).

The shift in SWP N cycling with temperature shown in this study suggests that the prevailing assumption of SWP N cycling (Gold et al., 2019a) may overestimate the ability of SWPs to function as net N sinks throughout the year. Though it is acknowledged that pond N retention changes seasonally with retention rates increasing during warmer weather (Rosenzweig et al., 2011), the unmeasured mechanism for retention is often attributed to denitrification due to a positive relationship between temperature and denitrification in other aquatic environments (Collins et al., 2010; Gold et al., 2019a; Rosenzweig et al., 2011). Results from this study show that this assumption of denitrification as an important fate of stormwater NO_x does not always hold true, especially during seasonal hot conditions where SWPs may appear to be strong NO_x sinks based on loading measurements. Furthermore, the current study does not incorporate NO_x uptake by actively photosynthesizing organisms (i.e., phytoplankton or plants) that can vary across seasons (Reed et al., 2016), so the low importance of denitrification estimated in this study during “hot” conditions may even be an overestimate of the actual importance of denitrification. Most loading studies on SWP N removal have spanned short time periods that may not capture seasonal variation (Koch et al., 2014), and the temporary uptake of NO_x observed in this study during “hot” conditions suggests that N removed by SWP sediments could be recycled as DON or particulate carbon (i.e., algae) at a later date. This transformation from inorganic to organic N can happen at varying rates (Rosenzweig et al., 2011) that may or may not be measured during the typically short time scales of previous studies (Koch et al., 2014).

Alternatively, NO_x retained but not denitrified could be denitrified later through remineralization and coupled nitrification-denitrification.

This potential recycling of N within ponds is also supported by recent research showing that stormwater ponds store, transform, and export other elements at varying time scales. SWPs process carbon from the watershed and have distinct spectral signatures of dissolved organic matter that signifies autochthonous production and remineralization (Gold et al., 2020; Kalev et al., 2020; Williams et al., 2016, 2013). Similarly, SWPs also store and release phosphorus from sediments, often converting inorganic forms to organic forms (Duan et al., 2016; Song et al., 2017; Taguchi et al., 2019). Future studies should further assess the fate of NO_x in SWPs throughout the year to help determine the full impact of ponds on downstream water quality.

Conditions between storms as the major control of SCM N cycling

We hypothesize that the ability of SWP sediments to permanently remove NO_x from stormwater is broadly controlled by the redox potential of the sediments, which in turn is controlled by the unique hydrology of SWPs, weather conditions between storms, and upstream nutrient supply (Figure 2.6). We suggest that during hotter conditions, long residence times between storms can lead to a lack of NO_x and oxygen at the sediment-water interface. A lack of NO_x and oxygen could cause pond sediments to become more reduced and promote temporary NO_x uptake over denitrification (Figure 2.6).

SWPs are designed to have long residence times in order to process nutrients and settle out particulates, but long residence times may lead to a depletion of NO_x at the sediment-water interface and anoxic conditions that inhibit NO_x production via nitrification. In order to achieve their primary goal of retaining stormwater runoff, SWPs do not have a constant source of water flowing into them; they are designed to collect and release water only during storm events and a few days immediately afterwards. This sporadic inflow leads to long residence times between storms ranging from hours to weeks (Jefferson et al., 2015), and long residence times can promote low-oxygen conditions at the sediment-water interface, especially during seasonal hot conditions (Burgin et al., 2011; Song et al., 2013). Generally, long residence times and low-oxygen conditions have been promoted as positive factors for NO_x removal and denitrification in SWPs (Bettez and Groffman, 2012; Collins et al., 2010; Mallin et al., 2002; Toet et al., 1990), but based on this study's consistently low ambient NO_x concentrations, even 1-2 days after rain events, we hypothesize that NO_x supplied from watersheds in this study is likely taken up rapidly within the SWPs. After the stormwater-supplied NO_x is processed within in the sediments or water column, the only source of NO_x until the next storm is from nitrification within the SWP, which may be inhibited in SWPs with low-oxygen conditions at the sediment-water interface (Rysgaard et al., 1994; Thompson et al., 2000). High NO_x demand from sediments, phytoplankton, and plants combined with limited NO_x supply during certain conditions suggests that sediments in some SWPs could experience long periods of time without exposure to NO_x. Although NO_x concentrations are influenced by the land use of the draining watershed, low NO_x concentrations have been observed in other coastal stormwater ponds as well (Gold et al., 2017a; Reed et al., 2016), suggesting that rapid NO_x uptake after storms is common.

There is increasing evidence that the sediment-water interface of SWPs can become highly biogeochemically-reduced between storms, and these conditions may promote temporary N removal processes over denitrification when stormwater runoff provides NO_x. With NO_x and oxygen depleted, inundated sediments can become highly biogeochemically reduced and produce methane (CH_4) through methanogenesis (Burgin et al., 2011). Recent research has found that small human-made water bodies, such as SWPs, are large and previously-unaccounted-for sources of methane (Grinham et al., 2018), and methane production in these systems is positively related to increased eutrophication and elevated temperatures (Bergen et al., 2019; Peacock et al., 2019; Zhou et al., 2019). For shallower stormwater wetlands or detention basins, methane production is higher in permanently submerged areas than in areas that fluctuate between wet and dry (Bledsoe et al., 2020; McPhillips and Walter, 2015), further suggesting that permanently inundated SWPs produce methane. The conditions that promote methane production in SCMs are similar to the conditions found in this study where NO_x uptake was high but denitrification was low or non-existent: higher temperatures, ambient DON concentrations, NO_x demand, and sediment oxygen demand. Anecdotally, methane bubbles were apparent during sediment coring in every study SWP, especially during “hot” sampling events. There may, in fact, be a direct link between methanogenesis and temporary N uptake, as some methanogens can perform nitrogen fixation (Bae et al., 2018) and high carbon/low nitrate environments can favor DNRA over denitrification (Burgin and Hamilton, 2007; Kessler et al., 2018). Further study is warranted to determine how the carbon and nitrogen cycle are related in SWPs and how high redox potentials may affect SWP N cycling.

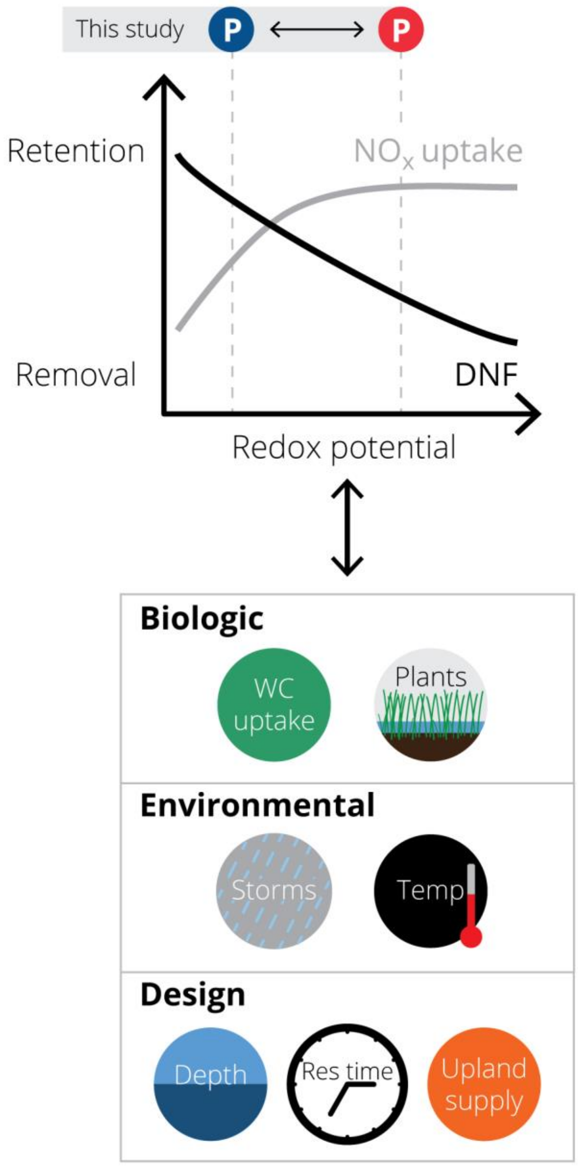

Figure 2.6. Conceptual diagram detailing possible drivers of redox potential and the hypothesized relationship between redox potential and N fate in SWP sediments. Blue circle ("P") represents "cool" conditions in this study, and the red circle represents "hot" conditions. DNF = denitrification.

Conclusions

Stormwater ponds (SWPs) are a common type of stormwater control measure (SCM), but how these SCMs process N from stormwater has not been extensively studied across seasons. To better characterize SWP N cycling and their efficacy as N sinks, we collected sediment cores from three SWPs (n = 7) in the southeastern US coastal plain and measured dissolved gas and nutrient fluxes during ambient and NO_x-enriched conditions. DON was the dominant form of N in the water column of all measured SWPs, and NO_x was below detection for the majority of sampling events. Sediment properties (SOM and C:N) varied between study SWPs and were significantly correlated with ambient total N (TN) fluxes. SWP sediments generally functioned as TN sinks during NO_x-enriched conditions, but the relative importance of denitrification as a fate of NO_x was significantly lower during sampling events at elevated water temperatures (> 25˚C). SWP sediments at elevated water temperatures also had significantly higher sediment oxygen demand and NO_x uptake. These results suggest that the efficacy of N removal by SWP sediments can change seasonally based on temperature, and NO_x retained within SWP sediments during hotter conditions has the potential to be recycled at a later date. We hypothesize that the lower relative importance of denitrification observed during hot conditions may be driven by prolonged periods of low-oxygen and low-NO_x conditions at the sediment-water interface between storms.

CHAPTER 3: THE EFFECTS OF URBANIZATION AND RETENTION-BASED STORMWATER MANAGEMENT ON COASTAL PLAIN STREAM NUTRIENT EXPORT[2]

Introduction

Urbanization changes watershed hydrology and increases stream nutrient export (O'Driscoll et al., 2010; Walsh et al., 2005), but understanding the specific effects of urbanization can allow for more effective municipal water management. The typical effects of urbanization are increased rates of stormflow and decreased rates of baseflow (Paul and Meyer, 2001; Walsh et al., 2005), but this change in hydrology (especially at low flows) is also influenced by changes in evapotranspiration, contributions from leaky wastewater infrastructure, and physical properties of watersheds or drainage networks (Bhaskar et al., 2016a; Meierdiercks et al., 2017; Price, 2011; Walsh et al., 2005). Various relationships between concentration and discharge can suggest mechanisms of nutrient delivery to a stream and sources of nutrients within a watershed (Duncan et al., 2017; Musolff et al., 2015), which can be important for management given that urbanization alters watershed biogeochemical processes, increases nutrient sources, and degrades nutrient sinks (Sarah E Hobbie et al., 2017; Kaushal et al., 2011; Newcomer Johnson et al., 2014; Reisinger et al., 2016). Understanding changes in hydrology,

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sources of nutrients, and pathways of nutrient delivery with urbanization can help determine what type of stormwater management strategy might be most effective (Jefferson et al., 2017).

Coastal plain streams in the southeastern US have unique hydrology and biogeochemistry that suggests they may have a different response to urbanization than streams from other regions. The effects of urbanization on watershed hydrology and stream nutrient dynamics can vary by region and depend on physiographic attributes (Hopkins et al., 2015; Utz et al., 2011). For example, a study comparing the Mid-Atlantic coastal plain and Piedmont found that urbanization affected stream water quality similarly between the two regions, but hydrologic metrics associated with high flows were more affected by urbanization in the coastal plain than the Piedmont (Utz et al., 2011). Many coastal plain streams in the southeastern US are characterized as “blackwater” streams due to high concentration of dissolved organic matter (DOM) derived from forested wetlands (Meyer, 1990) and watersheds with low slopes and sandy soils (Markewich et al., 1990). Dissolved organic nitrogen (DON) is the dominant form of dissolved nitrogen in these blackwater coastal plain streams while concentrations of dissolved inorganic nitrogen (DIN) and algal biomass are low (Meyer, 1990; Tufford et al., 2003; Wahl et al., 1997). Previous studies in this area have found that even small increases in DIN can cause algal blooms (Mallin et al., 2004), and urbanization increases the concentrations of DIN (Tufford et al., 2003; Wahl et al., 1997), the volume of streamflow (Wahl et al., 1997), and the flashiness of streamflow (Jayakaran et al., 2014). Further, coastal plain streams may have a disproportionate impact on nutrient sensitive coastal waters due to their close proximity that limits processing within the stream network compared to upland streams. Coastal environments are ecologically, economically, culturally, and recreationally important (Costanza et al., 1997), but nutrient enrichment from land-based nutrient export has degraded water quality and ecosystem function in many estuaries (Bricker et al., 2008; Deegan et al., 2012) and freshwater tidal creeks (Sanger et al., 2013).

Previous studies have reported some effects of urbanization on southeastern US coastal plain streams, but there are still gaps in understanding that must be addressed to inform management (O'Driscoll et al., 2010). The relative amount of particulate nitrogen (PN) has not been measured in either less-impacted or urban coastal plain streams, nutrient export for all nitrogen species during storm events has not been quantified due to methodological challenges (Mallin et al., 2009; Tufford et al., 2003; Wahl et al., 1997), and there are few records of long-term measurements of streamflow and nutrient export across a range of watershed ISC. The effects of stormwater control measures (SCMs) on watershed hydrology and nutrient export compared to unmitigated urban development is an especially critical gap in understanding given the mandated use of SCMs for new development in this region. Determining the effects of coastal plain watershed urbanization on stream nutrient export and discharge is critical for informing stormwater management policy for coastal areas and improving coastal water quality through effective mitigation.

To address these gaps in understanding, this study measured four years of streamflow and nutrient export (dissolved and particulate nitrogen, orthophosphate, and algal biomass) from five streams with watersheds spanning a range of imperviousness in the coastal plain of North Carolina. One of the three urban watersheds was drained by stormwater ponds, which allowed for comparisons in discharge and nutrient export between types of stormwater management strategies. The primary goal of this study was to determine the impacts of increased watershed ISC and retention-based stormwater management on stream discharge and nutrient export from coastal plain streams in the southeastern US. Specifically, this study analyzed the magnitude and timing of stream discharge and nutrient export and the relationships between nutrient concentrations and discharge.

Materials and Methods

Study Sites

Five streams with watersheds spanning a wide range of imperviousness (1-38%) on US Marine Corps Base Camp Lejeune (MCBCL) in Jacksonville, NC were selected for study (Figure 3.1, Table 3.1). Watersheds were delineated in ArcGIS 10.4 using 1-meter resolution elevation data provided by the Environmental Services division of MCBCL, and watershed impervious area was manually delineated using high-resolution orthoimagery collected by the MCBCL in 2013. The MCBCL is the largest Marine Corps base in the world and surrounds most of the New River Estuary. The study area lies in the outer coastal plain, an area comprised mostly of sandy soils that range from excessively-drained to very poorly drained (Soil Survey Staff, 2015) and was historically vegetated with longleaf pine savannah with bottomland hardwood species fringing the streams (Messina and Conner, 1997; Outcalt and Sheffield, 1996). Natural streams in this area are blackwater, low-gradient streams. The MCBCL provided an excellent location to study the impacts of urbanization on coastal plain stream nutrient export due to the range of impervious cover of watersheds within its boundaries and the fact that all study watersheds were owned by the same entity, thus constraining differences in management that could impact hydrology (e.g., groundwater withdrawal, stormwater control measure selection & maintenance, etc.). As a labeling convention, the percent watershed ISC is used to identify streams and watersheds (e.g., 1% ISC stream, 1% ISC watershed).

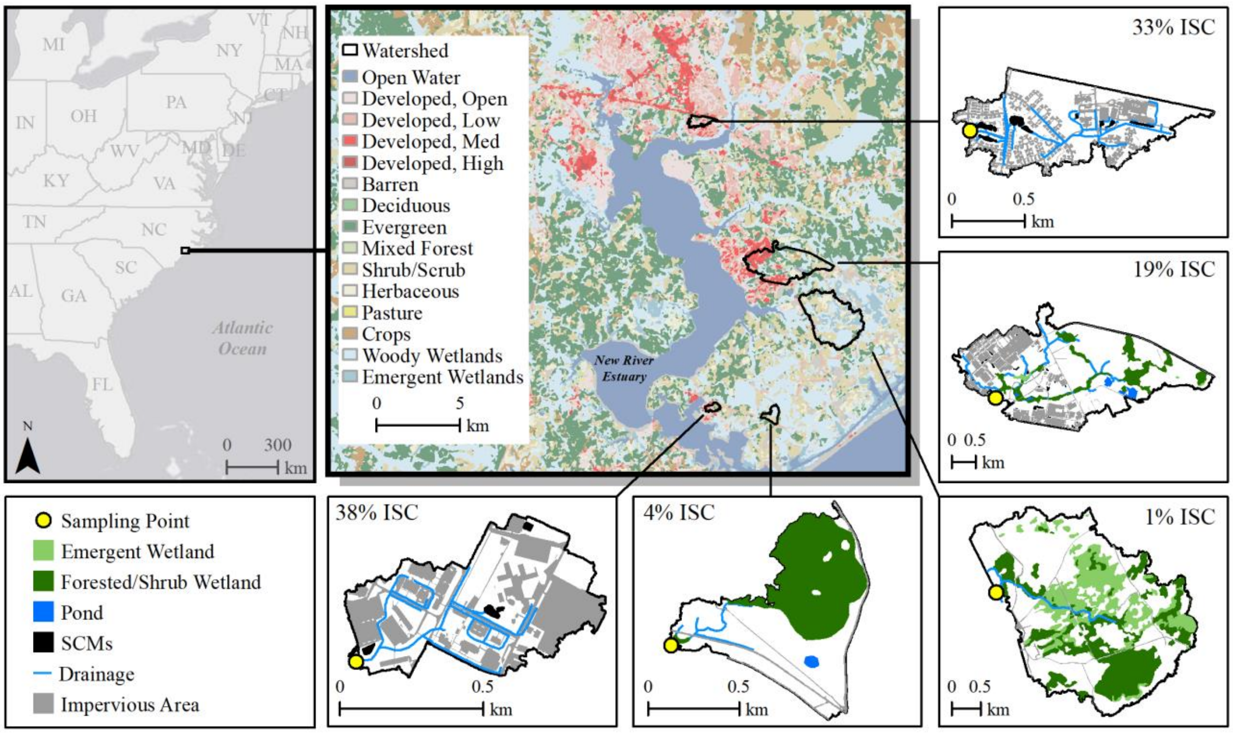

Figure 3.1. Overview map of study watersheds and stream sampling locations. Land cover data from the 2011 NLCD data set and the USFWS.

The study watersheds ranged in size and imperviousness but were all located along the eastern shore of the New River Estuary (Figure 3.1, Table 3.1). The two watersheds with the lowest levels of imperviousness (1% and 4% ISC) exemplified the two most common natural land cover types in this area. The 1% ISC watershed contains large areas of emergent wetlands, forested wetlands, and shrub/scrub land cover, while the 4% ISC watershed contains mostly forested wetlands and shrub/scrub land cover (Table B.1, Gold and others 2017a). The 19% ISC watershed contains high-density, commercial land cover and large amounts of forest and forested wetland cover (Table 3.1). The stormwater management in this watershed drains approximately half of the impervious area in the watershed using retention ponds and infiltration basins, and most of the stormwater is routed to stormwater control measures or the stream by a complex network of ditches along the road network (Table 3.1). The 33% ISC watershed contains mostly residential urban area, and 97% of the watershed area is drained by curb and gutter drainage to stormwater retention ponds (Gold et al., 2017a, Table 3.1). The most impervious watershed in this study (38% ISC) contains commercial development that is drained through a series of ditches along the roadways, and a parking lot drains to a stormwater retention pond near the sampling site (Table 3.1). The most impervious watershed was undergoing construction during data collection, resulting in increased watershed ISC from 24% to 38% between 2009 and 2013. The watershed was denoted as 38% ISC in this study because this amount of ISC was maintained for most of the study period. Watershed ISC was the main focus of this study because this metric was negatively correlated with wetland cover (R^2 = 0.95) and positively correlated with percent well-drained soils (Hydrologic class A or B)(R^2 = 0.94)(Table 3.1). Together, these sample sites capture variation in watershed ISC as well as differences in stormwater management at the higher limit of imperviousness.

Table 3.1. Study watershed statistics.

ISC (name)	ISC (%)	Area (ha)	Unmitigated impervious area (%)	Total wetland area (%)	Percent well-drained (%)
1% (French)	0.96	835.05	0.96	42.19	35.07
4 % (Traps)	3.93	61.48	3.92	44.37	23.17
19% (Cogdel)	19.24	725.41	9.49	12.37	70.03
33% (Tarawa)	33.27	70.16	0.98	0.44	82.87
38% (Courthouse Bay, CHB)	38.16	31.77	26.13	0.11	100.00

Discharge, export, and concentration measurements

Streams from the five study watersheds were gauged for discharge for a period of four years (June 2011 - June 2015) using Teledyne Isco automatic water samplers outfitted with flow sensors (acoustic Doppler velocity and pressure transducer level). Velocity and level measurements were recorded every 30 minutes, and stream cross-sections allowed for the conversion of level and velocity measurements to stream discharge. Twice-monthly water grab samples were collected, filtered through Whatman GF/F filters (25 mm diameter, 0.7 µm nominal pore size), and analyzed for nitrate-N (NO_x^-, detection limit = 0.05 µM), ammonium (NH_4^+, detection limit = 0.24 µM), dissolved organic nitrogen (DON, detection limit = 0.75 µM), and orthophosphate (PO_4^{3-}, detection limit = 0.02 µM) with a Lachat QuickChem 8000 nutrient autoanalyzer. Filters were then analyzed for chlorophyll-*a* (chl-*a*) as a proxy for algal biomass. Analysis for chl-*a* was conducted with a Turner Designs Trilogy fluorometer after sonicating and extracting frozen filters for 24 hours in a 90% acetone solution (Welschmeyer, 1994). Results for chl-*a* will be referred to interchangeably as algal biomass. Particulate nitrogen (PN) concentrations were measured during the final two years of the study (June 2013 – June 2015). PN was measured by filtering water samples with the filters specified above and analyzing filters for nitrogen content with a Costech Elemental Combustion System with Elemental Analysis software. Water samples were also collected at greater frequency during storm events for one storm a month with the Isco automatic water samplers using a velocity-based trigger and flow-paced sampling scheme set to span the entire storm hydrograph. Export was calculated for each 30-minute interval to match the frequency of discharge measurements. Baseflow and stormflow volumes were calculated by delineating discharge volume into baseflow or stormflow during manually identified storm events using a digital filter (Nathan and McMahon, 1990). During baseflow, export was estimated for each water quality variable by multiplying the most recent measured baseflow nutrient concentration by discharge (period-weighted approach - discussed by Aulenbach and others 2016). During storm events, concentration was interpolated between storm samples encompassing the hydrograph (regression-model approach - discussed by

Aulenbach and others 2016). Export during unsampled storm events was estimated by multiplying measured discharge by concentration calculated from discharge-concentration relationships for rising and falling limbs of sampled storms. All values of export and discharge were normalized by watershed area for comparisons between study streams. Data analysis was conducted in Microsoft Excel and R (R Core Team, 2020).

Streamflow and hydrologic metrics

Daily discharge values were calculated by summing measurements of discharge collected every thirty minutes for each day, and daily discharge values were used for all analyses. Average annual streamflow was calculated for each stream by taking the mean of annual discharge for each year of the sampling period (n = 4). Dates of missing streamflow data due to equipment failures were not estimated, but annual values of discharge and export were adjusted for missing days (48 missing days total, mostly 8/17/2011 – 9/20/2011 due to equipment removal prior to tropical storm). Daily discharge values sorted from low to high were used to calculate percentiles for each value of discharge as well as cumulative discharge for each stream following established methods (Duan et al., 2012; Pennino et al., 2016; Shields et al., 2008). Gini coefficients, which can be used as a measure of temporal inequality in discharge or nutrient export (Jawitz and Mitchell, 2011), were calculated from this sorted list of discharge values using the “ineq” R package. The Richards-Baker flashiness index was calculated for each month for each stream, although two months were removed due to missing data (August & September 2011) (Baker et al., 2004). Baseflow index (BFI) values were calculated, and average annual BFI values were calculated. Paired t-tests were performed on log-transformed annual streamflow and BFI values to test for significant differences between streams ($\alpha = 0.05$). Discharge values for each study stream were parsed into seasons (winter = D, J, F; spring = M, A, M; summer = J, J, A; fall = S, O, N), and differences between seasons were determined through non-parametric Kruskal-Wallis and Dunn's tests ($\alpha = 0.05$) because data could not be normalized with transformations.

Nutrient export and concentrations

Average annual export for each water quality constituent was calculated in the same way as average annual discharge, and paired t-tests were performed on log-transformed annual values to test for significant differences between streams ($\alpha = 0.05$). The ratios of dissolved nitrogen species from water samples were plotted on a ternary plot using the ggtern R package (Hamilton and Ferry, 2018). Differences in concentrations of various water quality constituents between study streams were analyzed using one-way ANOVAs and Tukey HSD post-hoc tests on log-transformed concentration measurements. To analyze the timing of export, the ranked discharge values from each stream were used to calculate cumulative export and cumulative percent export for each water quality constituent using the same methodology discussed previously for cumulative discharge.

Relationships between concentration, discharge, and export

Metrics that describe the influences of discharge and concentration on nutrient export were calculated for each study stream and water quality constituent. The metric CV_C/CV_Q, which compares the coefficient of variation of concentration measurements to the coefficient of variation of discharge measurements (Thompson et al., 2011), was calculated for manually sampled concentration and discharge measurements (n range = 211-249). The linear slope of the log-log relationship between measured concentration and discharge (b from the equation $C = aQ^b$

where C = concentration and Q = discharge) was calculated for each study stream and measured water quality constituent. Due to the inclusion of concentration and discharge measurements below detection limits, a value of 0.01 was added to all values of discharge and orthophosphate and a value of 0.1 was added to all values of nitrate, ammonium, and DON. The combination of the CV_C/CV_Q metric and C-Q slope can suggest nutrient sources and means of delivery from the watershed to the stream. For example, a water quality variable that has a low CV_C/CV_Q value (< 0.5) and low b value ($-0.2 < b < 0.2$) would be considered chemostatic (i.e., variability in discharge controls export). The b value can better inform the source of water quality variables that are chemodynamic ($CV_C/CV_Q > 0.5$, variability in concentration controls export), with positive b values indicating a flushing of material during storm events and negative b values indicating dilution of material due to increased discharge (Godsey et al., 2009).

To compare the export of nitrogen species across flows, values of discharge were binned every 10 percentiles, and the export of each species of nitrogen was summed within each bin. The ratio of export of each nitrogen species in each bin was then calculated.

Results

Streamflow and hydrologic metrics

Average annual stream discharge increased with watershed ISC, and this increase in overall discharge volume with watershed ISC was driven by increases in streamflow across all flows and more cumulative discharge at high flows (Figure 3.2). The 38% ISC stream had much higher flow than all of the other study watersheds, and had nearly twice the amount of discharge as precipitation (~1.3m/yr of precipitation) (Figure 3.2). In general, streamflow flashiness and the relative importance of high flows to overall discharge volume increased with watershed ISC and baseflow index (BFI) decreased with watershed ISC (Figure 3.2, Table B.2). However, the hydrologic metrics of the 4% ISC stream were similar to those of the streams with the most developed watersheds despite large differences in discharge volume. The timing of the “flashy” behavior of the 4% ISC stream differed from that of the more developed streams, with higher values of flashiness occurring during months with less discharge and low BFI values rather than more discharge and low BFI values (Figure B.2).

Stream discharge was highest during winter for every study stream, but there were differences in the seasonal patterns between the study streams for the other seasons (Figure B.1). The two least developed streams had significantly lower summer flows compared to all other seasons, which aligns with peak growing season and increased evapotranspiration. The 4% ISC stream had no flow during periods of the summer for the first two years of the study. The three more developed streams either exhibited a muted seasonal pattern or a different seasonal pattern than that of the less developed streams (Figure B.1, Table B.3). Streamflow in these three streams was continuous throughout the year.

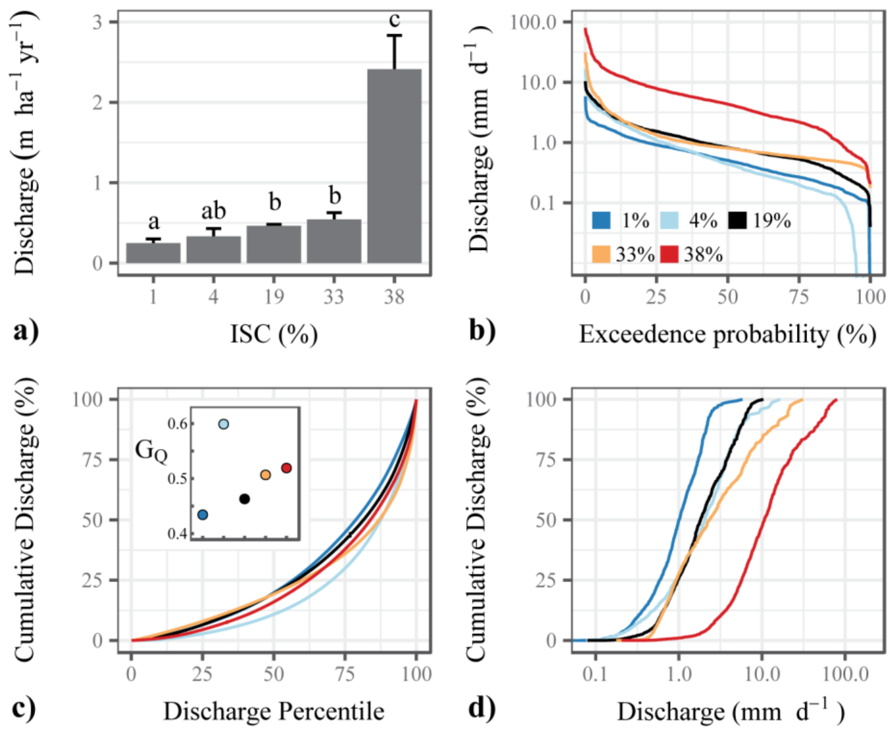

Figure 3.2. a) The mean annual volume of streamflow, **b)** flow duration curves, and **c)** Lorenz curves of discharge with Gini coefficients (inset), and **d)** cumulative flow distribution curves for each study stream. Letters indicate significant differences based on paired t-tests ($p < 0.05$). Error bars indicate standard error.

Nutrient export and concentrations

Average annual nutrient export increased with watershed ISC for all measured variables, but as with discharge, export from the 38% ISC stream was much higher than all other streams (Figure 3.3, Table B.4). DON export was similar between all streams except for the most urban stream which had much higher rates of export (Figure 3.3). Differences between the three more developed streams and the two less developed streams were largest for nitrate and algal biomass export (chl-*a*), while the two most developed streams had higher rates of export than all other watersheds for ammonium, orthophosphate, and PN (Figure 3.3). There were no discernable differences in seasonal patterns of nutrient export between watersheds (Figure B.1), and nutrient export from each watershed followed similar seasonal patterns as discharge (Figure B.1). Generally, nutrient export was highest in the winter during higher flows and was lowest in the summer or spring during lower flows (Figure B.1).

All water quality variables had more exports during higher flows with increasing watershed ISC (Figure B.4). This pattern was similar to discharge, with watersheds (except the most developed stream) grouping together at lower flows and diverging at high flows.

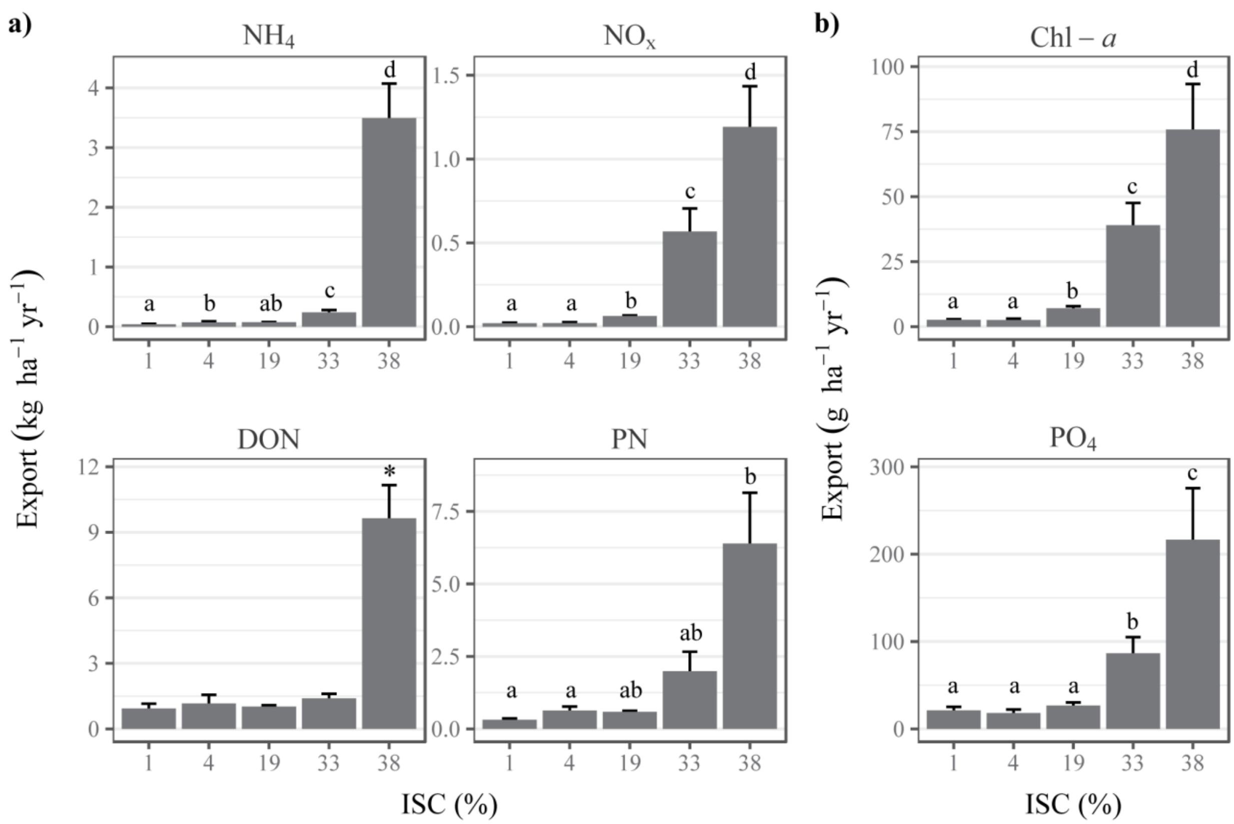

Figure 3.3. a) Mean annual export of measured variables over the entire study period (June 2011 – June 2015) in kg/ha and **b)** grams/ha. Note different y axes for each plot. Particulate nitrogen (PN) was only measured for the last two years of the study period (June 2013 – June 2015). Letters (or asterisk when only one group is different) indicate significant differences based on paired t-tests ($p < 0.05$). Error bars indicate standard error.

Concentrations generally increased with watershed imperviousness for all measured variables except DON and orthophosphate (Table 3.2). The 19% ISC stream had concentrations that were similar to the 2 least developed streams except for higher concentrations of nitrate and significantly lower concentrations of DON (Table 3.2). The 33% ISC stream had significantly higher concentrations of all measured variables except DON (2nd lowest concentrations) and ammonium (2nd highest concentrations) (Table 3.2). The most urban stream had much higher concentrations of ammonium than all other streams as well the highest or second highest concentrations of all other variables (Table 3.2). Different seasonal trends in concentrations between watersheds were only apparent for nitrate. Compared to other seasons, the two least developed streams had significantly higher summer concentrations of nitrate that coincided with higher seasonal temperatures and significantly less discharge (Figure B.1), while lower nitrate concentrations coincided with the coldest seasonal temperatures and the highest discharge (Figure B.1). In contrast, the three streams with more impervious watersheds had the highest concentrations of nitrate during the winter and followed the same pattern as discharge (Figure B.1).

Table 3.2. Summary of nutrient concentrations from study streams (mean $\pm$ SE).

ISC (%)	**NO_x (μM)**	**NH_4 (μM)**	**ON (μM)**	**PN (μg/L)***	**PO_4 (μM)**	**Chl-*a* (μg/L)**
1	0.75 ± 0.05^{a}	1.26 ± 0.04^{a}	26.38 ± 0.81^{ab}	137.68 ± 11.98^{a}	0.29 ± 0.01^{a}	1.39 ± 0.11^{a}
4	0.68 ± 0.08^{a}	1.59 ± 0.09^{a}	24.61 ± 0.76^{b}	156.35 ± 13.62^{a}	0.21 ± 0.01^{b}	0.97 ± 0.11^{b}
19	1.34 ± 0.11^{b}	1.2 ± 0.08^{b}	14.6 ± 0.34^{c}	167.88 ± 23.15^{a}	0.26 ± 0.01^{a}	1.55 ± 0.17^{a}
33	5.93 ± 0.26^{c}	3.96 ± 0.35^{c}	19.51 ± 0.51^{d}	313.86 ± 23.22^{b}	0.64 ± 0.03^{c}	11.27 ± 0.96^{c}
38	4.25 ± 0.29^{d}	12.69 ± 1.45^{d}	27.88 ± 0.73^{a}	229.14 ± 14.84^{b}	0.31 ± 0.02^{a}	4.79 ± 0.35^{d}

There were clear differences in the dominant forms of nitrogen export between study streams (Figure 3.4a, 2.4b). Overall, DON was the dominant form of nitrogen exported from all study streams except the 33% ISC stream with stormwater ponds, where particulate nitrogen was the dominant form of nitrogen exported (Figure 3.4b). PN export was generally the second largest species of nitrogen exported followed by either ammonium or nitrate. The relative importance of DON to total nitrogen export decreased with watershed ISC, while the relative importance of PN and DIN export increased (Figure 3.4b). The increase in the relative importance of DIN export was driven by different nitrogen species in the most urban study streams - the 33% ISC stream had more nitrate export than ammonium and the most urban stream had more ammonium export than nitrate (Figure 3.4b). The decreased relative importance of DON in the more urban watersheds also corresponded with increased chl-*a* concentrations and particulate N concentrations (Figure B.3).

The differences in the dominant forms of nitrogen between study streams can also be visualized by comparing the percent contribution of each dissolved nitrogen species to total dissolved nitrogen in collected water samples (Figure 3.4c). The two less developed streams cluster at high percentages of DON and low DIN percentages. The stream with the 19% ISC watershed also encompasses high % DON and low % DIN water samples, but it also extends farther out along the % NO_x and % NH_4 axes. Finally, the two most urban streams move away from high % DON (very few water samples near 100% DON) and extend out along the % NO_x and % NH_4 axes farther than the other study streams. Similar to Figure 3.4b showing the relative important of different nitrogen species to export, the 33% ISC has higher values of % NO_x and the most urban stream has higher values of % NH_4.

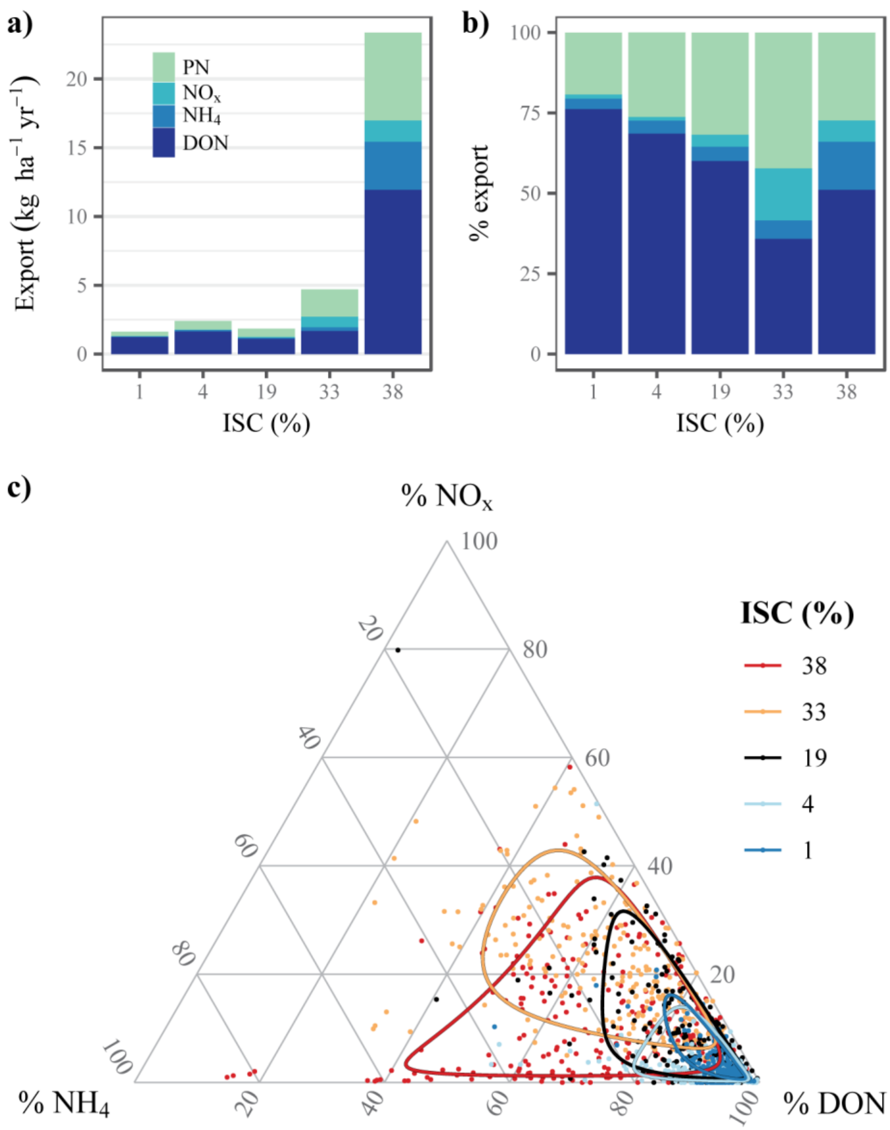

Figure 3.4. a) Mean annual total nitrogen export, **b)** the relative export of nitrogen species for each study stream between June 2013 – June 2015 when PN was measured, and **c)** a ternary plot showing the percent of each dissolved nitrogen species within water samples collected over the entire study period with outlines of 66% confidence intervals to illustrate groupings. ISC = impervious surface cover of watershed.

Relationships between concentration, discharge, and export

Plotting b, or the linear slope of the log-log relationship between concentration and discharge, versus CV_C/CV_Q can classify the export regime of a stream and point to possible sources within the watershed (Musolff et al., 2015). For ammonium, the 4% ISC stream was the only stream that was chemostatic, the 1% ISC stream and the 33% ISC stream were slightly chemodynamic with b values of approximately zero, and the 19% ISC stream and the 38% ISC stream were more chemodynamic with negative b values indicating the dilution of ammonium with increased discharge (Figure 3.5). Nitrate export from the two most developed streams was chemodynamic with small b values, the 19% ISC stream was chemodynamic with a positive b value, and the two least developed streams exhibited large, negative b values (Figure 3.5). DON export was chemostatic for all streams except the least developed stream, which was weakly chemodynamic and had a positive b value (Figure 3.5). All study streams had small b values for PN export, but the 4, 33, and 38% ISC streams were weakly chemodynamic and the 1 and 19% ISC streams were strongly chemodynamic (Figure 3.5). This grouping of streams aligns with differences in watershed size, which can influence CV_C/CV_Q values (Diamond and Cohen, 2018). Differences in chl-*a* CV_C/CV_Q values between streams were similar to that observed for PN, but the main difference in b values was that the 33% ISC stream with stormwater ponds had a large and positive b value while the other study streams had small b values (Figure 3.5). All study streams had orthophosphate CV_C/CV_Q values indicating chemostatic or weak chemodynamic behavior, and the b value generally increased with watershed ISC (Figure 3.5).

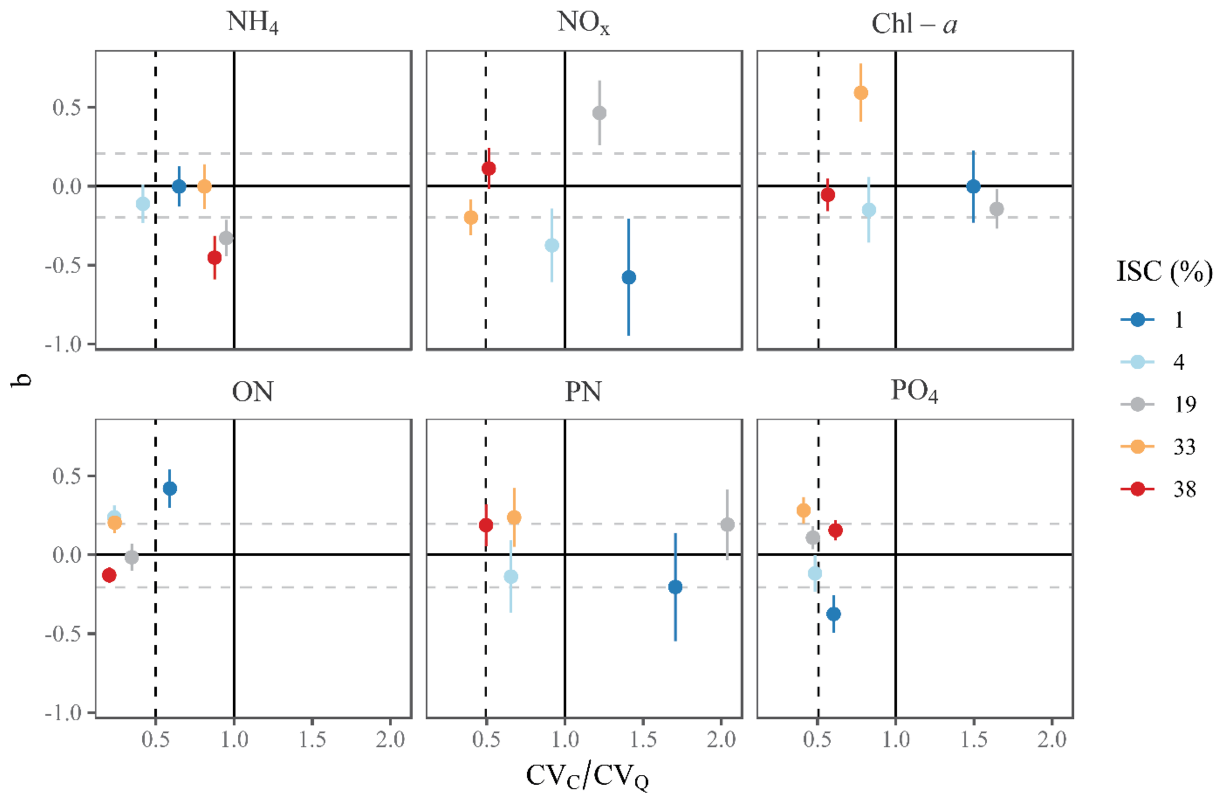

Figure 3.5. CV_C/CV_Q (proxy of export regime) and b (linear slope of log-log C and Q relationship) for each watershed and growing/dormant season. Values of CV_C/CV_Q that are less than 0.5 indicate chemostasis, and values of b between 0.2 and -0.2 (between horizontal grey lines) indicate weak flushing or dilution patterns.

There were small differences between cumulative nutrient export and cumulative discharge that can be seen by comparing the relationship between the two indices, and this comparison can highlight important periods of export in water quality variables that are chemodynamic (Figure B.5). Only patterns that differ from the C-Q slopes presented above are shown. For nitrate, the least developed stream had more cumulative export than discharge at lower flows compared to all other watersheds despite a wide range of b values among streams (Figure B.5). Every stream except for the least developed stream had relatively more ammonium export than discharge at lower flows (Figure B.5). Higher flows were important periods of PN export for all study streams despite differences in b and CV_C/CV_Q values (Figure B.5).

The speciation of nitrogen export across flows differed based on watershed ISC (Figure 3.6, Figure B.6). Relative to total nitrogen export, the relative amount of DON increased and PN decreased from low to high flows in both less developed streams (Figure 3.6b, Figure B.6). Also, the importance of ammonium decreased from low to high flows in the 4% ISC stream. The timing of export for all nitrogen species was similar for the two less developed streams except for nitrate in the 1% ISC stream and ammonium in the 4% ISC stream (Figure 3.6, Figure B.6). The three more urban streams had notable increases in the importance of PN export from low to high flows (Figure 3.6b, Figure B.6). There was also a slight decrease in the importance of DON and DIN export from low to high flows, although the speciation of inorganic species varied among the more urban streams (Figure 3.6b, Figure B.6). The more extreme differences in speciation of nitrogen export across flows in the three more urban streams led to larger differences in the timing of cumulative nitrogen export among nitrogen species (Figure 3.6c). PN was exported at higher flows than all other nitrogen species in the three more urban streams, followed by nitrate in the 19 and 38% ISC streams and DON in the 33% ISC stream (Figure 3.6c).

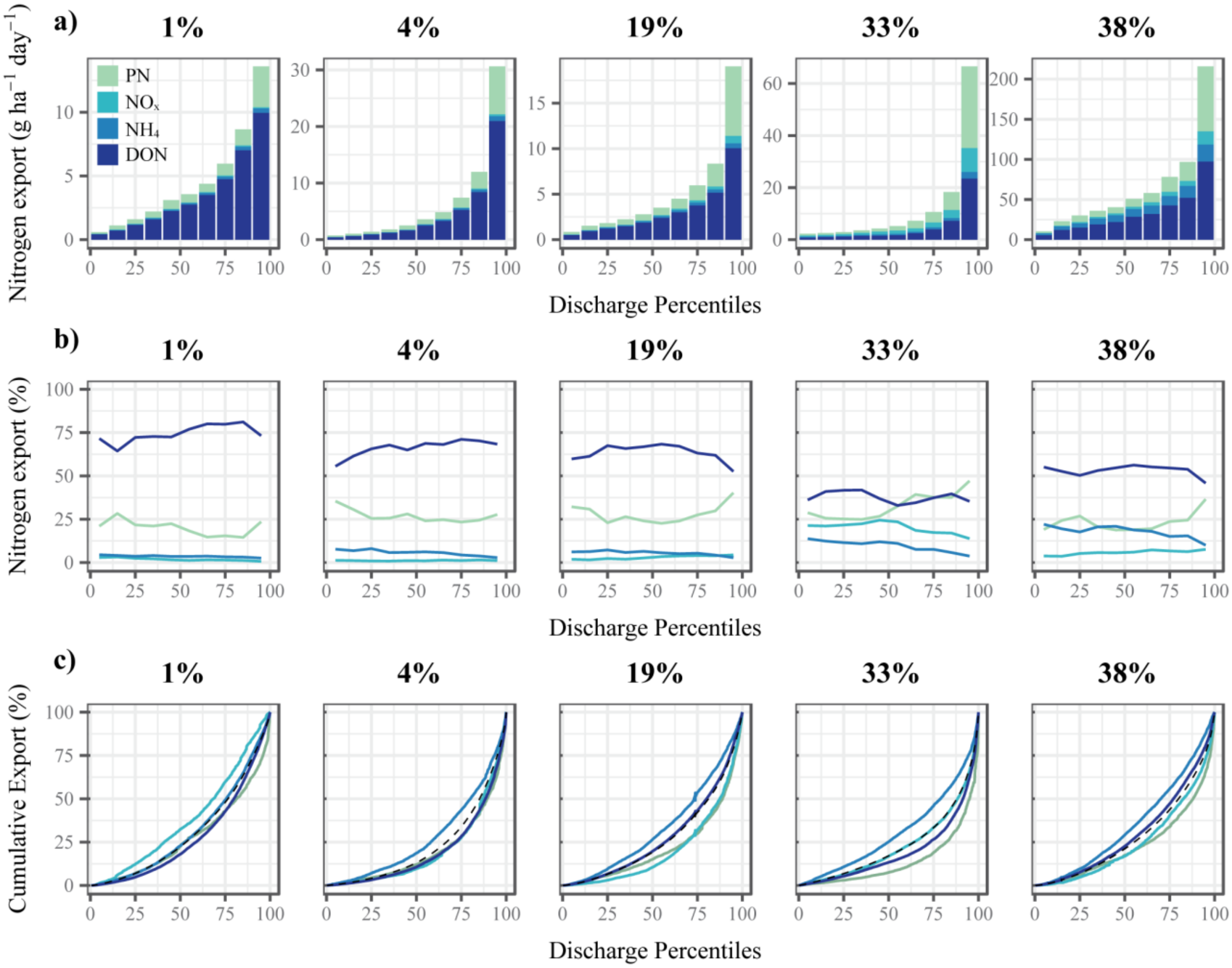

Figure 3.6. a) Total nitrogen export separated into nitrogen species over the full range of flows, **b)** The percent of each nitrogen species exported within each bin of discharge percentiles (bins = 10), and **c)** cumulative export for each nitrogen species across the full range of flows. Data are from the final two years of monitoring (June 2013 – June 2015).

Discussion

Watershed hydrology and ISC

This study found that streams with more developed watersheds had higher rates of discharge across all flows, more cumulative discharge at higher flows, and dampened seasonal patterns of discharge when compared to streams with less developed watersheds (Figure 3.2, Figure B.1, Table B.3). These findings agree with studies in other physiographic regions that observed increased high flows during storms but differ slightly from previous studies that found urbanization typically decreases discharge at low flows (Hardison et al., 2009; O'Driscoll et al., 2010; Walsh et al., 2005). Also, the shift towards more discharge at higher flows with watershed ISC appears to be less intense than in other areas, likely because of increased low flows. R-B flashiness values generally increased with watershed ISC which was also reported in past studies, but the 4% ISC stream was flashy at low and intermittent flows during the summer (Figure B.2, Table B.2). The flashy behavior at low flows in the 4% ISC stream due to storm events during intermittent summer flow highlights the fact that seasonal differences in discharge were dampened in the more impervious watersheds (Figure B.1, Table B.3).

The most likely mechanisms for the increased rates of discharge across all flows and dampening of seasonal trends with increasing ISC are increased stormwater runoff, reduced evapotranspiration, increased input from wastewater infrastructure, and increased surface water storage in the form of stormwater ponds. Elevated stormflow and decreased infiltration due to impervious surfaces is an extremely well-documented occurrence (Walsh et al., 2005) that was evident in this study. Increased discharge at low flows may be due to decreased evapotranspiration from forested and wetland area in the urban watersheds. Approximately 70% of precipitation in southeastern coastal plain wetlands is evapotranspired (Sun et al., 2002) and decreased evapotranspiration can lead to increased discharge (Mclaughlin et al., 2013). Increased discharge due to decreased evapotranspiration has been observed previously in urbanizing watersheds with well-drained soils (Barron et al., 2013) and in southeastern coastal plain watersheds that experience large losses of forested land for silviculture (Mclaughlin et al., 2013; Sun et al., 2010). Increased flow from decreased evapotranspiration in urban areas hypothesized here may be regionally specific, though, as a study of streams in the inner Coastal plain found that increasing watershed ISC led to deeper water tables and decreased baseflow (Hardison et al., 2009). Water inputs from leaky water and wastewater infrastructure can also lead to increases in discharge (Bhaskar et al., 2016a; Price, 2011), and this likely explains the consistently high flow in the most urban stream which was undergoing additional development during the study period. The extensive use of stormwater ponds, which are not designed to reduce stormwater volume but rather to reduce peak flows and extend the hydrograph (Hancock et al., 2010), may have contributed to reduced seasonality in discharge by supplementing low flows after storm events (2-5 day drawdown period). Decreased seasonality in baseflow has been observed in low impact development watersheds that have extensive stormwater infiltration (Bhaskar et al., 2016b), and while we observed a similar decrease in seasonality, flow from stormwater ponds to the stream could consist of either infiltration or flow to the stream due to drawdown of the temporary pond storage volume. Increased discharge and reductions in seasonality of flow have been noted in southeastern coastal plain streams previously (Jayakaran et al., 2014; Wahl et al., 1997), so this phenomenon is likely caused by decreased evapotranspiration and supplemented by stormwater ponds or wastewater infrastructure leaks.

Stream nutrient export and ISC

Stream nutrient export increased with watershed ISC, and this increase was caused by elevated discharge, inorganic nitrogen export, and PN export. More nutrients were exported at higher flows in the more urban streams as seen in past studies (Duan et al., 2012; O’Driscoll et al., 2010; Paul and Meyer, 2001; Walsh et al., 2005), but nitrate and PN export notably shifted to higher flows relative to other nitrogen species with increasing watershed ISC (Figure 3.6). The two streams with the least developed watersheds exhibited typical blackwater stream biogeochemistry– low N, high proportions of DON, and low concentrations of algal biomass and

PN. The three more urban streams maintained the same amount of DON export (or greater in the case of the 38% ISC stream), but were differentiated from the less developed streams by increased concentrations and export of DIN, PN, and algal biomass.

The quantity of DON exported from the study streams was similar to export from streams and rivers throughout the continental US (Lewis, 2002) and western Australia (Petrone, 2010), although concentrations were lower than those from forested watersheds in a review of DON concentrations (Pellerin et al., 2006). PN export is often not reported due to methodological constraints, but PN export from the two least developed streams was similar to minimally disturbed streams in the SE US and Maryland Coastal plain (Correll et al., 1999; Lewis, 2002), and PN export from the more urban streams was much higher than streams of similar imperviousness in western Australia (Petrone, 2010). The export of nitrate from the study streams was lower than previously reported values in streams with watersheds of similar impervious cover (Lewis, 2002; Pennino et al., 2016; Petrone, 2010; Shields et al., 2008), most likely because this study was conducted in a coastal area where the reference blackwater streams are characteristically low in nitrate (Mallin et al., 2004; Wahl et al., 1997). Ammonium export from the stream with the least impervious watershed in this study was much lower than that measured in a relatively undisturbed stream in the inner coastal plain of South Carolina (Lewis, 2002), but ammonium export for all of the study streams was similar to that measured in urbanized streams in the coastal plain of western Australia (Petrone, 2010). The magnitude of annual orthophosphate export in this study was also similar to previous studies (Duan et al., 2012; Pennino et al., 2016; Petrone, 2010), but concentrations of orthophosphate were not clearly related with watershed imperviousness as was found in a previous study on coastal plain streams (Mallin et al., 2009).

Nitrogen speciation and ISC

The three more developed streams exported more nutrients and had a smaller relative amount of DON than the less developed streams, and this pattern was driven by increased concentrations of PN and DIN (Figure 3.4). The relative amount of dissolved nitrogen export as DON for all streams was similar to results from previous studies in coastal plain blackwater streams (Tufford et al., 2003; Wahl et al., 1997) but much higher than reported values from upland areas (Groffman et al., 2004; Pellerin et al., 2006; Shields et al., 2008) and inner coastal plain streams (Lewis, 2002; Yarbro et al., 1984). Despite the higher relative amount of DON in the study, the decreased relative importance of DON shown here has been documented in many different geographic areas, including in nearby coastal South Carolina (Pellerin et al., 2006; Tufford et al., 2003). This phenomenon appears to occur regardless of reference stream chemistry, and is likely controlled by land use, wastewater discharges, and the abundance of wetlands in the watershed (Pellerin et al., 2006).

PN constituted a sizeable portion of the total nitrogen pool in all study streams (Figure 3.4B), but algal biomass was likely the driver of PN export for only the 33% ISC stream with stormwater ponds. Blackwater streams typically have low concentrations of algal biomass and particulate organic matter (Meyer, 1990; Yarbro et al., 1984), so the proportion of total nitrogen exported as particulates (19-26%) in the two least developed streams is somewhat unexpected. Although, this relative amount of particulate nitrogen is still low, and previous studies in natural coastal plain streams have shown that particulate phosphorus is the dominant form of phosphorus export (Tufford et al., 2003; Yarbro et al., 1984). Algal growth in blackwater streams can be stimulated with even small amendments of DIN or labile DON due to their typically low concentrations of DIN and slower flow velocities (Mallin et al., 2004), so increased DIN and chl-

a concentrations suggest that algal biomass likely contributes to the PN pool in the more urban streams (Figure B.3). However, differences in the timing of PN and algal biomass export for all study streams except the 33% ISC stream indicates that algal biomass was a major driver of increased PN export for only the 33% ISC stream.

Another consideration for PN is that PN was exported at higher flows than other types of nitrogen in the urban streams (Figure 3.6), and this may increase downstream impacts more than just an increase in the magnitude of PN export. Due to the close proximity of the study streams to coastal waters, this change in timing of PN export relative to other nitrogen species will likely lead to more intense pulses of PN to coastal waters during storm events. PN and other particulate material that is exported to coastal waters can immediately contribute to increased biological oxygen demand (BOD) which can negatively impact aquatic ecosystems (Mallin et al., 2009). This consideration is especially relevant for the stream with the 33% ISC watershed and stormwater ponds where nitrogen export was dominated by PN and large amounts of algal biomass export during high flows.

Changing nutrient sources with urbanization

This study found that relationships between concentration and discharge changed with watershed ISC, indicating that nutrient sources shifted from natural to urban sources that varied by watershed. To highlight differences in nutrient sources with watershed ISC, the two least developed streams (1 and 4% ISC) will be described as “minimally impacted”, the two streams with higher ISC and minimal retention-based stormwater management (19 and 38% ISC) will be grouped as “urban”, and the 33% ISC stream extensively drained by stormwater ponds will be referred to as “urban with retention-based stormwater management”.

Minimally impacted watersheds

Major nutrient sources in the two least developed streams were attributed to DON from extensive wetland area, PN from leaf material or other organic, non-algal sources, and inorganic nitrogen and phosphorus from groundwater or biogeochemical processes within the stream channel. DON export was chemostatic for both minimally impacted streams, and positive C-Q slopes (b values), higher concentrations of DON than the more urban streams, and extensive wetland area indicate that wetlands and forested area were the main source of DON. The timing of export aligns with past studies showing that wetlands and forested areas are the main sources of DON in minimally impacted coastal plain watersheds, and these sources are typically transported to streams during storm events when wetlands are flushed or inundated (Flint and McDowell, 2015; Lehrter, 2006; Pellerin et al., 2004). Negative C-Q slopes for PN that were not significantly different from zero, lower concentrations of algal biomass than the urban streams, and differences in the timing of PN and algal biomass export mean that algal biomass was not the main source of PN. However, algal biomass could constitute a portion of the particulate N pool in the two least impervious streams that is exported at lower flows when streamflow velocities are low (Figure B.5). The main source of PN in these two streams were likely leaf material (Newcomer et al., 2012), and a past study in coastal plain streams found that particulate material in a minimally disturbed stream was organic (Jayakaran et al., 2014). Nitrate export was low and chemodynamic with negative C-Q slopes, and concentrations were highest during summer when flow decreased or ceased. This pattern is indicative of a natural source of nitrate transported via groundwater or nitrified in the streambed or riparian zone during baseflow (Duncan et al., 2015). Ammonium export was lower than all other nitrogen species exported from the less developed streams, and chemostatic or weakly chemodynamic ammonium export with flat C-Q slopes suggests that the source is likely mineralization of organic matter during baseflows and ammonium from wetland processing during storm events. A chemostatic or weakly chemodynamic dilution pattern for orthophosphate hints at a consistent source at low flows, possibly in-stream processing such as mineralization and desorption from sediments (Hensley et al., 2017; Mallin et al., 2004).

Urban watersheds

The relationships between concentration and discharge for the 19% ISC stream suggested that DON was supplied by wetlands within the stream network and groundwater, nitrate from anthropogenic sources mobilized during stormflow (i.e., fertilizers, atmospheric deposition), and PN, ammonium, and orthophosphate from stream channel degradation and altered nutrient removal processes. DON export from 19% ISC stream was chemostatic with a flat C-Q slope that was different than those of the two less developed streams. This stream had the lowest DON concentrations of all study watersheds despite a moderate amount of wetland area (12.37% watershed area), so it is possible that increased discharge across all flows due to urbanization diluted DON concentrations relative to the less developed streams. PN export from the 19% ISC stream had a positive C-Q slope that was opposite that of the less developed streams, and storm events were more important times of export relative to other nitrogen species. Algal biomass export was significantly higher in the 19% ISC stream than the less developed streams, likely due to increased nutrient availability (Mallin et al., 2004; Smucker et al., 2013) and light availability (Reisinger et al., 2019; Tank et al., 2018), but differences in the timing of PN and algal biomass means that a PN source other than algal biomass was exported at higher flows. PN in urban streams can originate from leaf material, sediment, grass clippings, and periphyton

(Newcomer et al., 2012), and a study in a similar study area found that exported particulate material was largely mineral (as opposed to organic) and due to stream channel erosion (Jayakaran et al., 2014). Nitrate export from the 19% ISC stream was chemodynamic with a large, positive C-Q slope indicating a flushing of nitrate from the watershed during storm events. Potential sources of nitrate in more urbanized watersheds can include leaky wastewater infrastructure, lawn fertilizers, and atmospheric deposition of nitrate onto impervious surfaces (Kaushal et al., 2011). The 19% ISC stream had chemodynamic ammonium export with a negative C-Q slope suggesting that there were sources mobilized during baseflow and diluted during storms, although ammonium export from the 19% ISC stream was not higher than the two least developed streams. This shift in timing of ammonium export to lower flows may be driven by processes occurring during baseflow such as elevated net nitrogen mineralization within the floodplain and throughout the watershed (Reisinger et al., 2016), elevated rates of remineralization due to increased algal biomass (McMillan et al., 2010; O'Brien et al., 2012), or decreased rates of ammonium uptake due various effects of development (Meyer et al., 2005). Finally, orthophosphate C-Q slopes were positive rather than negative like the less developed streams, and this enrichment pattern aligns with previous studies that show that hydrologic change from urbanization can increase orthophosphate export via erosion within the watershed or stream (Withers and Jarvie, 2008).

The major sources of nutrients in the 38% ISC watershed were similar to those of the 19% ISC stream, but leaky sanitary sewers were likely the dominant source of ammonium and DON. A chemostatic, dilution pattern for DON in the 38% ISC stream was attributed to this persistent sanitary sewer leak that provided a consistent source of flow and nutrients. Leaky sanitary sewers can occur in urban areas and convey large amounts of water (Bhaskar et al., 2016a) and fecal bacteria, nitrate, and organic matter to streams (Cahoon et al., 2016; Hosen et al., 2014; Iverson et al., 2018; Kaushal et al., 2011; Pennino et al., 2016). The clearest indicators of leaky sanitary sewers in the most urban stream (besides abnormally high discharge volume) were ammonium concentrations that were nearly four times higher than the next highest stream and DON concentrations that were significantly higher than the other urban streams and similar to concentrations in the two less-impacted streams despite having no wetland area in the watershed. A strong dilution pattern for ammonium export was also likely the result of this leak. Nitrate export from the 38% ISC stream was chemostatic with a slope not significantly different from zero, so it is likely that this watershed had a large and consistent anthropogenic source of nitrate in the watershed derived from the urban sources mentioned for the 19% ISC stream. This shift in nitrate sources with watershed ISC from a natural, seasonally-variable, groundwater-transported source as seen in the less developed streams to a consistent, transport-limited source has been shown in previous studies (Duncan et al., 2017; Thompson et al., 2011). The relationships between discharge and concentration were similar to those of the 19% ISC stream for orthophosphate and PN (excluding differences in CV_C/CV_Q for particulate metrics), so PN and orthophosphate sources mobilized during stormflow were likely the results of stream channel and bank erosion.

Urban watershed with retention-based stormwater management

Nearly the entire watershed of the 33% ISC stream was drained by stormwater ponds, and these stormwater ponds appear to have been important transformers of dissolved nitrogen and large sources of PN. The 33% ISC stream had a positive DON C-Q slope similar to the two less developed streams, but low DON concentrations suggests a that a diluted natural source of

DON during baseflow (lack of wetlands in watershed) may have been supplemented during storm events by DON from stormwater ponds within the watershed. Stormwater ponds can be sources of DON downstream (Bell et al., 2019), have strong autochthonous nitrogen and carbon signatures (Williams et al., 2013), transform inorganic nitrogen to DON and PN (Gold et al., 2017b), and increase the biodegradability of DON (Mary G Lusk and Toor, 2016). The 33% ISC stream also had ammonium C-Q slopes that were similar to the less developed streams, so stormwater ponds may have also been sources of ammonium like natural wetlands in the less developed watersheds. Stormwater ponds were clearly large sources of algal biomass that was exported during storm events when ponds were flushed, and this algal biomass contributed to increased PN export. The 33% ISC stream had positive C-Q slopes for both PN and algal biomass, and while high flows were important times of export for both particulate N and algal biomass, the timing of algal biomass export was similar to PN export (opposite that of all other study streams). A previous study showed that a stormwater pond in the 33% ISC watershed had significantly higher chl-*a* concentrations than the draining stream (Gold et al., 2017b), and stormwater ponds in similar areas have also been shown to harbor high concentrations of algal biomass (DeLorenzo et al., 2012; Lewitus et al., 2008; Reed et al., 2016). Nitrate export was chemostatic with a dilution pattern, but nitrate was likely not supplied by the stormwater ponds given that nitrate concentrations in these ponds and other coastal stormwater ponds during baseflow conditions have been low to nonexistent (Gold et al., 2017b; Reed et al., 2016). Stormwater ponds can promote denitrification downstream if the area drained by ponds is less impervious, but denitrification downstream can be dampened if the drained area is very impervious (Rivers et al., 2018), possibly leading to higher nitrate concentrations during baseflow. Urban streams can also have increased rates of net nitrogen mineralization and nitrification (Reisinger et al., 2016), so this may have influenced the elevated nitrate concentrations during baseflow. For orthophosphate, a strong enrichment pattern shows that stormwater ponds may have been a source of orthophosphate. Stormwater ponds can decrease erosion in the draining stream (Tillinghast et al., 2011), thus decreasing orthophosphate export, but they can also be sources of orthophosphate during certain seasons due to low-oxygen conditions in pond sediments that cause desorption (Duan et al., 2016).

Additional impacts of changing nutrient sources

While rates of DON export were similar between most of the study streams, the growing importance of urban sources of DON with watershed ISC could increase the availability of DON to downstream ecosystems. The dilution of natural DON sources and increase in the urban DON sources presented here has been observed previously with measurements of DON bioavailability, which increases in urban streams (Mary G. Lusk and Toor, 2016; Pellerin et al., 2006; Petrone et al., 2009; Stanley and Maxted, 2008). Further, DON and dissolved organic matter (DOM) are derived from similar sources in blackwater streams, and DOM sources have also been shown to shift with increased watershed ISC (Hosen et al., 2014; Parr et al., 2015). Bioassay experiments have shown that urban sources of DON, such as wastewater effluent or stormwater, are more easily utilized by estuarine algae than natural sources of DON (Hounshell et al., 2017; Seitzinger et al., 2010), suggesting that a similar amount of DON export from urban streams compared to more natural streams may supply more bioavailable nitrogen.

PN removal is rarely measured when assessing nitrogen removal from stormwater ponds (Rosenzweig et al., 2011), but this may be a pathway of nitrogen export to streams in certain areas. Stormwater wet ponds are designed to retain water, nutrients, and suspended sediments, but total suspended solids measurements (TSS) that are often used as a measure of effectiveness are poor predictors of performance due to phytoplankton growth in stormwater ponds that can drive internal nutrient processing (Williams et al., 2013). There are few studies that assess PN export from coastal plain urban streams, but a previous study found that elevated particulate phosphorus concentrations in an urban stream was likely due to urban pond phytoplankton export (Tufford et al., 2003). Low N:P ratios and high rates of nitrogen uptake within coastal stormwater pond waters indicate that nitrogen uptake may be dominated by assimilative uptake by algae in the water column (Gold et al., 2017a; Reed et al., 2016). Assimilative uptake by coastal stormwater pond sediments, as opposed to denitrification, may be high when DIN:DIP ratios are low (as shown by differences in pond age) or during hot and dry periods (Gold et al., 2017a), and assimilated nitrogen could be remineralized. The nutrient cycling within stormwater ponds likely changes with season and physiographic region, and could influence the retention of dissolved versus particulate forms of nutrients. Stormwater ponds are often promoted as nitrogen sinks although the processes of nitrogen removal have not been well characterized (Gold et al., 2019a), and this topic requires further study to determine if and when algal biomass is the dominant pathway of nitrogen uptake in stormwater ponds and if it is a source of PN downstream in other physiographic areas.

Implications for coastal water quality management

The results of this study indicate that multiple management actions could be used to address or prevent excessive stream nutrient export stemming from coastal plain urbanization. The first management action is stormwater volume reduction, which should aim to reduce the volume of stormwater to restore the pre-development water balance and hydrologic flowpaths (Askarizadeh et al., 2015; Dietz, 2007). The second management action is to preserve or restore wetland area within the watershed to act as DIN sinks. The third management action is to reduce contemporary anthropogenic sources of nutrients that may be contributing to increased nutrient export.

Reducing the overall volume of discharge would reduce nutrient export (Jefferson et al., 2017), and a stormwater volume reduction approach may be more effective than retention-based stormwater management in this region. Retention-based stormwater management is designed to decrease peak flows and extend the storm hydrograph (Hancock et al., 2010), but this study shows that by retaining nutrient-rich stormwater in nitrogen-limited stormwater ponds in the study area, a large amount of algal biomass was produced and exported downstream as PN. Based on these negative water quality impacts of retention-based stormwater management and increased flow across all rates of discharge in the urban study streams, stormwater volume reduction with an emphasis on stormwater harvesting may be a more effective mitigation strategy in the study area than a retention-based approach. A well-known way to reduce stormwater volume is to utilize low impact development (LID) structures that promote evapotranspiration of stormwater, the reuse of stormwater through harvesting, and stormwater infiltration. However, extensive stormwater infiltration practices in urbanizing areas can sometimes lead to increases in baseflow due to decreased evapotranspiration and increased infiltration (Barron et al., 2013; Bhaskar et al., 2016b). This increase in baseflow with excessive infiltration could be a concern for development in this study region based on the observed increases in discharge across all flows and dampened seasonal patterns in discharge with watershed ISC. Stormwater harvesting would help reduce discharge during baseflow as well as discharge volume over annual and seasonal time scales (Askarizadeh et al., 2015; Jefferson et al., 2017), but it may not address decreased stormflow lag times as effectively as retention-based or infiltration-based stormwater management (Jefferson et al., 2017). A combination of stormwater harvesting and infiltration would likely be effective at reducing discharge and nutrient export (Askarizadeh et al., 2015), but additional studies in this area are needed. LID structures have not been extensively studied in coastal plain regions, but the few studies on this topic suggest that bioretention cells (Page et al., 2015), permeable pavement (Bean et al., 2007; Page et al., 2015) and regenerative stormwater conveyance systems (RSCs) (Cizek et al., 2017; Fanelli et al., 2017) may be able to improve water quality and reduce the volume of stormwater.

Adding wetland area within the watershed (or conserving wetlands during urbanization) provides an inorganic nitrogen sink for the removal of current nutrient pollution and "legacy" nutrient pollution (Basu et al., 2010; Collins et al., 2010) and could shift DON towards natural sources (Flint and McDowell, 2015; Petrone et al., 2011). Chemostatic behavior of nitrate and orthophosphate suggests that there may be a legacy store within the watershed that could keep nutrient export elevated for a long period of time (Basu et al., 2010; Goyette et al., 2018; Van Meter and Basu, 2015), and wetlands throughout the watershed, especially in areas with short travel times to the stream (Van Meter and Basu, 2015), may help lower values of export (Basu et al., 2010). This addition of wetlands would likely be part of a larger stormwater volume reduction strategy as discussed above.

Finally, reducing nonpoint sources (e.g., fertilizers, lawn waste, pet waste, etc.) and point sources (e.g., leaky sewers)(Hobbie et al., 2017; Kaushal et al., 2011) remains an effective approach to reduce nutrient export. Nitrate from non-point urban sources was evident from chemostatic export and positive C-Q slopes in the more urban watersheds. Also, leaky sewers can contribute large amounts of water and nutrients to streams, as shown by the 38% ISC watershed, and should be repaired to reduce nutrient export.

Conclusions

This study found that urban coastal plain streams had higher rates of annual discharge, more cumulative discharge at high flows, and dampened seasonal patterns of discharge compared to less impacted streams. Differences in hydrology at high flows were attributed to increased watershed ISC, and differences at low flows were attributed to decreased evapotranspiration with watershed ISC, leaky wastewater infrastructure, and stormwater ponds. The magnitude of nutrient export for all measured nutrients increased with watershed ISC due to elevated stream discharge and increased concentrations of PN and DIN that varied by watershed and were more reliant on high flows. The relative importance of DON to total nitrogen export decreased with watershed ISC due to increased DIN and PN export, but DON was the dominant form of nitrogen in all but one study stream. Nitrogen export in the urban watershed drained by stormwater ponds was dominated by PN export due to pond algal production. Based on these findings, this study suggests that stormwater volume reduction emphasizing stormwater harvesting and evapotranspiration rather than retention-based management, the preservation or addition of wetland area, and the reduction of anthropogenic nutrient sources could reduce nutrient export from urban coastal plain streams.

Effective management of urban areas benefits from an understanding of ecological processes in more natural systems. By including a wide spectrum of development with a more natural end member, this study provides new information and insights that can be used to manage coastal plain watersheds and improve downstream water quality.

CHAPTER 4: URBANIZATION ALTERS COASTAL PLAIN STREAM CARBON EXPORT AND DISSOLVED OXYGEN DYNAMICS [3]

Introduction

Streams are important conduits and transformers of material from terrestrial landscapes (Alexander et al., 2007; Cole et al., 2007; Newcomer Johnson et al., 2016), but urbanization alters their function (Kaushal and Belt, 2012). Urbanization, often measured by increased impervious surface cover (ISC) in a watershed, amplifies the export and concentrations of nutrients as well as carbon, hydrocarbons, heavy metals, and emerging organic contaminants (Paul and Meyer, 2001; Walsh et al., 2005). Stream ecosystems respond differently to urbanization based on geographic location and prior land use (Brown et al., 2009; Utz et al., 2016), but in general, urban stream ecosystems are degraded by increased pollutant concentrations and stormflow-induced streambed scour. Degraded urban streams can have less diverse macroinvertebrate populations (Brown et al., 2009), reduced rates of nutrient removal (Meyer et al., 2005; O'Driscoll et al., 2010), and extended periods of low dissolved oxygen (DO) (Blaszczak et al., 2019). Alterations in stream function, geomorphology, and stream export due to urbanization are so common as to have been characterized as the "urban stream syndrome"

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(Vietz et al., 2015; Walsh et al., 2005) and, more recently, watershed “chemical cocktails” (Kaushal et al., 2018).

The composition of organic material and nutrients exported from a watershed also changes with urbanization, and these changes have implications for the health of streams and downstream waters (Hosen et al., 2014; Newcomer et al., 2012; Parr et al., 2015; Smith and Kaushal, 2015; Williams et al., 2016). For nitrogen and phosphorus, the relative contribution of inorganic species to nutrient export increases with % ISC (Pellerin et al., 2006; Withers and Jarvie, 2008), which can increase the bioavailability and utilization of excess nutrients. The composition of dissolved organic matter (DOM) and particulate organic matter (POM) also change with increases in % ISC by shifting towards autochthonous or anthropogenic sources (Hosen et al., 2014; Imberger et al., 2014; Parr et al., 2015; Williams et al., 2016). Elevated autochthonous production of carbon in streams delivers excess labile particulate and dissolved carbon to streams and can result in the aforementioned low dissolved oxygen concentrations, reduced nutrient removal, and reduced macroinvertebrate biodiversity (Kaushal et al., 2014; Meyer et al., 2005; Paul and Meyer, 2001).

Streams in the coastal plain of the southeastern US supply nutrients and carbon for important estuarine ecosystems (Leech et al., 2016; Spencer et al., 2013), but the effects of urbanization on carbon composition and export in these systems have not been extensively studied. Many coastal plain streams in the southeastern US are classified as blackwater streams, which are unique ecosystems that are named for their dark brown, tea-colored water that contains exceptionally high concentrations of chromophoric dissolved organic matter (CDOM) and dissolved organic carbon (DOC) and low concentrations of suspended sediments and phytoplankton (Meyer, 1990; Spencer et al., 2013). DOM in blackwater streams or rivers in the southeastern US is derived from wetland and forest land cover within the watershed (Dosskey and Bertsch, 1994; Hosen et al., 2018; Petrone et al., 2011; Spencer et al., 2013), and this aromatic and high molecular weight DOM in blackwater streams is minimally bioavailable within the stream (Textor et al., 2018). While some studies have investigated various aspects of DOM and land use in larger blackwater rivers in the southeastern US (e.g., Bhattacharya and Osburn, 2020; Leech et al., 2016), the few studies that focused on smaller blackwater streams and the effects of urbanization have measured nutrients, such as nitrogen and phosphorus, rather than carbon (Gold et al., 2019b; Mallin et al., 2009; Tufford et al., 2003). The unique "blackwater" characteristics of these streams suggest that changes in carbon export and composition in response to urbanization may differ from prevailing models of inland streams, and understanding how urbanization affects carbon export and composition from coastal blackwater streams could promote more effective coastal watershed management.

This study aimed to determine the effects of urbanization on (a) the amount of exported carbon, (b) the composition of exported carbon, and (c) DO dynamics in coastal plain streams in the southeastern US. Metrics of DOM quality were measured for one year (2009) in ten streams that spanned a range of watershed ISC. For an additional two years (2013 - 2015), DOM quality, the magnitude and timing of DOC and particulate carbon (PC) export, and DO concentrations were measured in five streams that were a representative subset of the original ten streams.

Methods

Study sites

Ten streams on Marine Corps Base Camp Lejeune (MCBCL) located near Jacksonville, NC (Figure 4.1) were selected for this study. The watersheds of these study streams ranged in

ISC from 0.96% to 52.9% (Table 4.1). To obtain the most accurate assessment of watershed ISC at the time of sampling, watershed ISC was calculated by hand-delineating the impervious surfaces of each watershed using USDA NAIP imagery for the initial year of sampling (2009). While the hand-delineated ISC allowed for high spatial and temporal accuracy of watershed ISC metrics, the hand-delineated ISC was linearly correlated to percent National Land Cover Database (NLCD 2011) developed area (high, medium, and low developed area combined)(R^2 = 0.92, $p < 0.01$, Table C.1). The percent ISC of each watershed was significantly negatively correlated with percent NLCD total wetland land cover (Homer et al., 2015) based on a negative logarithmic relationship (R^2 = 0.78, $p < 0.01$, Table 4.1). Additional land cover data is presented in Table C.1.

Spectral analyses were conducted on water samples from all ten streams over a single calendar year (Jan – Dec 2009) to measure the amount and quality of DOM. A subset of five streams were subsequently gauged for discharge, DOC export, PC export, and streamwater spectral analyses over a two-year span (June 2013 – June 2015)(Figure 4.1, Table C.2). Of the five gauged streams, the three with the highest watershed ISC (i.e., Cogdel, CHB, and Tarawa) had increases in imperviousness between the initial sampling for spectral analysis (2009) and the gauging for export (2013)(Table C.2). These differences in imperviousness were determined by comparing hand-delineated watershed ISC from 2009 (USDA NAIP imagery) to hand-delineated watershed ISC from 2013 (aerial imagery provided by the MCBCL Environmental Services division). Development over this time frame included the installation of stormwater wet ponds in the Tarawa watershed that drained 97% of the watershed (Gold et al., 2017b) and an in-line wetland upstream of the sampling point at CHB. Stream canopy cover, estimated for the five gauged streams using 2011 NLCD USFS Tree Canopy data that intersected the stream network, was much higher in the three least developed streams (~70%) than the two most developed streams (15-25%)(Table C.2).

Table 4.1. Watershed information for study streams in 2009. Gauged sample points sampled for additional two years are named, and ungauged sample points are labeled S1 – S5.

Stream name	Area (ha)	ISC (%)	Wetland (%)*
French	835.1	0.96	47.08
S1	468.5	1.45	30.86
S2	433.2	2.91	42.71
Traps	61.5	3.93	44.18
S3	25.3	4.47	24.81
S4	74.9	13.2	24.13
Cogdel	725.4	18.0	14.45
CHB	31.8	24.2	0.15
Tarawa	70.2	26.4	0.00
S5	142.1	52.9	5.50

*Data from 2011 NLCD (Homer et al., 2015)

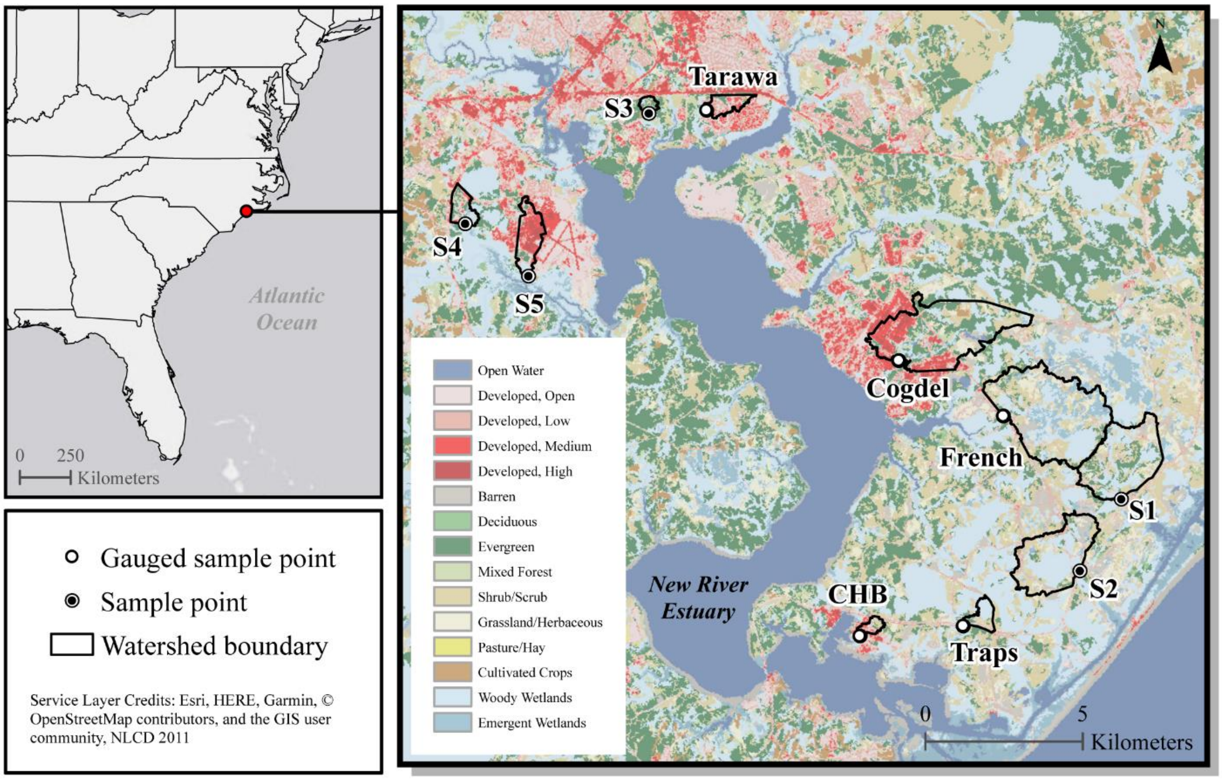

Figure 4.1. Map of study sites and watersheds on Marine Corps Base Camp Lejeune (MCBCL) near Jacksonville, NC. All ten streams were sampled for streamwater spectral analysis, and five streams were gauged for discharge and nitrogen and carbon export.

Stream export and DO concentrations

In the five gauged streams, water level and velocity were measured at 30 minute intervals with a Teledyne ISCO water level and velocity sensor, and DO concentrations were measured at 30 minute intervals with a YSI 600XL multiparameter sonde deployed in the middle of the stream channels. Stream discharge was calculated from continuous measurements of water level and velocity that were applied to stream cross-sectional areas. Samples of streamwater were manually collected from the middle of each stream twice monthly and during select storm events using automated flow-based sampling for a period of two years (June 2013 – June 2015, n = 117 - 135). Manually collected water samples were immediately refrigerated for transport and storage while automated flow-based samples were collected from the ISCO autosamplers and refrigerated within 24 hours of collection. Upon arrival at the UNC Institute of Marine Sciences, water samples were filtered (combusted Whatman GF/F, 25 mm diameter & 0.7 µm nominal pore size), and filters were frozen. Filters were then dried, ground, and analyzed for PC (and PN) with a Costech Elemental Combustion System with Elemental Analysis software. Filtered streamwater samples were frozen in precombusted glass vials, and concentrations of DOC were measured on thawed samples using a Shimadzu Total Organic Carbon 5000 analyzer that was calibrated with potassium biphthalate. Water samples were filtered (washed, dried and pre-weighed GF/F 47 mm diameter filters) for total suspended solids (TSS) concentrations within 24 hours of sampling and frozen for subsequent analysis by weight (Clesceri et al., 1998).

The load of carbon species and TSS was estimated by multiplying measured discharge by concentration that was estimated for every thirty minutes using a period-weighted step function during baseflow and a piece-wise linear function during “measured” storm events (Aulenbach et al., 2016), which was defined as 4 or more samples during a designated storm event. Storm events were manually classified based on stream discharge. To estimate concentrations during “unmeasured” storm events (3 or less samples), concentration-discharge (C-Q) relationships (Godsey et al., 2009) were created for each season (i.e., W, Sp, Su, F) using log-transformed data with outliers removed (values > 6 times the mean Cook’s distance)(Table C.3). Seasonal C-Q relationships were used to capture seasonal variation in mean concentrations, as C-Q slopes were often flat for overall PC and TSS. To limit extrapolation, the estimated concentrations for unmeasured storms were constrained by the minimum and maximum measured concentrations multiplied by 0.8 and 1.25, respectively. Upper and lower estimates of load were calculated by multiplying discharge by the upper and lower 95% confidence intervals for concentration estimates during unmeasured storms (seasonal C-Q relationships, 8 – 17% of concentration estimates) and ± 10% of the period-weighted and linear piece-wise concentration estimates. Watersheds of each study stream were delineated using ESRI ArcMap 10 and a 1-meter resolution DEM provided by the MCBCL, and stream load values were divided by watershed areas to calculate export.

Spectral analyses

Water was collected from the middle of the ten streams twice monthly for one calendar year (Jan. 2009 – Dec. 2009), and these samples (n = 22 – 25 per stream) were analyzed for various spectral properties and water quality parameters. Water samples were refrigerated immediately after collection until spectral analyses were performed, within 24 hours of sample collection. Streamwater sampling for spectral metrics did not target storms, so these samples represent conditions ranging from baseflow to moderate stormflow. The absorbance of the streamwater samples between 250 and 800 nm wavelengths were measured using a Shimadzu UV-mini 1240 spectrophotometer and 1 cm quartz cuvette. These absorption spectra were obtained from filtered streamwater samples (Whatman GF/F, 25 mm diameter & 0.7 µm nominal pore size) within one day after collection from stream headwaters. Baseline corrections to DI water were conducted at the start of the analysis and all samples were at room temperature when scanned. Absorbance values between 250 and 700 nm for each sample were corrected for background noise and other sources of error by subtracting the average absorbance between the 700 and 800 nm wavelengths (Green and Blough, 1994). Napierian absorption coefficients were then calculated using corrected absorbance data following the equation, $a_\lambda = 2.303 \times A_\lambda / l$, where a_λ is the Napierian absorption coefficient, A_λ is the measured absorbance at wavelength λ, and l is the cuvette path length in meters (Green and Blough, 1994). The absorbance at 350 nm was used to measure the concentration of CDOM (Moran et al., 2000), where higher values of absorbance indicate higher concentrations of CDOM. The ratio between the absorbance values at 254 nm and 365 nm (E_2:E_3, Leech et al., 2016) is a proxy for DOM molecular weight (Peuravuori and Pihlaja, 1997), where higher molecular weight corresponds with a lower E_2:E_3 (modified from De Haan et al. (1982) where E_2:E_3 = absorbance at 250:365 nm). The spectral slope ratio (S_r) was calculated by comparing the linear slope of log-transformed absorbance data between the ranges 275-295 nm and 350-400 nm. S_r was used as an indicator of DOM source because it captures differences in DOM molecular weight and photodegradation that are distinct for autochthonous and allochthonous material (Helms et al., 2014, 2008). Higher values of S_r correspond with autochthonous DOM (i.e., lower molecular weight, more photodegraded), and lower values of S_r are indicative of allochthonous DOM (Helms et al., 2014).

Five of the original ten streams were sampled for an additional period of two years (June 2013 – June 2015, n = 55 – 67 per stream) and analyzed for the spectral measurements listed above as well as the specific UV absorbance at 254 nm ($SUVA_{254}$) and 350 nm ($SUVA_{350}$). $SUVA_{254}$ is a proxy of CDOM aromaticity that is calculated as the absorbance at 254 nm / DOC concentration (Weishaar et al., 2003). Higher values of $SUVA_{254}$ indicate CDOM from terrestrial sources (Leech et al., 2016). $SUVA_{350}$ represents the contribution of CDOM to the entire pool of DOC (Moran et al., 2000).

Particulate organic matter quality

Particulate organic matter (POM) quality was assessed using molar ratios of carbon to nitrogen (C:N from elemental analysis described above) and concentrations of chlorophyll-*a* (chl-*a*). The general term "POM" here refers to suspended particulates within the stream, while

"PC" refers specifically to measurements of carbon export. Particulate nitrogen concentrations were measured on the same filters analyzed for PC concentrations (see section 2.2). Chl-*a* concentrations, a proxy for algal biomass, were measured by filtering water samples through GF/F filters, sonicating and extracting frozen filters for 24 hours in a 90% acetone solution, and measuring the fluorescence of the solution with a Turner Designs Trilogy fluorometer (Welschmeyer, 1994).

Data analysis

All collected data were assessed for normality and homogeneity of variance using a Shapiro-Wilk test and Bartlett test, respectively. Even after various data transformations, data did not meet the assumptions of parametric tests, so non-parametric Kruskal-Wallis and Dunn's post-hoc test with Bonferroni adjustments ($\alpha = 0.05$) were used to test for significant differences in measured variables between study streams (Dinno, 2017). All statistical analyses were performed in R (R Core Team, 2020).

To illustrate differences in the timing of export between carbon species, the percent of cumulative carbon export was calculated for each value of discharge. Instantaneous carbon export rates for both DOC and PC were arranged in ascending order based on rates of instantaneous discharge, and a cumulative sum of each carbon species was calculated for each value of export. Cumulative values of export were then converted to percent of cumulative carbon export by dividing cumulative export by the total sum of export and multiplying by 100. Gini coefficients, a measure of the temporal inequality in export (Jawitz and Mitchell, 2011), were calculated for DOC and PC export as well. C-Q slopes (Godsey et al., 2009) and CV_C/CV_Q values (Musolff et al., 2017) for entire study period were calculated and used to describe the carbon export regime and potential sources of carbon within the watershed. For example, a low CV_C/CV_Q value (< 0.5) and a relatively flat C-Q slope (-0.2 – 0.2) would indicate that variation in discharge rather than concentration drive the variation in export, and this export regime would be described as chemostatic. A chemodynamic export regime would mean that variation in export is driven by variation in concentration rather than discharge ($CV_C/CV_Q > 0.5$), and the direction of C-Q slope would indicate the source of material (i.e., flushing vs. dilution during storm events).

To characterize the relationship between ISC and DOM quality, the relationship between median values of spectral indices for the ten streams sampled in 2009 and watershed ISC were fit with a linear or logarithmic regression. Differences in DOM quality between the five intensively-sampled streams were visualized using non-metric multidimensional scaling (NMDS) ordination of the metrics of CDOM, $SUVA_{254}$, E_2:E_3, and S_r created with the *vegan* package in R (Oksanen et al., 2019). Prior to NMDS, the variable inflation factor (VIF) for each spectral metric was assessed, and the metrics of $SUVA_{350}$ and a_{254} were excluded due to VIF values greater than 10. All input data were log-transformed, centered, and scaled and outliers were removed (values > 4 times the mean Cook's distance). The NMDS used Euclidean distances and two dimensions. The influence of discharge on carbon quality was assessed using linear regressions between log-transformed carbon quality metrics and discharge.

Dissolved oxygen data were converted from mg/L to percent saturation using measured water temperature data (Garcia and Gordon, 1992). Exceedance values were calculated for DO percent saturation values to visualize the distribution of DO values, which can provide information about stream DO and biogeochemical patterns (Blaszczak et al., 2019). Daily ranges of DO data were calculated by subtracting the minimum DO percent saturation values from the maximum values for each day. Average diel patterns of DO were visualized by taking the mean of DO percent saturation values for the gauged study period (June 2013 – June 2015) for each thirty-minute sampling time step. Diel patterns of DO can represent the amount of gross primary productivity within a stream (Bernhardt et al., 2018).

Results

Stream carbon export and concentrations

Magnitude of export and concentration

Carbon export was higher for the two least developed streams (French and Traps) than the urban Cogdel and Tarawa streams, but lower than the most developed stream, CHB (Table 4.2). PC export generally increased with watershed ISC while DOC export decreased with watershed ISC, except for the CHB stream which had extremely high rates of DOC export (Table 4.2). DOC was the dominant form of organic carbon export from all study streams, and the relative amount of DOC to PC was highest in the least developed streams and lowest in the Tarawa stream (Table 4.2). The export of suspended solids also increased with imperviousness (Table 4.2).

Concentrations of PC, DOC, and TSS exhibited similar patterns with watershed ISC as export – PC concentrations were significantly higher in the two most developed streams (Tarawa and CHB), DOC concentrations were significantly lower in Cogdel and Tarawa streams, and TSS concentrations were highest in the Tarawa and CHB streams and lowest in the least developed stream (French) (Table 4.2). Despite having the highest rates of export, concentrations of PC, DOC, and TSS in the CHB stream were not the highest of the study streams (Table 4.2).

Table 4.2. Export and concentrations of C species and TSS. Letters indicate significant differences in stream concentrations based on Kruskal-Wallis and Dunn's tests.

			Export (kg ha^{-1} yr^{-1})			% of total C export		Median concentrations (IQR) (mg/L)		
Name	**ISC (%)**	**Discharge (m yr^{-1})**	**PC**	**DOC**	**TSS**	**PC**	**DOC**	**PC**	**DOC**	**TSS**
French	0.96	0.32	4.74 (4.0 – 5.71)	45.08 (40.34 – 50.0)	10.44 (8.58 – 13.23)	9.52	90.48	1.5 (1.46)^{a}	14.57 (6.48)^{a}	3.2 (6.69)^{a}
Traps	3.93	0.46	8.26 (6.77 – 10.76)	59.25 (52.97 – 65.9)	52.25 (41.89 – 87.33)	12.23	87.77	1.76 (2.14)^{ab}	12.55 (3.93)^{ad}	6.06 (12.47)^{b}
Cogdel	19.24	0.49	8.24 (6.93 – 9.94)	32.81(29.5 – 36.19)	80.59 (63.75 – 111.42)	20.08	79.92	1.55 (1.43)^{a}	5.98 (2.52)^{b}	7.01 (23.07)^{bc}
Tarawa	33.27	0.67	25.58 (18.12 – 41.02)	31.48 (27.33 – 35.48)	211.47 (122.95 – 393.12)	44.83	55.17	2.42 (2.3)^{c}	4.4 (1.89)^{c}	9.55 (21.39)^{c}
CHB	38.16	3.04	82.39 (68.78 – 100.89)	353.80 (317.9 – 390.2)	541.62 (447.76 – 689.21)	18.89	81.11	2.09 (1.7)^{bc}	10.35 (6.75)^{d}	8.73 (11.53)^{c}

Timing of export

The timing of DOC and PC export varied by stream based on watershed size and watershed ISC (Figure C.1), but there were notable differences in the timing of DOC export relative to PC export based on watershed ISC (Figure 4.2, Figure C.1). Streams with lower watershed ISC had DOC and PC export at similar values of discharge, whereas PC was exported at higher values of discharge than DOC in the more developed streams (Figure 4.2a, Figure C.1). DOC C-Q slopes differed greatly between streams (Figure 4.2b), but the variance in DOC concentrations relative to discharge was low ($CV_C/CV_Q < 0.5$, Figure C.2), showing that discharge generally controlled the timing of DOC export (i.e., chemostatic export regime). PC export was chemodynamic for all streams (i.e., $CV_C/CV_Q > 0.5$, Figure C.2), meaning that the strength and direction of PC C-Q relationships impacted the timing of PC export. High flows were more important times for PC export in the more developed streams because the C-Q relationships became stronger and more positive with increasing watershed ISC (Figure 4.2).

Though DOC export was chemostatic, all but one stream (Traps) had a significant relationship between discharge and DOC concentrations (Figure 4.2b). French and Tarawa streams had positive relationships between DOC concentration and discharge, indicating a flushing of DOC during high flows. PC C-Q slopes were slightly positive for all streams, but only the two most developed streams had significant C-Q relationships (Figure 4.2c). TSS C-Q slopes increased with watershed ISC, and the three most urban streams were the only streams that had significant relationships with discharge (Figure C.3).

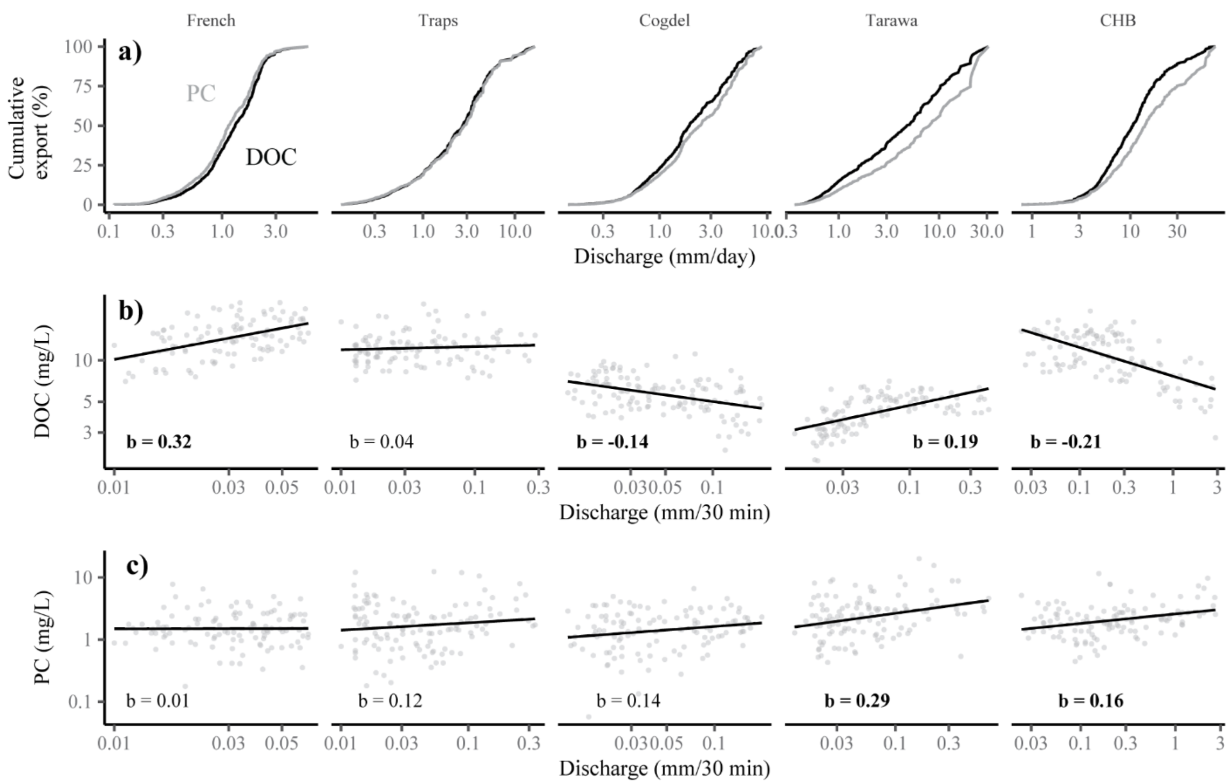

Figure 4.2. a) Cumulative export of DOC and PC across values of discharge. **b)** Relationships between DOC and discharge, and **c)** PC and discharge. Overall slopes of the C-Q relationships are presented as b, with bold values indicating significant C-Q relationships (α = 0.05)

Carbon Quality

Relationship with ISC

Watershed ISC was significantly correlated with streamwater CDOM concentration (a_{350}) based on a negative logarithmic relationship (Figure 4.3a, Table C.4). Streamwater E_2:E_3 and S_r were both significantly correlated with watershed ISC as well, exhibiting positive relationships with ISC (Figure 4.3b, 3.3c, Table C.4). Plotting S_r versus CDOM showed that streams with higher watershed ISC (>15%) had low CDOM and high S_r values and streams with less developed watersheds had higher concentrations of CDOM and lower S_r values (Figure 4.3d). The subset of five streams selected for additional monitoring exhibited the same relationships between spectral indices (CDOM, E_2:E_3, and S_r) and watershed ISC illustrated in Figure 4.3, although the relationship between S_r and watershed ISC was not significant (Figure C.4). Both $SUVA_{254}$ and $SUVA_{350}$ were significantly correlated with watershed ISC based on negative logarithmic relationships (Figure C.4).

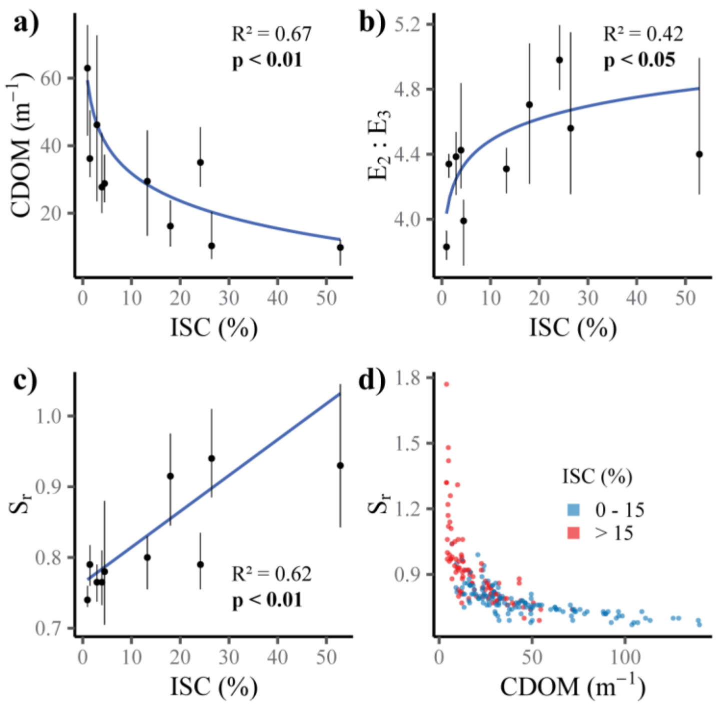

Figure 4.3. a) Concentrations of CDOM (a_{350}), **b)** E_2:E_3 (a_{254}:a_{350}), and **c)** spectral slope ratios (S_r) in streamwater samples from ten streams across a range of watershed ISC. Points indicate median values and error bars show the 25th and 75th percentiles. **d)** Relationship between CDOM and S_r for ten sampled streams which showed a distinct relationship with watershed ISC.

An NMDS ordination of DOM quality metrics from the five gauged streams further illustrated the differences in carbon quality with watershed ISC (Figure 4.4). Samples from the more developed streams had lower values of CDOM and aromaticity ($SUVA_{254}$) and higher values of S_r and E_2:E_3 than less developed streams (Figure 4.4). While not shown in the NMDS, the more developed streams also had lower relative values of CDOM to DOC ($SUVA_{350}$).

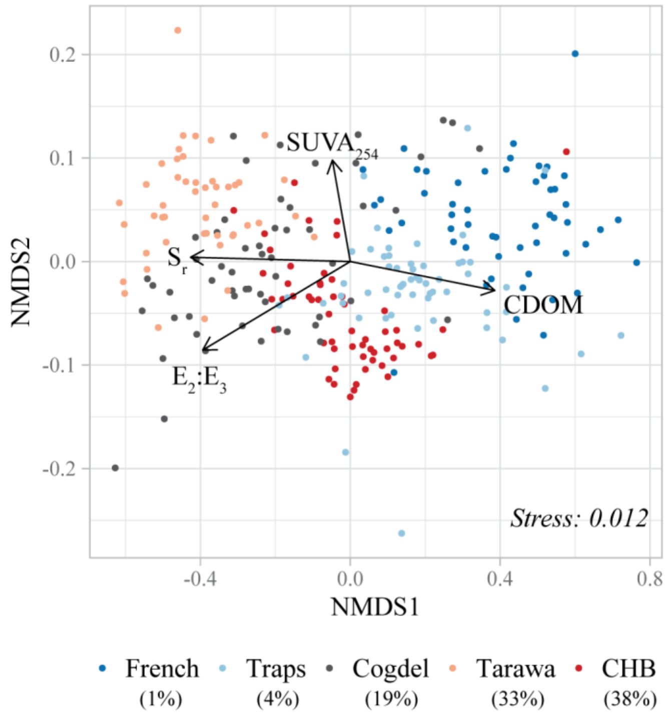

Figure 4.4. NMDS ordination of spectral indices from five gauged streams across a gradient of watershed ISC.

The carbon to nitrogen ratio (C:N) of POM, an indicator of organic matter lability and source, was significantly higher in the three streams with lower watershed ISC than the two most developed streams (Figure 4.5a, Table C.5). The two streams with higher ISC and lower C:N also had significantly higher chl-*a* concentrations than the three streams with lower watershed ISC (Figure 4.5b, Table C.5). C:N decreased as chl-*a* increased based on a log-log relationship, and this relationship was significant but highly variable (Figure C.6).

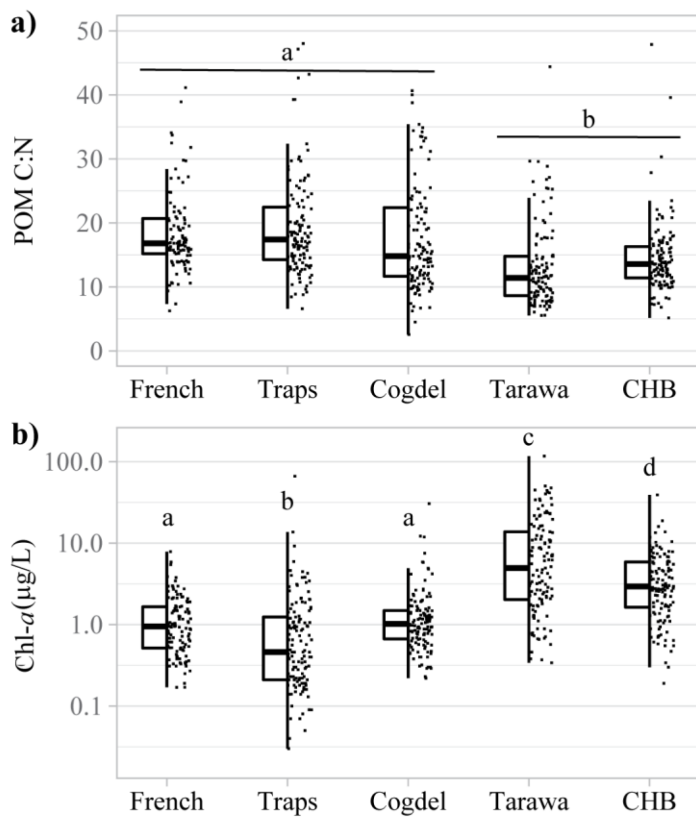

Figure 4.5. a) Boxplot of particulate C:N and **b)** chl-*a* concentrations (log-scale) for each watershed. Letters indicated significant differences based on a Kruskal-Wallis and Dunn's post-hoc test with Bonferroni adjustments ($\alpha = 0.05$).

Changes in carbon quality with discharge

Indices of carbon quality for both dissolved and particulate carbon changed with discharge, although the effect of discharge differed based on watershed ISC (Figure 4.6). The two least developed streams had significant, positive relationships between CDOM and discharge, but neither stream had significant relationships between any other spectral metrics and discharge. In contrast, the three more developed streams had varying relationships with discharge for S_r and CDOM, but all three streams had significant, positive relationships between $SUVA_{350}$ (proxy of CDOM:DOC) and discharge. All streams had positive relationships between discharge and $SUVA_{254}$ and negative relationships between discharge and E_2:E_3, but for both spectral indices, two of the three more developed streams had a significant relationship with discharge. Particulate C:N ratios decreased with discharge in every study stream, and chl-a concentrations were only significantly related to discharge in the Tarawa stream where there was a positive relationship.

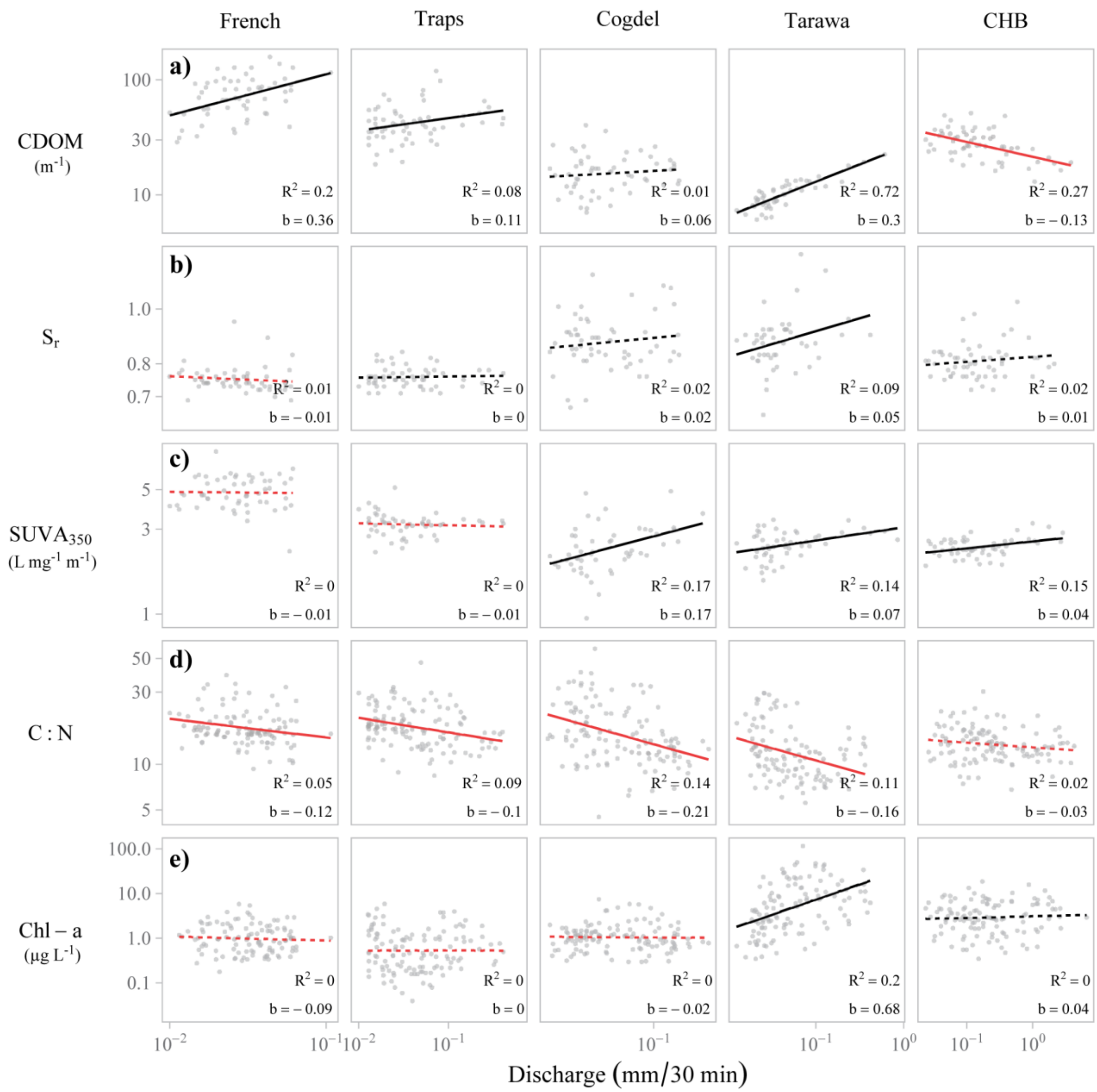

Figure 4.6. a – c) The relationship between DOM spectral metrics and discharge. **d & e)** The relationship between POM quality indices and discharge. Regression lines indicate if the slope

(b) is positive (black) or negative (red) and significant (full line, α = 0.05) or not significant (dashed line).

Dissolved oxygen concentrations

Dissolved oxygen concentrations were significantly different between study streams, but the concentrations did not correspond with watershed ISC (Table C.6). There were large differences in mean DO concentrations and DO exceedance distributions between streams with similar watershed ISC, such as the two least developed streams, French and Traps (Figure 4.7a). Higher flows appeared to elevate DO in all study streams, but the two less developed streams had significantly less diel variation of DO during typical baseflow conditions. The diel range of DO percent saturation increased with watershed ISC (Figure 4.7b), and this can be visualized by comparing the average diel pattern of DO concentrations (Figure 4.7c).

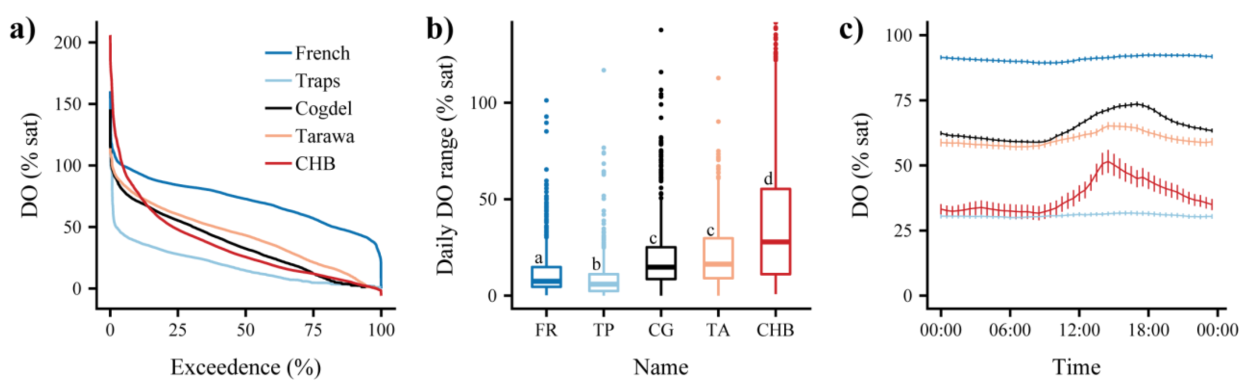

Figure 4.7. a) Exceedance plot of dissolved oxygen. **b)** Daily DO range for each stream with letters indicating significant differences based on a Kruskal-Wallis and Dunn's post-hoc test with Bonferroni adjustments (α = 0.05). **c)** Average diel pattern of DO during baseflow over study period (bars indicate SE).

Discussion

Streams in the southeastern US coastal plain have an outsized impact on carbon supply and ecosystem function in coastal waters due to their proximity and high carbon concentrations (Leech et al., 2016; Spencer et al., 2013), but the effects of urbanization on carbon composition and export in streams have not been extensively studied. Results from this study show that DOC export generally decreased with watershed ISC while PC export increased, although watershed-specific characteristics of the urban study streams were important controls on the magnitude of carbon export. Differences in the timing of DOC and PC export and indices of carbon quality suggested that exported carbon shifted towards autochthonous or anthropogenic sources with increasing watershed ISC. Finally, significantly larger diel DO patterns in the urban study streams showed the impact of urbanization and shifting carbon sources on stream function. While these results align with past studies in other areas (Hassett et al., 2018; Hosen et al., 2014; Parr et al., 2015; Smith and Kaushal, 2015; Williams et al., 2016), the changes in stream carbon export may be especially large and ecologically impactful in the study area or streams in similar physiographic regions due to the naturally high concentrations of streamwater DOC and CDOM.

Urbanization effects on dissolved carbon

The strong relationships between streamwater spectral properties and watershed ISC suggest that the sources and processing of carbon changed with urbanization, and these changes were nonlinear (Figures 3 and 4). For the ten study streams, CDOM concentrations decreased rapidly with increased watershed ISC, but at a certain point (approximately 15% ISC in this study), further increases in watershed ISC were accompanied by minimal changes in CDOM concentrations and large changes in streamwater S_r. This relationship indicates that urbanization as measured by ISC appeared to reduce the characteristic color of the blackwater study streams and shift the dissolved C pool towards autochthonous or anthropogenic sources. Results from the two year monitoring period of five streams exhibited a similar pattern in DOM quality, as well as a general reduction in DOC export with watershed ISC. DOC export was chemostatic for all five gauged study streams ($CV_C/CV_Q < 0.5$), so despite large differences in streamwater DOC concentrations with watershed ISC, the timing of DOC export strongly followed the timing of discharge.

At lower watershed ISC, the spectral properties of DOM were similar to those of coastal plain streams or rivers measured previously (Hosen et al., 2018, 2014; Leech et al., 2016; Spencer et al., 2013). These characteristics included high concentrations of CDOM and DOC, CDOM constituting a larger part of the DOC pool (i.e., high $SUVA_{350}$), and spectral indices that indicate high molecular weight DOM that is more aromatic, minimally photodegraded, and indicative of allochthonous terrestrial sources such as wetlands or forests (i.e., low E_2:E_3, high $SUVA_{254}$, low S_r)(Bhattacharya and Osburn, 2020; Dosskey and Bertsch, 1994; Hosen et al., 2018; Petrone et al., 2011; Spencer et al., 2013). While this study did not directly analyze the relationship between wetland and forest cover on DOM quality, the measured spectral indices (Figure 4.3), patterns of both DOC and CDOM enrichment with stream discharge (Figure 4.4, Figure 4.6a), and a significant relationship between % ISC and % wetland land cover in the study watersheds (R^2 = 0.78, p < 0.01, Table C.1) suggests that wetland and forest land cover was a large source of DOM for the minimally impacted streams. Rates of DOC export were high (45 – 59 kg ha^{-1} yr^{-1}) in the two least developed gauged streams (French and Traps) compared to DOC export from minimally impacted streams and rivers in other temperate physiographic regions (mean: 37.9 kg ha^{-1} yr^{-1}, median: 18.0 kg ha^{-1} yr^{-1}, Hope et al., 1994). Rates of DOC export from blackwater headwater streams in the southeastern US coastal plain are lacking, but the rates presented here for the two minimally impacted streams were comparable to DOC export from larger blackwater rivers such as the Chowan river in North Carolina (22.3 [dry year]– 69.1 [wet year] kg ha^{-1} yr^{-1}, Leech et al., 2016) and the Edisto river in South Carolina (58.3 kg ha^{-1} yr^{-1}, Spencer et al., 2013). Rates of DOC export from the two minimally impacted streams were also similar to rates of total carbon export from blackwater stream-wetland ecosystems in the coastal plain of North Carolina (18.9 – 83.7 kg ha^{-1} yr^{-1}, Mulholland and Kuenzler, 1979).

At higher watershed ISC, streamwater spectral indices indicated that DOM had lower aromaticity, lower molecular weight, and was more photodegraded (i.e., low $SUVA_{254}$, high E_2:E_3, high S_r). These spectral indices suggest that the pool of natural DOM from wetland and forest sources (Dosskey and Bertsch, 1994; Huang and Chen, 2009) was reduced (i.e., lower CDOM, $SUVA_{350}$, DOC), and the pool of carbon shifted towards autochthonous or anthropogenic sources of DOM. Rates of DOC export from the Cogdel and Tarawa streams (31 – 32 kg ha^{-1} yr^{-1}) were much lower than the two least developed streams, and measured spectral indices strongly suggest that this lower DOC export was due to a lack of wetland- or forest-derived DOM that was prevalent in the less developed streams. This reduced amount of allochthonous DOM in the more developed streams could be attributed to less wetland area in the watershed and riparian zone (Bhattacharya and Osburn, 2020; Pisani et al., 2020) or to decreased connectivity between the stream and floodplain due to stream incision and stormwater discharge directly to the stream (O'Driscoll et al., 2010). Rates of DOC export from the Cogdel and Tarawa streams were similar to those from urban streams in the Baltimore/DC metro area (7.2 - 39 kg ha^{-1} yr^{-1}, Pennino et al., 2016; 9 -23 kg ha^{-1} yr^{-1}, Smith & Kaushal, 2015) and western Australia (11 - 35 kg ha^{-1} yr^{-1}, Petrone, 2010). The most developed stream had significantly more DOC export than all other streams (353.80 kg ha^{-1} yr^{-1}), but this unexpectedly high rate of DOC export may be attributed to a suspected failing sanitary sewer system in the watershed that could explain increased rates of discharge as well as ammonium and organic nitrogen export (Gold et al., 2019b).

There was variability in DOM quality among urban streams, and the more intensive monitoring of the five study streams indicated that this was likely due to watershed-specific attributes such as stream canopy cover, the type of stormwater management, and wastewater infrastructure. Stream canopy cover of Cogdel (19% ISC) was high (~70%, similar to the two least developed streams), and wetland cover was nearly 13% of the watershed area. The low concentration and export of DOC from Cogdel as well as highly variable carbon quality metrics that overlapped with the two least developed streams (Figure 4.4) suggest that natural sources of DOM were present but diminished (Figure 4.4, Figure 4.6). The Tarawa stream, fed primarily by stormwater ponds that are flushed during storm events, exhibited a distinct autochthonous DOM signature (Figure 4.4) that increased with discharge (Figure 4.6). The most developed stream, CHB (38% ISC), had a mean DOC and CDOM concentration that was similar to the two least developed streams, but both were diluted with increased discharge and had much lower molecular weight DOM (higher E_2:E_3) than all other study streams (Figures 2, 3, 6). These results could suggest a sanitary sewer leak as the dominant source of DOC in at this site.

Additional anthropogenic sources of DOM found in urban streams can include yard waste leachate, wastewater, and hydrocarbons from roadways (Hosen et al., 2014; Newcomer et al., 2012; Williams et al., 2016). While not measured in this study, previous studies have also demonstrated a shift from humic-like DOM derived from allochthonous sources to protein-like DOM derived from autochthonous production within stream or stormwater networks (Hassett et al., 2018; Hosen et al., 2018, 2014; Newcomer et al., 2012; Parr et al., 2015; Williams et al., 2016).

Urbanization effects on particulate carbon

The qualities and timing of PC export measured in this study point to algal biomass as an important constituent of POM in the urban study streams, particularly in the Tarawa stream that was fed by a watershed drainage system of stormwater ponds. The C:N of POM was significantly lower in the two most urban study streams relative to the other study streams, and this difference corresponded with significantly higher concentrations of algal biomass (as chl-*a*) and higher rates of PC and TSS export (Figure 4.5, Table 4.2). Rates of particulate nitrogen and algal biomass export also increased with watershed ISC in the same study streams as shown by Gold et al., 2019. Higher S_r values in the urban streams suggest that this algal material was likely an important contributor to the DOM pool as well, and this has been previously observed in urban streams (Hassett et al., 2018; Hosen et al., 2018, 2014; Newcomer et al., 2012; Parr et al., 2015; Williams et al., 2016).

We suggest that physical changes to the stream network and increased nutrient availability promoted autochthonous carbon production in the more urban study streams that impacted both POM and DOM pools. The timing of PC export shifted towards higher flows with increasing watershed ISC compared to DOC (Figure 4.2, Figure C.1), meaning that a large amount of PC in more developed streams was likely supplied from within the watershed or stormwater network and transported during stormflows. The two most developed streams had lower canopy cover than the other study streams (Table C.2), and lower canopy cover can promote more algal growth within urban streams (Arango et al., 2008; Bernot et al., 2010;

Reisinger et al., 2019) as well as in minimally-disturbed blackwater streams (Carey et al., 2007). Stormwater ponds can export a large amount of algal-derived particulate nitrogen during high flows when they are flushed (Gold et al., 2019b, 2017b), and catchment-scale stormwater networks in general promote more autochthonous production within the stream (Imberger et al., 2014). Stormwater ponds located in the Tarawa watershed appeared to modify the particulate and dissolved carbon pools by generating algal biomass, as shown in the same ponds previously (Gold et al., 2019b, 2017b). Nutrient availability (NO_x & NH_4 concentrations) increased with watershed ISC in the same five gauged streams during the same period (Gold et al., 2019b), and coupled with the physical changes to the stream network, likely promoted the observed increase in algal biomass and decrease in C:N of POM in the urban streams. Less impacted blackwater streams typically have low concentrations of inorganic forms of nitrogen and algal biomass, but excess nitrogen has been shown to promote algal production (Mallin et al., 2004) and algal-derived DOC (Reed et al., 2015).

Specific sources of POM in urban streams determined from previous studies include phytoplankton, leaf litter, periphyton, soil, and lawn clippings (Imberger et al., 2014; Newcomer et al., 2012). Methods used in this study were not able to distinguish these sources of POM, but the signal of increased autotrophic production by algal biomass appeared to be an important source of POM in the urban study streams.

Changing DO dynamics with urbanization

Diel variation of DO was greater in streams with higher watershed ISC (Figure 4.7b, c), illustrating how the impacts of urbanization, including the demonstrated shift in the composition of exported carbon, affected stream function. More specifically, the increased diel variation of

DO with watershed ISC is a signal of increased primary production, as large amounts of diel variation in DO can signify high rates of gross primary production within the stream (Bernhardt et al., 2018). Greater diel variation in DO as an indicator of increased primary productivity is further supported by the finding that streamwater from the urban study streams had elevated concentrations of algal biomass (as chl-*a*) and more labile PC. While not measured in the current study, benthic algae could also contribute to the increased diel DO variation in the urban study streams. Benthic algal growth is typically low in southeastern US coastal plain streams due to light limitation and seasonally low flows (or no flow) during the summer (Carey et al., 2007), but the urban study streams have less seasonal flow variation and less canopy cover than the less developed streams (Gold et al., 2019b). The observed differences in spectral indices suggesting a shift in the DOM pool towards autochthonous and anthropogenic sources with watershed ISC may also play a role in elevated diel variation in DO. Anthropogenic DOM in urban streams can be more bioavailable and have quicker turnover times than DOM from natural sources (Hosen et al., 2014; Parr et al., 2015; Williams et al., 2016), and this can increase rates of stream metabolism (Kaushal et al., 2014). In inland streams, changes in stream metabolism with urbanization can have deleterious effects on macroinvertebrate communities and nutrient removal rates (Paul and Meyer, 2001; Walsh et al., 2005). Though rates of metabolism are not presented here, the elevated primary production seen in the urban study streams can cause hypoxic conditions that have negative consequences for the ecological integrity of coastal plain streams (Mallin et al., 2006, 2004; Sanger et al., 2013).

Concentrations of DO did not correspond with watershed ISC and were significantly different among streams of lower imperviousness (Table C.6). The mechanisms behind these differences are unclear, especially since DO concentrations in minimally impacted blackwater streams have been found to be relatively low due to high biological oxygen demand from heterotrophic bacteria and high concentrations of DOC (Mallin et al., 2004; Meyer, 1990). The differences in mean DO concentrations between the two minimally impacted streams suggests that this factor alone may not be a good indicator of stream health in these coastal plain streams.

Managing coastal watersheds to support coastal ecosystems

This study shows that urbanization in coastal watersheds can alter the magnitude and composition of exported carbon and have effects on stream function, but coastal urbanization can also have profound impacts further downstream in important coastal water bodies. DOC, and specifically CDOM in blackwater streams, is an important source of carbon for myriad estuarine processes that positively influence estuarine trophic status (Leech et al., 2016). A shift to more bioavailable DOM (Hosen et al., 2014; Parr et al., 2015) and increased export of labile autochthonous POM from urban streams (this study, Imberger et al., 2014) may further impair receiving waters by increasing algal production and bacterial metabolism (Wear et al., 2014). While the shift towards autochthonous DOM and POM shown in this study is especially relevant for high-DOC blackwater streams in the southeastern US, other blackwater streams or streams in similar physiographic regions may be similarly affected. To promote the health of downstream coastal ecosystems, changes in carbon export quality and quantity as well as elevated nutrient export due to urbanization should be addressed (Stanley et al., 2012).

Management actions to mitigate the effects of urbanization on carbon composition and export could include the protection and restoration of natural wetlands within the watershed, implementing constructed wetlands for stormwater management, and stream restoration that improves floodplain connectivity and restores stream canopy cover. In the lower range of watershed ISC in this study (approximately < 15%), increases in ISC corresponded with large reductions in CDOM concentrations, so management strategies that enhance the delivery of CDOM from natural sources could help maintain typical blackwater carbon and nitrogen composition. These strategies could include maintaining larger amounts of natural wetland and forest area and implementing stormwater control measures (SCMs) that promote infiltration and evapotranspiration of stormwater rather than open-water, retention-based SCMs that promoted the growth of algal biomass. Constructed stormwater wetlands are likely a better SCM for coastal stormwater management because they can act as inorganic nitrogen sinks (Messer et al., 2017) and also help maintain CDOM, organic nitrogen and DOC concentrations, although the quality of the DOM may be different than that from natural wetlands (Hosen et al., 2018). At higher values of ISC (approximately > 15% ISC), concentrations of CDOM were much lower than minimally impacted streams, and the main distinctions in spectral indices between the more urban watersheds were related to different amounts of photodegradation and autochthonous DOM production (S_r). Stream restoration that reestablishes floodplain connectivity and stream canopy cover may help mitigate negative effects of development on carbon export in urban streams by producing natural DOM (Dosskey and Bertsch, 1994; Stanley et al., 2012), removing inorganic nitrogen that can fuel autotrophic production (Klocker et al., 2009), and increasing canopy cover to reduce autochthonous production and stream metabolism (Tank et al., 2018). In the study area, management actions that aim to restore the pre-development hydrologic balance could reduce nutrient export that helps fuel autochthonous production (Gold et al., 2019b) and erosive stormflows that lead to stream channel incision (Hardison et al., 2009).

The spectral indices of DOM used in this study can serve as reliable indicators of anthropogenic impact on blackwater coastal plain streams. While not as robust as excitationemission matrices (commonly known as "EEMs"), these spectral indices require less sophisticated equipment, have a deep history in the literature, and are straightforward to interpret. Spectral indices indicative of typical blackwater streams do not ensure that a stream has not been impacted by urbanization, but it does suggest that water quality is likely better than that of a stream with spectral indices related to low CDOM concentrations, low molecular weight (E_2:E_3), and higher levels of photodegradation (S_r)(Gold et al., 2019b). Measuring the simple spectral indices of streamwater used in this study can provide an approximate indicator of impact from impervious surfaces and help managers track changes over time.

Conclusions

This study measured the spectral properties of streamwater from ten coastal blackwater streams in North Carolina along with carbon export and DO concentrations from a subset of five streams. The quality of DOM appeared to change with watershed ISC, with spectral indices from urban streams indicating lower concentrations of CDOM, DOM aromaticity, and DOM molecular weight than less impacted streams. Differences in spectral indices and their relationships with discharge suggest that natural DOM sources, such as wetland and forest land cover, were reduced and replaced with autochthonous and anthropogenic DOM sources as watershed ISC increased. The urban study streams had apparent differences in DOM quality and export that corresponded with watershed-specific attributes such as wetland and canopy cover, the presence of stormwater ponds, and perhaps point source inputs. In general, DOC export was much lower in the urban streams (31 – 32 kg ha^{-1} yr^{-1}) than the minimally impacted streams (45 – 59 kg ha^{-1} yr^{-1}), except for a single urban stream with abnormally high rates of DOC export (354 kg ha^{-1} yr^{-1}) suspected as a point source sewage leak. POM in the urban streams was indicative of more labile autochthonous sources (i.e., algal biomass) than that of the less impacted streams, especially in the stream draining stormwater ponds. Rates of PC export increased with watershed ISC (5 – 82 kg ha^{-1} yr^{-1}) and the relative importance of PC export to DOC export from the three more urban streams was higher than the minimally impacted streams. PC export occurred at higher flows than DOC due to increasingly strong positive relationships between PC and discharge. Diel variation of DO percent saturation increased with watershed ISC, representing an impact of urbanization-linked changes on stream function. The effects of urbanization on carbon export in the study streams were similar to those measured in other regions, but the uniquely high CDOM and DOC concentrations of coastal plain streams and coastal receiving waters may make them especially susceptible to negative ecological impacts from altered carbon and nutrient export. We suggest that the ecological integrity of southeastern US coastal plain streams and downstream coastal water bodies may be better maintained by mitigating the observed effects of urbanization on C export. Suggested management actions include protecting and restoring natural wetlands within the watershed, implementing constructed wetlands for stormwater management, and restoring stream floodplain connectivity and stream canopy cover.

APPENDIX A: SUPPLEMENTARY FIGURES AND TABLES FOR CHAPTER 2

Table A.1. Spearman correlation values between ambient pond water quality measurements (n=20) and sediment properties (n=18). Bold values indicate $p < 0.05$.

	Surface Temperature	RTRM	[ON]	[NH_4]	[PO_4]	[Chl-a]	OM
RTRM	0.4						
[ON]	**0.59**	0.37					
[NH_4]	-0.13	0.29	0.24				
[PO_4]	-0.03	0.17	0.03	0.16			
[Chl-a]	0.22	-0.31	0.37	-0.07	-0.02		
OM	-0.3	**0.56**	0.03	**0.52**	0.23	**-0.50**	
C:N	-0.14	**0.57**	0.05	0.44	0.33	**-0.51**	**0.87**

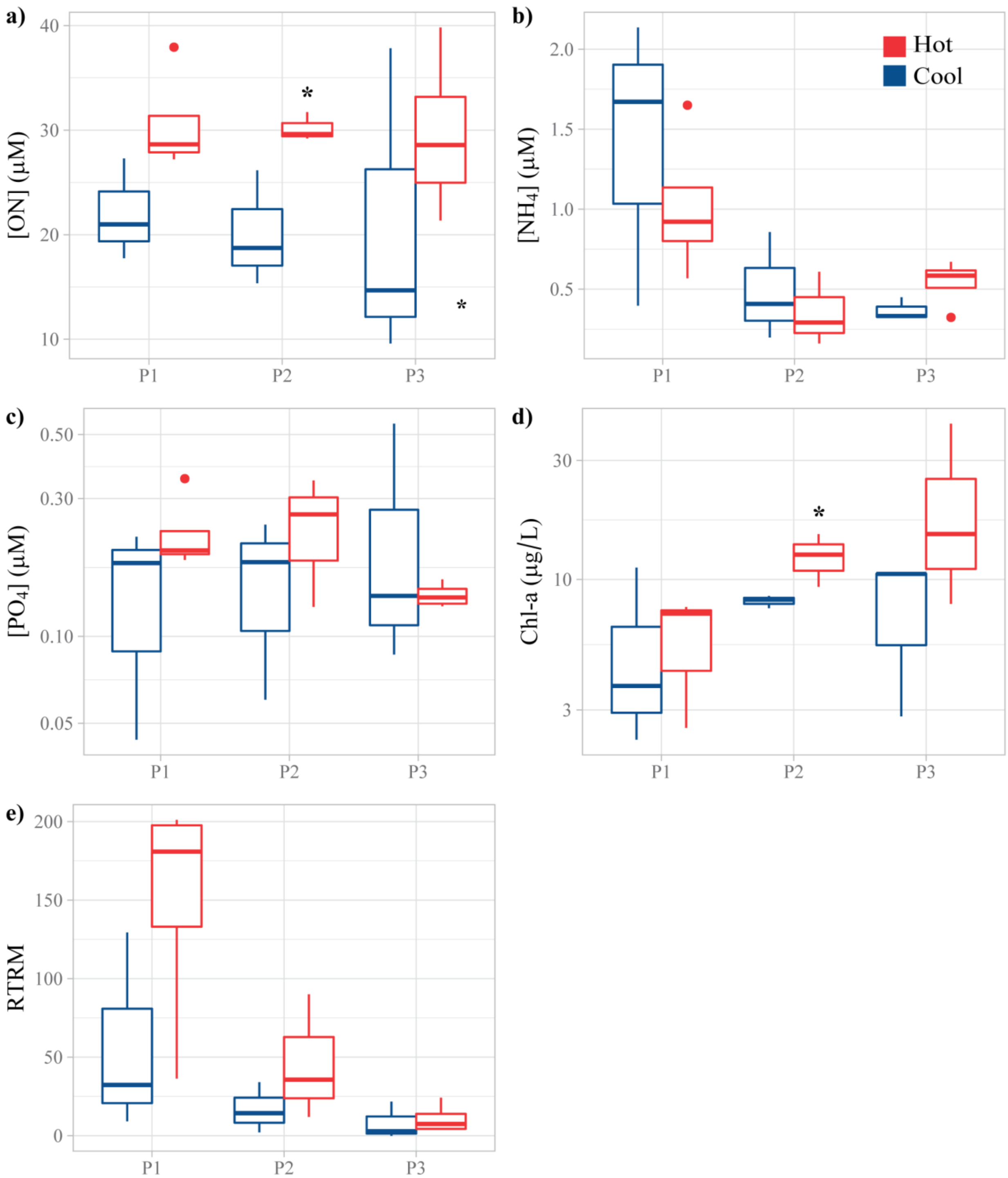

Figure A.1. Ambient measurements for **a)** dissolved organic nitrogen (DON), **b)** ammonium (NH_4), **c)** orthophosphate (PO_4), **d)** chlorophyll-a (Chl-a), and **e)** RTRM of ponds. Asterisks indicate significant differences between temperature groups (blue vs. red) based on a Kruskal-Wallis test ($\alpha = 0.05$).

Table A.2. Spearman correlation values between core flux measurements (n=58) and sediment properties (n=51). Bold values indicate $p < 0.05$. Correlation values for NO_x during ambient conditions were not calculated because the majority of values were below detection.

Ambient

	TN	N_2	O_2	DON	NO_X	NH_4	OM
N_2	-0.06						
O_2	0	0.16					
DON	**0.96**	-0.1	-0.03				
NO_X	-	-	-	-			
NH_4	**0.3**	0.21	-0.03	0.09	-		
OM	**0.32**	-0.08	0.09	**0.4**	-	-0.22	
C:N	**0.44**	0.05	0.24	**0.45**	-	0.04	**0.82**

NO_x-enriched

	TN	N_2	O_2	DON	NO_X	NH_4	OM
N_2	0.22						
O_2	**0.28**	0.1					
DON	**0.74**	0.18	-0.11				
NO_X	0.2	**0.3**	**0.73**	**-0.35**			
NH_4	0.17	-0.17	0.04	0.02	0.14		
OM	-0.02	0.08	0.1	0.09	-0.25	**-0.46**	
C:N	0.1	-0.15	**0.29**	0.1	-0.1	**-0.32**	**0.82**

APPENDIX B: SUPPLEMENTARY FIGURES AND TABLES FOR CHAPTER 3

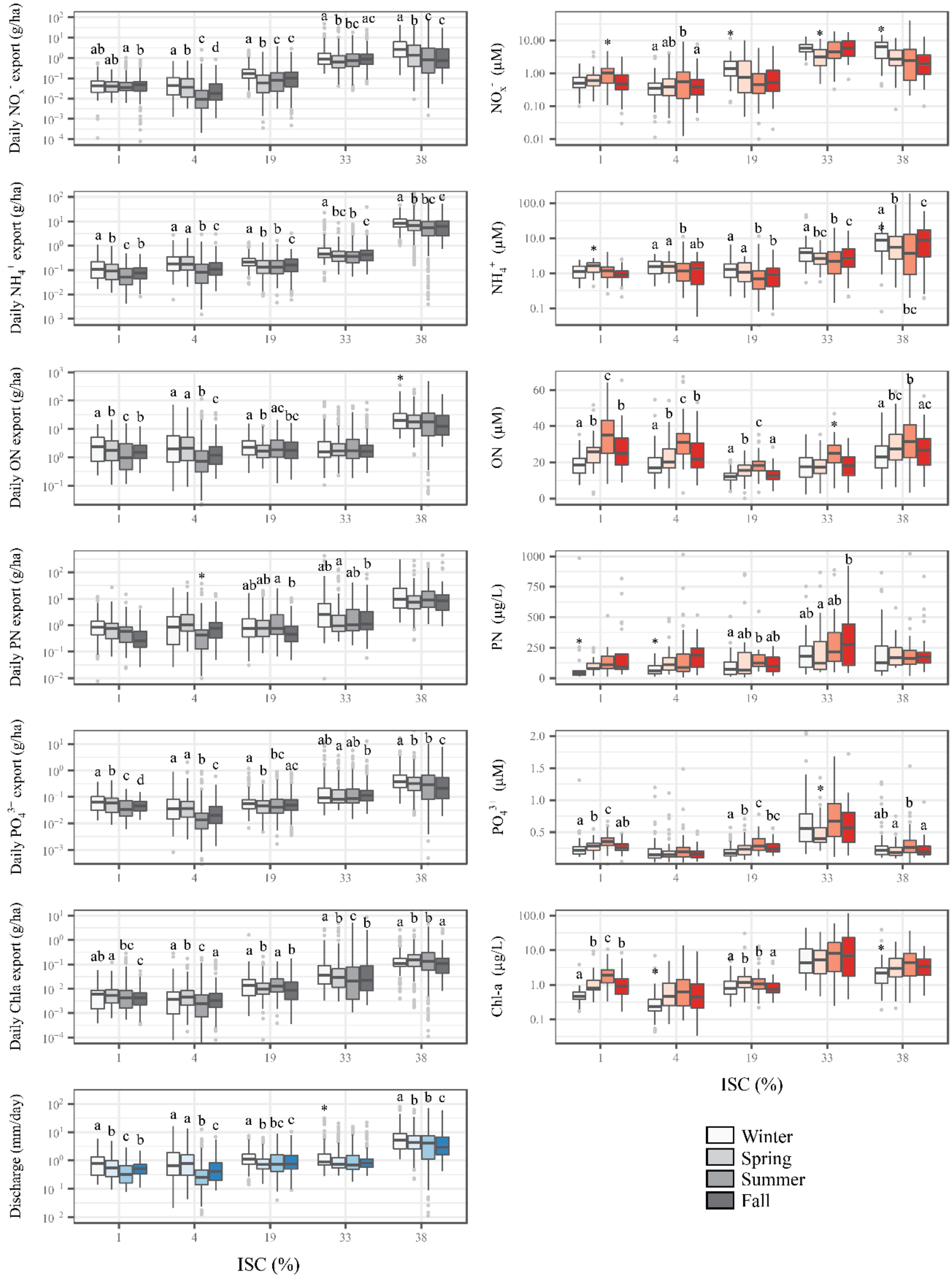

Figure B.1. Seasonal boxplots of discharge, export, and concentration. Letters or asterisk indicate significant differences based on Dunn's test ($p < 0.05$)

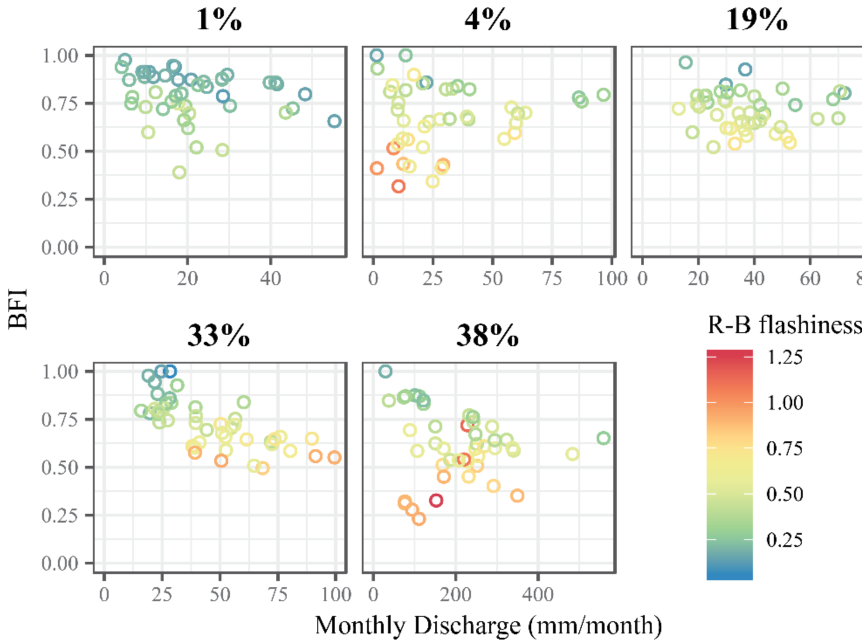

Figure B.2. Monthly discharge, baseflow index (BFI) values, and flashiness for each study stream.

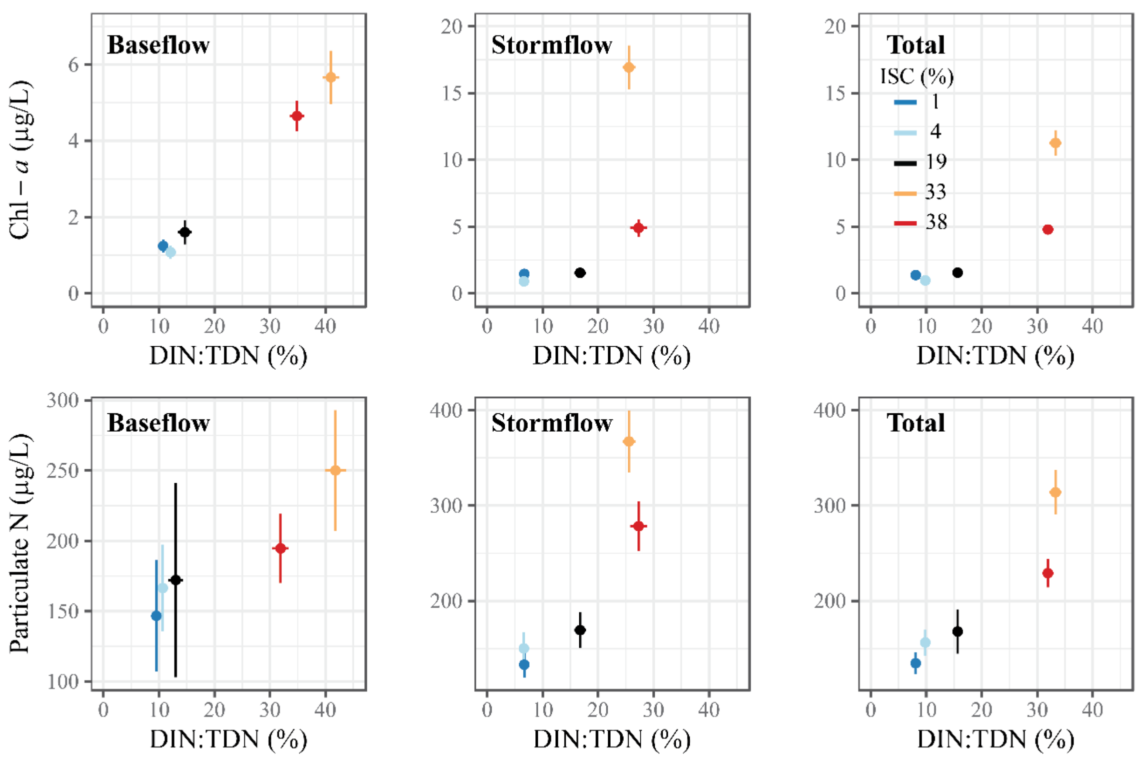

Figure B.3. Chl-*a* and particulate N concentrations versus the ratio of DIN to total dissolved nitrogen (TDN) for Baseflow, Stormflow, and all flows.

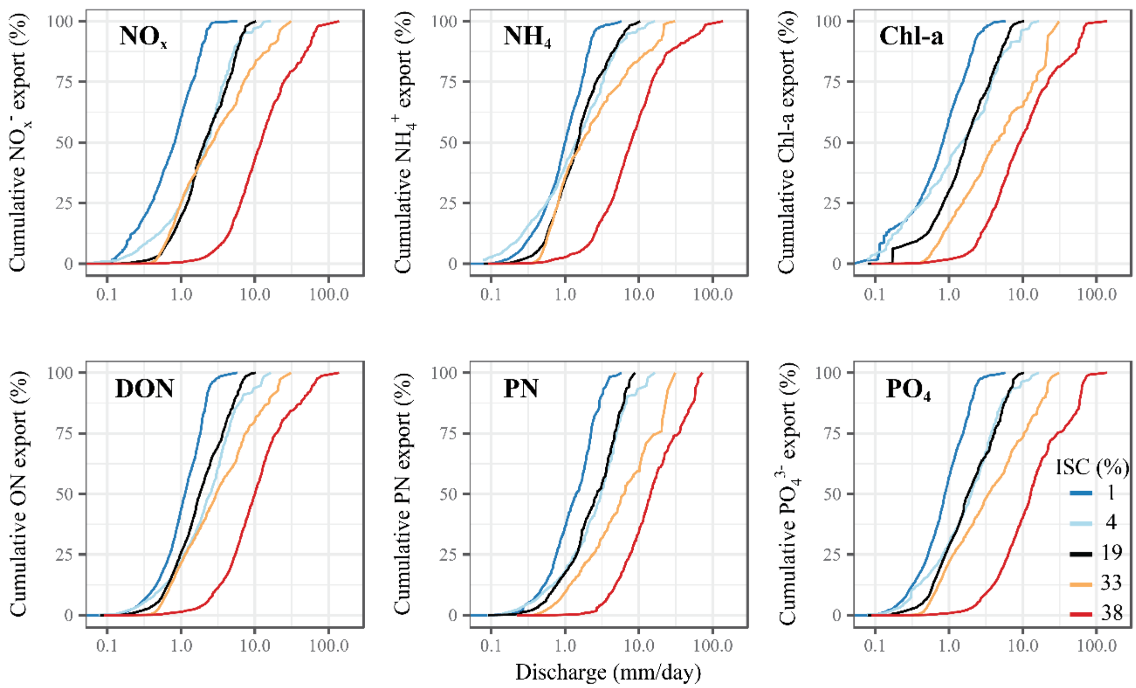

Figure B.4. Nutrient flow distribution curves for each study stream and water quality variable.

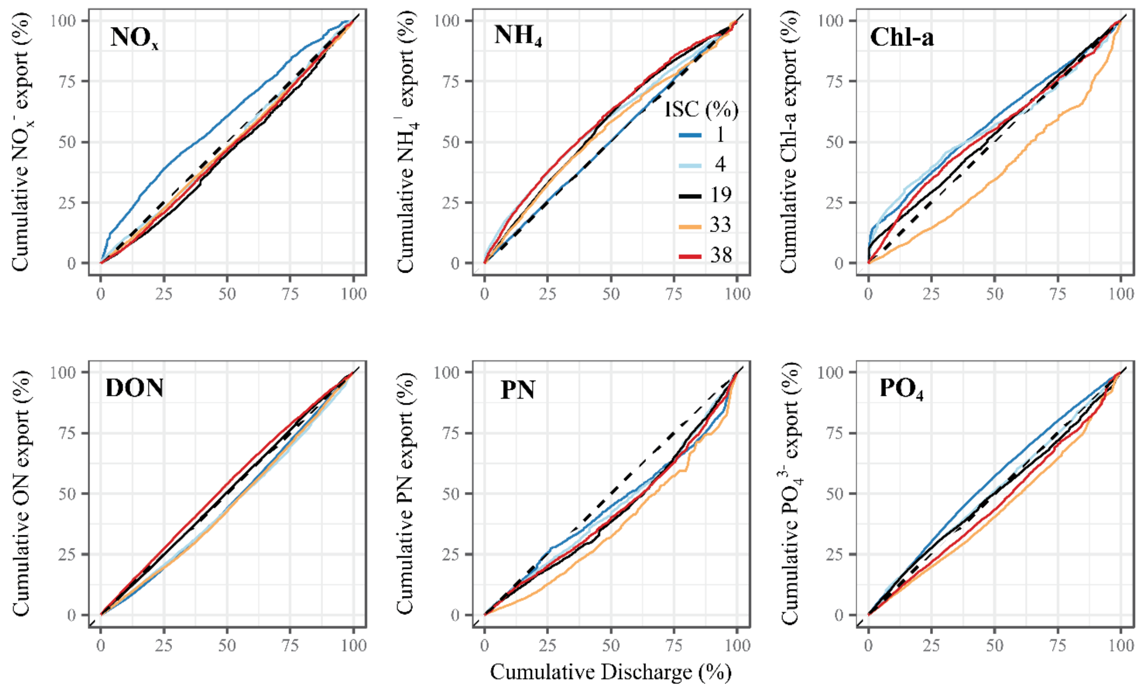

Figure B.5. Cumulative nutrient exports versus cumulative discharge. The dashed 1:1 line indicates that the flow distribution curve and export flow distribution curves for a particular watershed are identical.

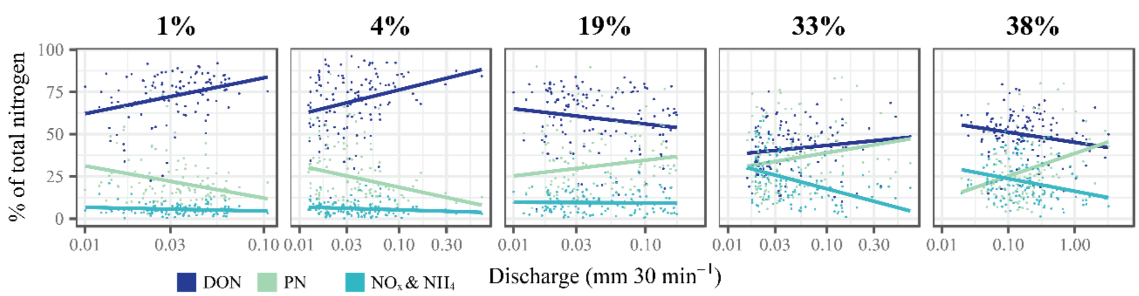

Figure B.6. Percent of each dissolved nitrogen species versus discharge.

Table B.1. 2011 NLCD land use percent of watershed area.

Name	French	Traps	Cogdel	Tarawa	CHB
Barren Land	4.90	3.40	3.04	0.90	4.82
Cultivated Crops	0.00	0.00	1.52	2.82	0.00
Deciduous Forest	0.06	0.00	0.00	0.00	0.00
Developed, High Intensity	0.00	0.00	8.00	1.59	0.99
Developed, Low Intensity	2.55	8.49	7.61	36.65	27.93
Developed, Medium Intensity	0.15	0.24	12.09	20.46	16.64
Developed, Open Space	2.12	12.73	6.88	25.54	21.85
Emergent Herbaceuous Wetlands	17.77	0.00	1.28	0.00	0.00
Evergreen Forest	6.58	9.99	23.54	9.79	12.59
Herbaceuous	12.73	0.00	5.97	0.00	0.00
Mixed Forest	0.78	0.00	3.03	0.00	0.00
Open Water	0.33	0.00	1.39	0.00	0.00
Shrub/Scrub	22.71	20.97	12.48	2.24	15.03
Woody Wetlands	29.30	44.18	13.17	0.00	0.15

Table B.2. Flow statistics from all study streams

ISC (Name)	Study Year	Discharge (m ha^{-1} yr^{-1})	BFI (%)	Mean flashiness
1% (French)	1	0.118	88.227	
	2	0.237	86.224	
	3	0.359	77.035	
	4	0.287	68.237	
	Mean (SE)	0.25 (0.04)	79.93 (3.98)	0.254 (0.015)
4% (Traps)	1	0.108	57.235	
	2	0.306	60.836	
	3	0.326	67.425	
	4	0.588	75.370	
	Mean (SE)	0.33 (0.09)	65.22 (3.45)	0.547 (0.033)
19% (Cogdel)	1	0.434	75.294	
	2	0.433	70.079	
	3	0.505	68.722	
	4	0.479	71.819	
	Mean (SE)	0.46 (0.02)	71.48 (1.23)	0.437 (0.022)
33% (Tarawa)	1	0.357	68.589	
	2	0.476	71.151	
	3	0.581	65.942	
	4	0.755	66.796	
	Mean (SE)	0.54 (0.07)	68.12 (1)	0.498 (0.032)
38% (CHB)	1	1.701	58.057	
	2	1.915	47.814	
	3	2.559	62.382	
	4	3.543	63.783	
	Mean (SE)	2.43 (0.36)	58.01 (3.13)	0.599 (0.039)

Table B.3. Seasonal median daily discharge (mm/day) and Winter-Summer differences (calculated as: Winter – Summer / Winter).

Name	Winter	Spring	Summer	Fall	Winter - Summer difference (%)
French	0.798	0.538	0.322	0.507	59.635
Traps	0.659	0.775	0.176	0.419	73.369
Cogdel	1.120	0.717	0.733	0.754	34.579
Tarawa	0.904	0.741	0.703	0.806	22.245
CHB	5.213	4.271	3.833	2.963	26.467

Table B.4. Rates of nutrient export from study watersheds

		kg ha^{-1} yr^{-1}				g ha^{-1} yr^{-1}	
ISC (Name)	**Study Year**	**NO_x**	**NH_4**	**ON**	**PN**	**PO_4**	**Chl-*a***
1% (French)	1	0.012	0.019	0.369	-	10.484	2.414
	2	0.027	0.037	0.898	-	23.433	2.353
	3	0.028	0.059	1.405	0.245	28.957	3.331
	4	0.015	0.045	1.079	0.382	22.525	2.546
	Mean (SE)	0.02 (0)	0.04 (0.01)	0.94 (0.19)	0.31 (0.05)	21.35 (3.37)	2.66 (0.2)
4% (Traps)	1	0.009	0.043	0.314	-	8.856	1.501
	2	0.020	0.060	1.043	-	17.520	2.281
	3	0.023	0.070	1.094	0.436	17.203	2.743
	4	0.034	0.123	2.217	0.830	28.997	3.870
	Mean (SE)	0.02 (0)	0.07 (0.02)	1.17 (0.34)	0.63 (0.14)	18.14 (3.58)	2.60 (0.43)
19% (Cogdel)	1	0.059	0.070	0.828	-	21.679	5.811
	2	0.055	0.064	1.025	-	21.497	5.688
	3	0.067	0.076	1.114	0.534	26.928	8.015
	4	0.071	0.086	1.106	0.640	36.677	8.826
	Mean (SE)	0.06 (0)	0.07 (0)	1.02 (0.06)	0.59 (0.04)	26.7 (3.08)	7.09 (0.68)
33% (Tarawa)	1	0.248	0.141	0.904	-	43.066	17.986
	2	0.497	0.281	1.313	-	89.603	36.211
	3	0.606	0.226	1.454	1.038	80.738	41.902
	4	0.915	0.315	1.921	2.939	132.923	59.747
	Mean (SE)	0.57 (0.12)	0.24 (0.03)	1.4 (0.18)	1.99 (0.67)	86.58 (15.98)	38.96 (7.45)
38% (CHB)	1	0.635	4.831	7.203	-	114.582	64.961
	2	1.089	2.208	7.675	-	149.254	48.208
	3	1.285	3.176	10.166	3.922	224.458	70.979
	4	1.796	3.823	13.716	8.867	379.344	124.867
	Mean (SE)	1.2 (0.21)	3.51 (0.48)	9.69 (1.29)	6.39 (1.75)	216.91 (50.92)	77.25 (14.36)

APPENDIX C: SUPPLEMENTARY FIGURES AND TABLES FOR CHAPTER 4

Table C.1. 2011 NLCD land use percent of watershed area.

Name	French	S1	S2	Traps	S3	S4	Cogdel	CHB	Tarawa	S5
Barren Land	4.90	4.14	10.07	3.40	0.00	2.88	3.04	4.82	0.90	0.00
Cultivated Crops	0.00	0.00	0.53	0.00	0.00	0.00	1.52	0.00	2.82	0.00
Deciduous Forest	0.06	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Developed, High Intensity	0.00	0.00	0.00	0.00	0.00	0.74	8.00	0.99	1.59	27.02
Developed, Low Intensity	2.55	3.87	6.63	8.49	1.33	12.82	7.61	27.93	36.65	16.63
Developed, Medium Intensity	0.15	0.04	0.13	0.24	0.53	7.74	12.09	16.64	20.46	28.37
Developed, Open Space	2.12	6.36	5.05	12.73	1.01	14.98	6.88	21.85	25.54	13.66
Emergent Herbaceuous Wetlands	17.77	1.40	2.64	0.00	0.00	1.92	1.28	0.00	0.00	0.00
Evergreen Forest	6.58	20.65	5.65	9.99	44.59	23.94	23.54	12.59	9.79	7.74
Herbaceuous	12.73	8.94	7.55	0.00	0.00	2.37	5.97	0.00	0.00	0.04
Mixed Forest	0.78	0.23	0.18	0.00	15.68	1.92	3.03	0.00	0.00	0.71
Open Water	0.33	0.15	0.39	0.00	0.00	0.00	1.39	0.00	0.00	0.00
Shrub/Scrub	22.71	24.75	21.11	20.97	12.05	8.48	12.48	15.03	2.24	0.32
Woody Wetlands	29.30	29.46	40.07	44.18	24.81	22.21	13.17	0.15	0.00	5.50

Table C.2. Watershed information for the five watersheds gauged for discharge and export.

Name	Imperviousness at time of gauging (%)	Area (ha)	Mean stream canopy cover (%)*	Notes
French	0.96	835.1	69.38	
Traps	3.93	61.5	69.47	
Cogdel	19.24	725.4	69.7	
Tarawa	33.27	70.2	27.89	Stormwater wet ponds drain watershed at time of gauging
CHB	38.16	31.8	14.96	In-line wetland at time of gauging

*Data from 2011 NCLD USFS Analytical Tree Canopy data set

Table C.3. Seasonal C-Q relationships used to estimate concentrations during unmeasured storms.

		TSS			PC			DOC		
Name	**Season**	**b**	**R^2**	**n**	**b**	**R^2**	**n**	**b**	**R^2**	**n**
French	summer	0.4	0.18	31	0.07	0.01	30	0.34	0.65	31
	fall	0.24	0.02	30	0.28	0.05	30	0.3	0.26	30
	winter	0.28	0.02	26	0.25	0.04	27	0.14	0.13	26
	spring	-0.21	0.03	25	-0.04	0	26	0.1	0.08	24
Traps	summer	0.09	0	41	0.23	0.04	42	0.05	0.02	43
	fall	0.01	0	29	0.08	0.01	25	0.14	0.13	24
	winter	0.62	0.12	31	0.4	0.23	30	0.05	0.03	30
	spring	0	0	24	0.1	0	26	0.04	0.01	25
Cogdel	summer	0.27	0.09	35	-0.05	0.01	36	-0.13	0.12	36
	fall	0.18	0.04	32	-0.03	0	33	-0.02	0.01	32
	winter	1.19	0.37	32	0.68	0.29	30	-0.25	0.39	30
	spring	0.94	2.60E-01	25	0.28	0.1	25	-0.23	0.5	24
Tarawa	summer	0.11	1.00E-02	42	0.09	0.01	41	0.19	0.49	41
	fall	0.26	1.00E-02	27	0.37	0.09	27	0.55	0.48	26
	winter	1.18	0.4	27	0.73	0.32	27	0.18	0.31	27
	spring	1.19	0.4	24	0.74	0.34	25	0.21	0.37	23
CHB	summer	0.23	1.00E-01	39	0.17	0.11	39	-0.24	0.49	38
	fall	0.17	6.00E-02	31	0.28	0.24	29	-0.2	0.17	28
	winter	0.44	0.09	30	0.24	0.04	30	-0.29	0.54	30
	spring	0.27	1.40E-01	25	0.2	0.16	24	-0.22	0.4	22

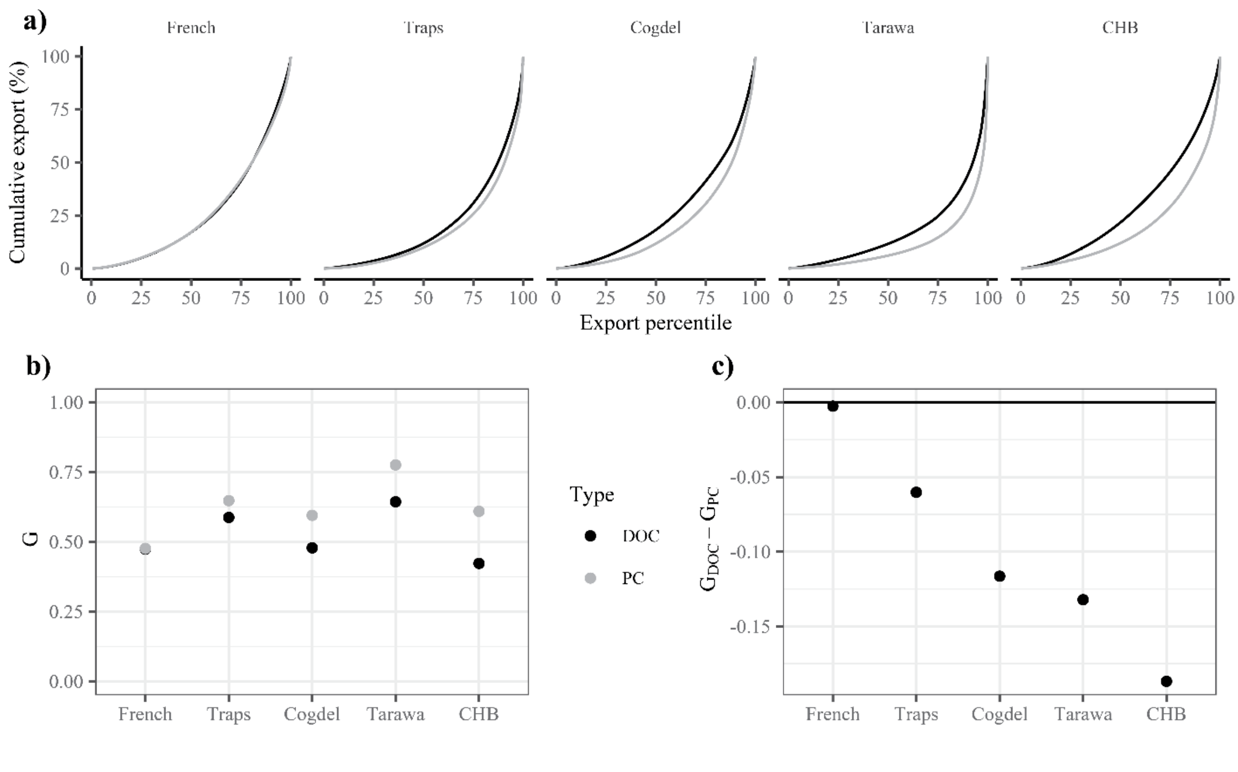

Figure C.1. a) Lorenz curves of DOC and PC export, **b)** Gini coefficients for DOC and PC export, **c)** the differences between Gini coefficients for DOC and PC.

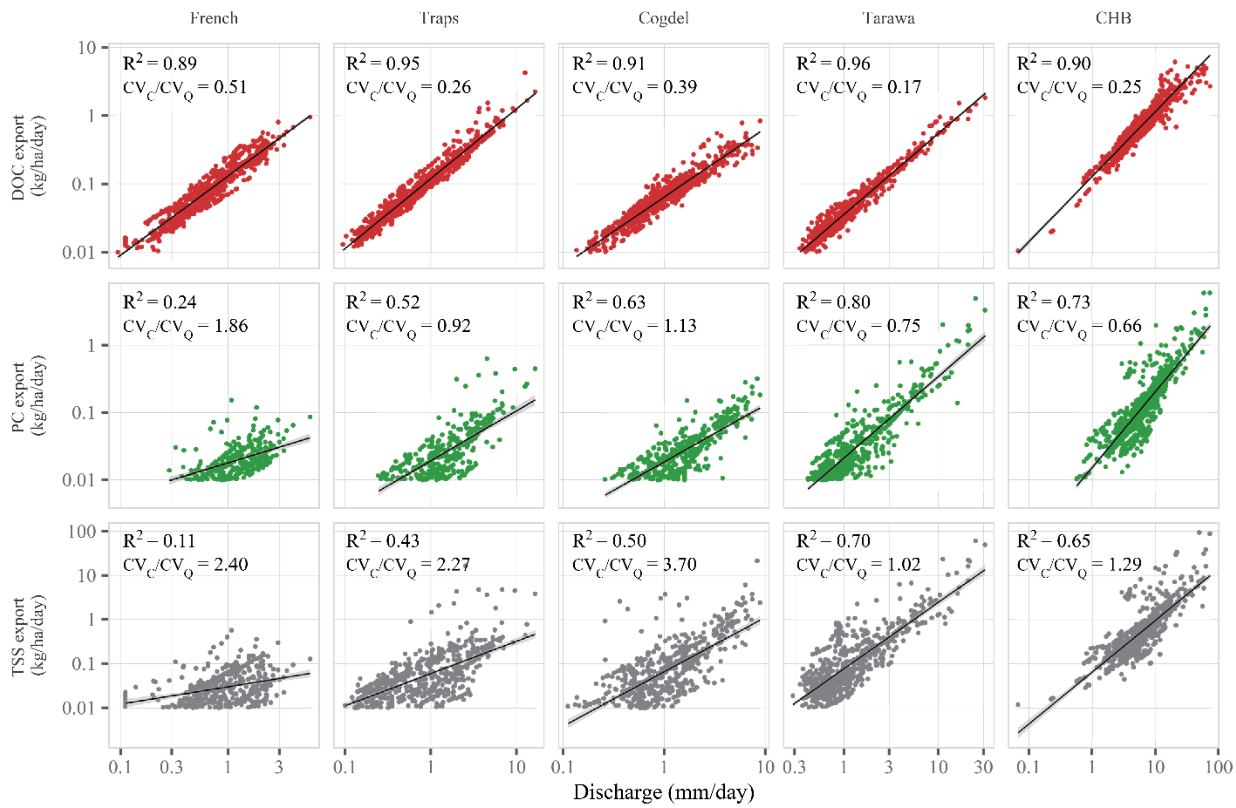

Figure C.2. The relationships between export and discharge for DOC, PC, and TSS. CV_C/CV_Q values indicate if variance in export is controlled by variance in concentrations ($CV_C/CV_Q > 1$) or discharge ($CV_C/CV_Q < 1$). $CV_C/CV_Q < 0.5$ is considered chemostatic.

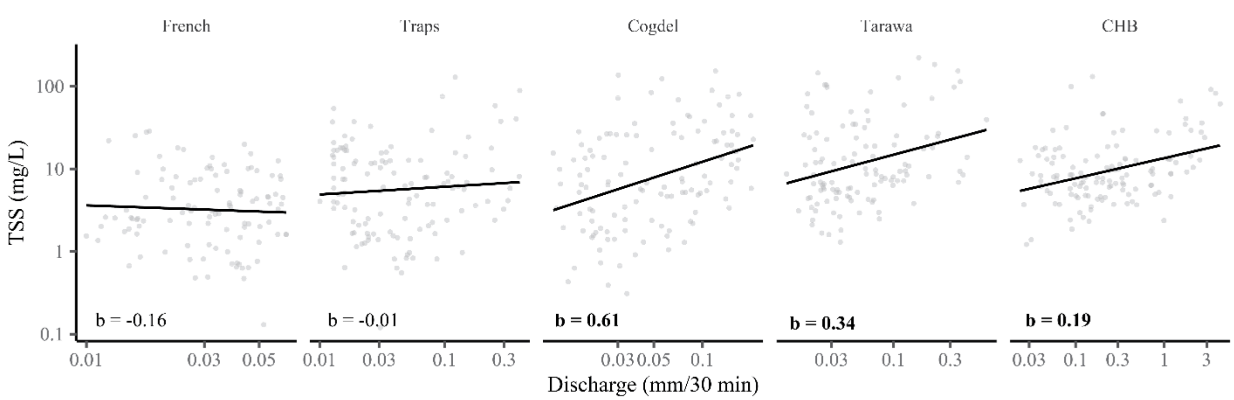

Figure C.3. Discharge-concentration relationships and C-Q slope (b) for TSS. Bolded b values indicate a significant relationship between TSS concentration and discharge ($\alpha = 0.05$)

Table C.4. Spectral scan medians (IQR) for 10 watersheds collected over 1 year (2009).

Name	Imperviousness (%)	a^{350} (m^{-1})	E_2:E_3	S_r
French	0.96	62.95 (32.74)	3.83 (0.18)	0.74 (0.03)
S1	1.45	36.17 (19.8)	4.34 (0.15)	0.79 (0.06)
S2	2.91	46.17 (49.13)	4.38 (0.39)	0.76 (0.05)
Traps	3.93	27.74 (23.71)	4.42 (0.65)	0.76 (0.08)
S3	4.47	28.8 (14.08)	3.99 (0.41)	0.78 (0.18)
S4	13.2	29.47 (31.25)	4.31 (0.28)	0.8 (0.07)
Cogdel	18	16.2 (13.66)	4.7 (0.87)	0.92 (0.13)
CHB	24.2	35.04 (17.64)	4.98 (0.4)	0.79 (0.08)
Tarawa	26.4	10.34 (13.96)	4.56 (1)	0.94 (0.12)
S5	52.9	9.86 (7.68)	4.4 (0.84)	0.93 (0.2)

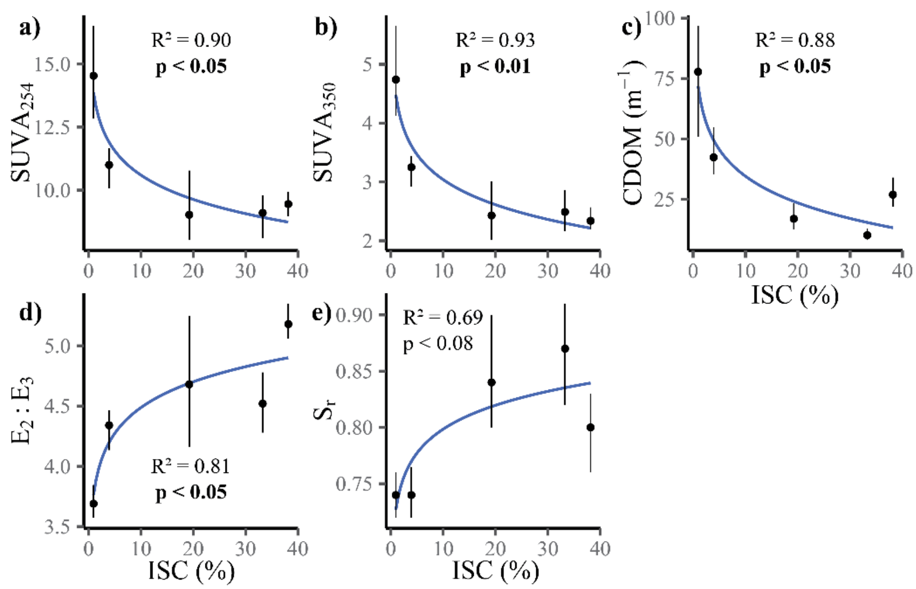

Figure C.4. Spectral indices for the five gauged streams. Points represent medians, and error bars represent 25th and 75th percentiles.

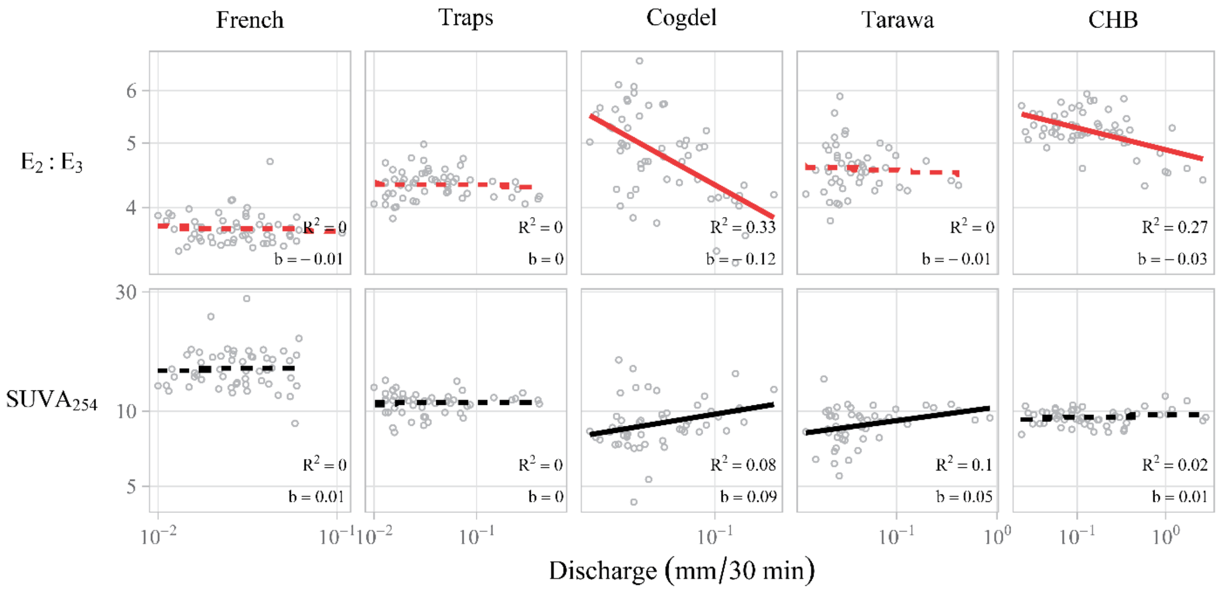

Figure C.5. Relationships between spectral metrics and discharge for each study watershed.

Table C.5. Median and IQR values of chl-*a* and C:N of POM. Letters indicate significant differences based on Kruskal-Wallis and Dunn's tests.

Name	Median chl-*a* (IQR), µg/L	Median C:N (IQR)
French	0.95 (1.14)[ab]	16.81 (5.49)[a]
Traps	0.46 (1.03)[a]	17.41 (8.2)[a]
Cogdel	1.02 (0.82)[b]	14.81 (10.74)[b]
Tarawa	4.95 (11.77)[c]	11.41 (6.15)[c]
CHB	2.94 (4.26)[c]	13.57 (4.88)[d]

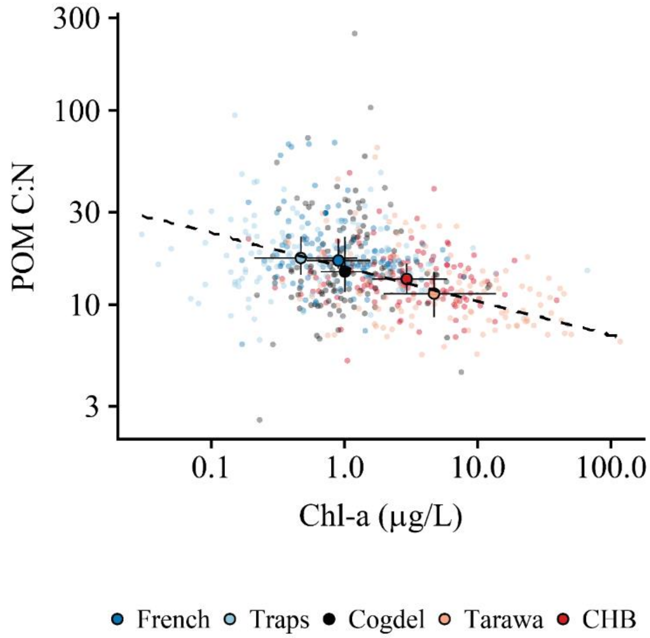

Figure C.6. Relationship between C:N and chl-*a* for individual samples (semi-transparent dots) and median values (large dots). Error bars show the 75th and 25th percentiles.

Table C.6. Physiochemical variables of each stream. Mean (SD).

Name	DO (mg/L)	DO (% sat)	Temperature (C)	Conductivity (µS/cm^2)
French	7.03 (2.58)	71.04 (18.78)	16.89 (6.58)	97.84 (33.34)
Traps	1.85 (1.58)	18.28 (15.41)	17 (5.32)	135.14 (54.54)
Cogdel	3.74 (3.02)	36.02 (25.77)	17.82 (7.04)	203.38 (59.62)
Tarawa	4.19 (2.8)	42.33 (24.88)	18.06 (6.57)	176.46 (40.83)
CHB	3.44 (3.26)	34.6 (31.55)	17.2 (6.5)	298.64 (77.5)

REFERENCES

Addy, K., Kellogg, D.Q., Gold, A.J., Groffman, P.M., Ferendo, G., Sawyer, C., 2002. In Situ Push – Pull Method to Determine Ground Water Denitrification in Riparian Zones. J. Environ. Qual. 31, 1017–1024. doi:10.2134/jeq2002.1017

Alexander, R.B., Boyer, E.W., Smith, R.A., Schwarz, G.E., Moore, R.B., 2007. The Role of Headwater Streams in Downstream Water Quality. J. Am. Water Resour. Assoc. 43, 41–59. doi:10.1111/j.1752-1688.2007.00005.x

Andersson, B., Sundbäck, K., Hellman, M., Hallin, S., Alsterberg, C., 2014. Nitrogen fixation in shallow-water sediments: Spatial distribution and controlling factors. Limnol. Oceanogr. 59, 1932–1944. doi:10.4319/lo.2014.59.6.1932

Arango, C.P., Tank, J.L., Johnson, L.T., Hamilton, S.K., 2008. Assimilatory uptake rather than nitrification and denitrification determines nitrogen removal patterns in streams of varying land use. Limnol. Oceanogr. 53, 2558–2572. doi:10.4319/lo.2008.53.6.2558

Askarizadeh, A., Rippy, M.A., Fletcher, T.D., Feldman, D.L., Peng, J., Bowler, P., Mehring, A.S., Winfrey, B.K., Vrugt, J.A., Aghakouchak, A., Jiang, S.C., Sanders, B.F., Levin, L.A., Taylor, S., Grant, S.B., 2015. From Rain Tanks to Catchments: Use of Low-Impact Development To Address Hydrologic Symptoms of the Urban Stream Syndrome. Environ. Sci. Technol. 49, 11264–11280. doi:10.1021/acs.est.5b01635

Aulenbach, B.T., Burns, D.A., Shanley, J.B., Yanai, R.D., Bae, K., Wild, A.D., Yang, Y., Yi, D., 2016. Approaches to stream solute load estimation for solutes with varying dynamics from five diverse small watersheds. Ecosphere 7, 1–22. doi:10.1002/ecs2.1298

Bae, H.S., Morrison, E., Chanton, J.P., Ogram, A., 2018. Methanogens are major contributors to nitrogen fixation in soils of the Florida Everglades. Appl. Environ. Microbiol. 84, 1–16. doi:10.1128/AEM.02222-17

Baker, D.B., Richards, R.P., Loftus, T.T., Kramer, J.W., 2004. A NEW FLASHINESS INDEX: CHARACTERISTICS AND APPLICATIONS TO MIDWESTERN RIVERS AND STREAMS. J. Am. Water Resour. Assoc. 40, 503–522. doi:10.1111/j.1752-1688.2004.tb01046.x

Barron, O. V., Barr, A.D., Donn, M.J., 2013. Effect of urbanisation on the water balance of a catchment with shallow groundwater. J. Hydrol. 485, 162–176. doi:10.1016/j.jhydrol.2012.04.027

Basu, N.B., Destouni, G., Jawitz, J.W., Thompson, S.E., Loukinova, N. V., Darracq, A., Zanardo, S., Yaeger, M., Sivapalan, M., Rinaldo, A., Rao, P.S.C., 2010. Nutrient loads exported from managed catchments reveal emergent biogeochemical stationarity. Geophys. Res. Lett. 37, 1–5. doi:10.1029/2010GL045168

Bean, E.Z., Hunt, W. rederick, Bidelspach, D.A., 2007. Evaluation of Four Permeable Pavement Sites in Eastern North Carolina for Runoff Reduction and Water Quality Impacts. J. Irrig.

Drain. Eng. 133, 583–592. doi:10.1061/(ASCE)0733-9437(2007)133:6(583)

Bell, C.D., Tague, C.L., McMillan, S.K., 2019. Modeling Runoff and Nitrogen Loads From a Watershed at Different Levels of Impervious Surface Coverage and Connectivity to Storm Water Control Measures. Water Resour. Res. 55, 2690–2707. doi:10.1029/2018WR023006

Bergen, T.J.H.M., Barros, N., Mendonça, R., Aben, R.C.H., Althuizen, I.H.J., Huszar, V., Lamers, L.P.M., Lürling, M., Roland, F., Kosten, S., 2019. Seasonal and diel variation in greenhouse gas emissions from an urban pond and its major drivers. Limnol. Oceanogr. 64, 2129–2139. doi:10.1002/lno.11173

Bernhardt, E.S., Heffernan, J.B., Grimm, N.B., Stanley, E.H., Harvey, J.W., Arroita, M., Appling, A.P., Cohen, M.J., McDowell, W.H., Hall, R.O., Read, J.S., Roberts, B.J., Stets, E.G., Yackulic, C.B., 2018. The metabolic regimes of flowing waters. Limnol. Oceanogr. doi:10.1002/lno.10726

Bernot, M.J., Sobota, D.J., Hall, R.O., Mulholland, P.J., Dodds, W.K., Webster, J.R., Tank, J.L., Ashkenas, L.R., Cooper, L.W., Dahm, C.N., Gregory, S. V., Grimm, N.B., Hamilton, S.K., Johnson, S.L., McDowell, W.H., Meyer, J.L., Peterson, B., Poole, G.C., Maurice Valett, H.M., Arango, C., Beaulieu, J.J., Burgin, A.J., Crenshaw, C., Helton, A.M., Johnson, L., Merriam, J., Niederlehner, B.R., O'Brien, J.M., Potter, J.D., Sheibley, R.W., Thomas, S.M., Wilson, K., 2010. Inter-regional comparison of land-use effects on stream metabolism. Freshw. Biol. 55, 1874–1890. doi:10.1111/j.1365-2427.2010.02422.x

Bettez, N.D., Groffman, P.M., 2012. Denitrification potential in stormwater control structures and natural riparian zones in an urban landscape. Environ. Sci. Technol. 46, 10909–17. doi:10.1021/es301409z

Bhaskar, A.S., Beesley, L., Burns, M.J., Fletcher, T.D., Hamel, P., Oldham, C.E., Roy, A.H., 2016a. Will it rise or will it fall? Managing the complex effects of urbanization on base flow. Freshw. Sci. 35, 293–310. doi:10.1086/685084

Bhaskar, A.S., Hogan, D.M., Archfield, S.A., 2016b. Urban base flow with low impact development. Hydrol. Process. 30, 3156–3171. doi:10.1002/hyp.10808

Bhattacharya, R., Osburn, C.L., 2020. Spatial patterns in dissolved organic matter composition controlled by watershed characteristics in a coastal river network: The Neuse River Basin, USA. Water Res. 169, 115248. doi:10.1016/j.watres.2019.115248

Blaszczak, J.R., Delesantro, J.M., Urban, D.L., Doyle, M.W., Bernhardt, E.S., 2019. Scoured or suffocated: Urban stream ecosystems oscillate between hydrologic and dissolved oxygen extremes. Limnol. Oceanogr. 64, 877–894. doi:10.1002/lno.11081

Blaszczak, J.R., Steele, M.K., Badgley, B.D., Heffernan, J.B., Hobbie, S.E., Morse, J.L., Rivers, E.N., Hall, S.J., Neill, C., 2018. Sediment chemistry of urban stormwater ponds and controls on denitrification. Ecosphere 9. doi:10.1002/ecs2.2318

Bledsoe, R., Austin, S., Bean, E., Peralta, A., 2020. A microbial perspective on balancing tradeoffs in ecosystem functions in a constructed stormwater wetland. Ecol. Eng. 158, 106000. doi:10.1101/2020.04.01.020776

Booth, D.B., 1990. STREAM-CHANNEL INCISION FOLLOWING DRAINAGE-BASIN URBANIZATION. JAWRA J. Am. Water Resour. Assoc. 26, 407–417. doi:10.1111/j.1752-1688.1990.tb01380.x

Bricker, S.B., Longstaff, B., Dennison, W., Jones, A., Boicourt, K., Wicks, C., Woerner, J., 2008. Effects of nutrient enrichment in the nation's estuaries: A decade of change. Harmful Algae 8, 21–32. doi:10.1016/j.hal.2008.08.028

Brown, L.R., Cuffney, T.F., Coles, J.F., Fitzpatrick, F., McMahon, G., Steuer, J., Bell, A.H., May, J.T., 2009. Urban streams across the USA: lessons learned from studies in 9 metropolitan areas. J. North Am. Benthol. Soc. 28, 1051–1069. doi:10.1899/08-153.1

Burgin, A.J., Hamilton, S.K., 2007. Have we overemphasized the role of denitrification in aquatic ecosystems? A review of nitrate removal pathways. Front. Ecol. Environ. 5, 89–96. doi:10.1890/1540-9295(2007)5[89:HWOTRO]2.0.CO;2

Burgin, A.J., Yang, W.H., Hamilton, S.K., Silver, W.L., 2011. Beyond carbon and nitrogen: How the microbial energy economy couples elemental cycles in diverse ecosystems, in: Frontiers in Ecology and the Environment. pp. 44–52. doi:10.1890/090227

Burgis, C.R., Hayes, G.M., Zhang, W., Henderson, D.A., Macko, S.A., Smith, J.A., 2020. Tracking denitrification in green stormwater infrastructure with dual nitrate stable isotopes. Sci. Total Environ. 747, 141281. doi:10.1016/j.scitotenv.2020.141281

Burns, M.J., Fletcher, T.D., Walsh, C.J., Ladson, A.R., Hatt, B.E., 2012. Hydrologic shortcomings of conventional urban stormwater management and opportunities for reform. Landsc. Urban Plan. 105, 230–240. doi:10.1016/j.landurbplan.2011.12.012

Cahoon, L.B., Hales, J.C., Carey, E.S., Loucaides, S., Rowland, K.R., Toothman, B.R., 2016. Multiple modes of water quality impairment by fecal contamination in a rapidly developing coastal area: southwest Brunswick County, North Carolina. Environ. Monit. Assess. 188, 89. doi:10.1007/s10661-015-5081-6

Carey, R.O., Vellidis, G., Lowrance, R., Pringle, C.M., 2007. Do Nutrients Limit Algal Periphyton in Small Blackwater Coastal Plain Streams? J. Am. Water Resour. Assoc. 43, 1183–1193. doi:10.1111/j.1752-1688.2007.00103.x

Chen, X., Peltier, E., Sturm, B.S.M., Young, C.B., 2013. Nitrogen removal and nitrifying and denitrifying bacteria quantification in a stormwater bioretention system. Water Res. 47, 1691–1700. doi:10.1016/j.watres.2012.12.033

Chimney, M.J., Wenkert, L., Pietro, K.C., 2006. Patterns of vertical stratification in a subtropical constructed wetland in south Florida (USA). Ecol. Eng. 27, 322–330. doi:10.1016/j.ecoleng.2006.05.017

Cizek, A.R., Hunt, W.F., Winston, R.J., Lauffer, M.S., 2017. Hydrologic Performance of Regenerative Stormwater Conveyance in the North Carolina Coastal Plain. J. Environ. Eng. 143, 05017003. doi:10.1061/(ASCE)EE.1943-7870.0001198

Clesceri, L.S., Greenberg, A.E., Eaton, A.D., 1998. Standard Methodsfor the Examination of Water and Wastewater, 20th ed. American Public Health Association, American Water Works Association, Water Environment Federation, Washington, DC.

Cole, J.J., Prairie, Y.T., Caraco, N.F., McDowell, W.H., Tranvik, L.J., Striegl, R.G., Duarte, C.M., Kortelainen, P., Downing, J.A., Middelburg, J.J., Melack, J., 2007. Plumbing the Global Carbon Cycle: Integrating Inland Waters into the Terrestrial Carbon Budget. Ecosystems 10, 172–185. doi:10.1007/s10021-006-9013-8

Collins, K.A., Lawrence, T.J., Stander, E.K., Jontos, R.J., Kaushal, S.S., Newcomer, T.A., Grimm, N.B., Cole Ekberg, M.L., 2010. Opportunities and challenges for managing nitrogen in urban stormwater: A review and synthesis. Ecol. Eng. 36, 1507–1519. doi:10.1016/j.ecoleng.2010.03.015

Correll, D.L., Jordan, T.E., Weller, D.E., 1999. Transport of nitrogen and phosphorus from rhode river watersheds during storm events. Water Resour. Res. 35, 2513. doi:10.1029/1999WR900058

Costanza, R., D'Arge, R., de Groot, R., Farber, S., Grasso, M., Hannon, B., Limburg, K., Naeem, S., O'Neill, R. V., Paruelo, J., Raskin, R.G., Sutton, P., van den Belt, M., 1997. The value of the world's ecosystem services and natural capital. Nature 387, 253–260.

Datry, T., Malard, F., Vitry, L., Hervant, F., Gibert, J., 2003. Solute dynamics in the bed sediments of a stormwater infiltration basin. J. Hydrol. 273, 217–233. doi:10.1016/S0022-1694(02)00388-8

De Haan, H., De Boer, T., Kramer, H.A., Voerman, J., 1982. Applicability of light absorbance as a measure of organic carbon in humic lake water. Water Res. 16, 1047–1050. doi:10.1016/0043-1354(82)90040-9

Deegan, L.A., Johnson, D.S., Warren, R.S., Peterson, B.J., Fleeger, J.W., Fagherazzi, S., Wollheim, W.M., 2012. Coastal eutrophication as a driver of salt marsh loss. Nature 490, 388–392. doi:10.1038/nature11533

DeLorenzo, M.E., Thompson, B., Cooper, E., Moore, J., Fulton, M.H., 2012. A long-term monitoring study of chlorophyll, microbial contaminants, and pesticides in a coastal residential stormwater pond and its adjacent tidal creek. Environ. Monit. Assess. 184, 343–59. doi:10.1007/s10661-011-1972-3

Diamond, J.S., Cohen, M.J., 2018. Complex patterns of catchment solute–discharge relationships for coastal plain rivers. Hydrol. Process. 32, 388–401. doi:10.1002/hyp.11424

Dietz, M.E., 2007. Low Impact Development Practices: A Review of Current Research and Recommendations for Future Directions. Water. Air. Soil Pollut. 186, 351–363.

doi:10.1007/s11270-007-9484-z

Dinno, A., 2017. dunn.test: Dunn's Test of Multiple Comparisons Using Rank Sums.

Dosskey, M.G., Bertsch, P.M., 1994. Forest sources and pathways of organic matter transport to a blackwater stream: a hydrologic approach. Biogeochemistry.

Duan, S., Kaushal, S.S., Groffman, P.M., Band, L.E., Belt, K.T., 2012. Phosphorus export across an urban to rural gradient in the Chesapeake Bay watershed. J. Geophys. Res. Biogeosciences 117, n/a-n/a. doi:10.1029/2011JG001782

Duan, S., Newcomer-Johnson, T., Mayer, P., Kaushal, S., 2016. Phosphorus Retention in Stormwater Control Structures across Streamflow in Urban and Suburban Watersheds. Water 8, 390. doi:10.3390/w8090390

Duncan, J.M., Band, L.E., Groffman, P.M., Bernhardt, E.S., 2015. Mechanisms driving the seasonality of catchment scale nitrate export: Evidence for riparian ecohydrologic controls. Water Resour. Res. 51, 3982–3997. doi:10.1002/2015WR016937

Duncan, J.M., Welty, C., Kemper, J.T., Groffman, P.M., Band, L.E., 2017. Dynamics of nitrate concentration-discharge patterns in an urban watershed. Water Resour. Res. 53, 7349–7365. doi:10.1002/2017WR020500

Dunn, R.J.K., Robertson, D., Teasdale, P.R., Waltham, N.J., Welsh, D.T., 2013. Benthic metabolism and nitrogen dynamics in an urbanised tidal creek: Domination of DNRA over denitrification as a nitrate reduction pathway. Estuar. Coast. Shelf Sci. 131, 271–281. doi:10.1016/j.ecss.2013.06.027

Elser, J.J., Bracken, M.E.S., Cleland, E.E., Gruner, D.S., Harpole, W.S., Hillebrand, H., Ngai, J.T., Seabloom, E.W., Shurin, J.B., Smith, J.E., 2007. Global analysis of nitrogen and phosphorus limitation of primary producers in freshwater, marine and terrestrial ecosystems. Ecol. Lett. 10, 1135–1142. doi:10.1111/j.1461-0248.2007.01113.x

Eyre, B.D., Maher, D.T., Squire, P., 2013. Quantity and quality of organic matter (detritus) drives N 2 effluxes (net denitrification) across seasons, benthic habitats, and estuaries. Global Biogeochem. Cycles 27, 1083–1095. doi:10.1002/2013GB004631

Fanelli, R., Prestegaard, K., Palmer, M., 2017. Evaluation of infiltration-based stormwater management to restore hydrological processes in urban headwater streams. Hydrol. Process. 31, 3306–3319. doi:10.1002/hyp.11266

Flint, S.A., McDowell, W.H., 2015. Effects of headwater wetlands on dissolved nitrogen and dissolved organic carbon concentrations in a suburban New Hampshire watershed. Freshw. Sci. 34, 456–471. doi:10.1086/680985

Foster, S.Q., Fulweiler, R.W., 2014. Spatial and historic variability of benthic nitrogen cycling in an anthropogenically impacted estuary. Front. Mar. Sci. 1, 1–16. doi:10.3389/fmars.2014.00056

Fulweiler, R.W., Brown, S.M., Nixon, S.W., Jenkins, B.D., 2013. Evidence and a conceptual model for the co-occurrence of nitrogen fixation and denitrification in heterotrophic marine sediments. Mar. Ecol. Prog. Ser. 482, 57–68. doi:10.3354/meps10240

Fulweiler, R.W., Heiss, E.M., Rogener, M.K., Newell, S.E., LeCleir, G.R., Kortebein, S.M., Wilhelm, S.W., 2015. Examining the impact of acetylene on N-fixation and the active sediment microbial community. Front. Microbiol. 6, 418. doi:10.3389/fmicb.2015.00418

Fulweiler, R.W., Nixon, S.W., Buckley, B.A., Granger, S.L., 2007. Reversal of the net dinitrogen gas flux in coastal marine sediments. Nature 448, 180–182. doi:10.1038/nature05963

Gao, Y., Zhang, Z., Liu, X., Yi, N., Zhang, L., Song, W., Wang, Y., Mazumder, A., Yan, S., 2016. Seasonal and diurnal dynamics of physicochemical parameters and gas production in vertical water column of a eutrophic pond. Ecol. Eng. 87, 313–323. doi:10.1016/j.ecoleng.2015.12.007

Garcia, H.E., Gordon, L.I., 1992. Oxygen solubility in seawater: Better fitting equations. Limnol. Oceanogr. 37, 1307–1312. doi:10.4319/lo.1992.37.6.1307

Gardner, W.S., McCarthy, M.J., 2009. Nitrogen dynamics at the sediment-water interface in shallow, sub-tropical Florida Bay: Why denitrification efficiency may decrease with increased eutrophication. Biogeochemistry 95, 185–198. doi:10.1007/s10533-009-9329-5

Godsey, S.E., Kirchner, J.W., Clow, D.W., 2009. Concentration-discharge relationships reflect chemostatic characteristics of US catchments. Hydrol. Process. 23, 1844–1864. doi:10.1002/hyp.7315

Gold, A.C., Thompson, S.P., Magel, C.L., Piehler, M.F., 2020. Urbanization alters coastal plain stream carbon export and dissolved oxygen dynamics. Sci. Total Environ. 747, 141132. doi:10.1016/j.scitotenv.2020.141132

Gold, A.C., Thompson, S.P., Piehler, M.F., 2019a. Nitrogen cycling processes within stormwater control measures: A review and call for research. Water Res. 149, 578–587. doi:10.1016/j.watres.2018.10.036

Gold, A.C., Thompson, S.P., Piehler, M.F., 2019b. The Effects of Urbanization and Retention-Based Stormwater Management on Coastal Plain Stream Nutrient Export. Water Resour. Res. 55, 7027–7046. doi:10.1029/2019WR024769

Gold, A.C., Thompson, S.P., Piehler, M.F., 2017a. Coastal stormwater wet pond sediment nitrogen dynamics. Sci. Total Environ. 609, 672–681. doi:10.1016/j.scitotenv.2017.07.213

Gold, A.C., Thompson, S.P., Piehler, M.F., 2017b. Water quality before and after watershed-scale implementation of stormwater wet ponds in the coastal plain. Ecol. Eng. 105, 240–251. doi:10.1016/j.ecoleng.2017.05.003

Goyette, J.-O., Bennett, E.M., Maranger, R., 2018. Low buffering capacity and slow recovery of anthropogenic phosphorus pollution in watersheds. Nat. Geosci. 11, 921–925.

doi:10.1038/s41561-018-0238-x

Green, S.A., Blough, N. V., 1994. Optical absorption and fluorescence properties of chromophoric dissolved organic matter in natural waters. Limnol. Oceanogr. 39, 1903–1916. doi:10.4319/lo.1994.39.8.1903

Grinham, A., Albert, S., Deering, N., Dunbabin, M., Bastviken, D., Sherman, B., Lovelock, C.E., Evans, C.D., 2018. The importance of small artificial water bodies as sources of methane emissions in Queensland , Australia. Hydrol. Earth Syst. Sci. 22, 5281–5298. doi:10.5194/hess-22-5281-2018

Groffman, P.M., Altabet, M.A., Böhlke, J.K., Butterbach-Bahl, K., David, M.B., Firestone, M.K., Giblin, A.E., Kana, T.M., Nielsen, L.P., Voytek, M.A., 2006. METHODS FOR MEASURING DENITRIFICATION: DIVERSE APPROACHES TO A DIFFICULT PROBLEM. Ecol. Appl. 16, 2091–2122. doi:10.1890/1051-0761(2006)016[2091:MFMDDA]2.0.CO;2

Groffman, P.M., Law, N.L., Belt, K.T., Band, L.E., Fisher, G.T., 2004. Nitrogen Fluxes and Retention in Urban Watershed Ecosystems. Ecosystems 7, 393–403. doi:10.1007/s10021-003-0039-x

Hamilton, N.E., Ferry, M., 2018. **ggtern** : Ternary Diagrams Using **ggplot2**. J. Stat. Softw. 87, 1–17. doi:10.18637/jss.v087.c03

Hancock, G.S., Holley, J.W., Chambers, R.M., 2010. A Field-Based Evaluation of Wet Retention Ponds: How Effective Are Ponds at Water Quantity Control?1. JAWRA J. Am. Water Resour. Assoc. 46, 1145–1158. doi:10.1111/j.1752-1688.2010.00481.x

Hardison, E.C., O'Driscoll, M.A., Deloatch, J.P., Howard, R.J., Brinson, M.M., 2009. Urban land use, channel incision, and water table decline along coastal plain streams, North Carolina. J. Am. Water Resour. Assoc. 45, 1032–1046. doi:10.1111/j.1752-1688.2009.00345.x

Hardy, R.W.F., Holsten, R.D., Jackson, E.K., Burns, R.C., 1968. The acetylene - ethylene assay for N_2 fixation: laboratory and field evaluation. Plant Physiol. 43, 1185–1207. doi:10.1104/pp.43.8.1185

Harrison, M.D., Groffman, P.M., Mayer, P.M., Kaushal, S.S., Newcomer, T.A., 2011. Denitrification in Alluvial Wetlands in an Urban Landscape. J. Environ. Qual. 40, 634. doi:10.2134/jeq2010.0335

Hartzog, P.E., Sladek, M., Kelly, J.J., Larkin, D.J., 2017. Bottle effects alter taxonomic composition of wetland soil bacterial communities during the denitrification enzyme activity assay. Soil Biol. Biochem. 110, 87–94. doi:10.1016/j.soilbio.2017.03.006

Hassett, B.A., Sudduth, E.B., Somers, K.A., Urban, D.L., Violin, C.R., Wang, S.-Y., Wright, J.P., Cory, R.M., Bernhardt, E.S., 2018. Pulling apart the urbanization axis: patterns of physiochemical degradation and biological response across stream ecosystems. Freshw. Sci.

000–000. doi:10.1086/699387

Helms, J.R., Mao, J., Stubbins, A., Schmidt-Rohr, K., Spencer, R.G.M., Hernes, P.J., Mopper, K., 2014. Loss of optical and molecular indicators of terrigenous dissolved organic matter during long-term photobleaching. Aquat. Sci. 76, 353–373. doi:10.1007/s00027-014-0340-0

Helms, J.R., Stubbins, Aron, Ritchie, J.D., Minor, E.C., David, J., Mopper, K., Helms, R., Stubbins, Avon, Kieber, D.J., 2008. Absorption Spectral Slopes and Slope Ratio as indicators of molecular source , slopes and slope ratios Absorption spectral of chromophoric and photobleaching dissolved matter organic 53, 955–969.

Hensley, R.T., McLaughlin, D.L., Cohen, M.J., Decker, P.H., 2017. Stream phosphorus dynamics of minimally impacted coastal plain watersheds. Hydrol. Process. 31, 1636–1649. doi:10.1002/hyp.11132

Hobbie, Sarah E., Finlay, J.C., Janke, B.D., Nidzgorski, D.A., Millet, D.B., Baker, L.A., 2017. Contrasting nitrogen and phosphorus budgets in urban watersheds and implications for managing urban water pollution. Proc. Natl. Acad. Sci. 114, 4177–4182. doi:10.1073/pnas.1618536114

Hobbie, Sarah E, Finlay, J.C., Janke, B.D., Nidzgorski, D.A., Millet, D.B., Baker, L.A., Hobbie, S.E., Baker, L.A., by L Turner, E.B., 2017. Correction for Hobbie et al., Contrasting nitrogen and phosphorus budgets in urban watersheds and implications for managing urban water pollution. Proc. Natl. Acad. Sci. 114, 4177–4182. doi:10.1073/pnas.1706049114

Hoffman, D.K., McCarthy, M.J., Newell, S.E., Gardner, W.S., Niewinski, D.N., Gao, J., Mutchler, T.R., 2019. Relative Contributions of DNRA and Denitrification to Nitrate Reduction in Thalassia testudinum Seagrass Beds in Coastal Florida (USA). Estuaries and Coasts 42, 1001–1014. doi:10.1007/s12237-019-00540-2

Homer, C., Dewitz, J., Yang, L., Jin, S., Danielson, P., Xian, G., Coulston, J., Herold, N., Wickham, J., Megown, K., 2015. Completion of the 2011 National Land Cover Database for the Conterminous United States - Representing a Decade of Land Cover Change Information. Photogramm. Eng. Remote Sensing 81.

Hope, D., Billett, M.F., Cresser, M.S., 1994. A review of the export of carbon in river water: Fluxes and processes. Environ. Pollut. 84, 301–324. doi:10.1016/0269-7491(94)90142-2

Hopkins, K.G., Morse, N.B., Bain, D.J., Bettez, N.D., Grimm, N.B., Morse, J.L., Palta, M.M., Shuster, W.D., Bratt, A.R., Suchy, A.K., 2015. Assessment of regional variation in streamflow responses to urbanization and the persistence of physiography. Environ. Sci. Technol. doi:10.1021/es505389y

Hosen, J.D., Armstrong, A.W., Palmer, M.A., 2018. Dissolved organic matter variations in coastal plain wetland watersheds: The integrated role of hydrological connectivity, land use, and seasonality. Hydrol. Process. 32, 1664–1681. doi:10.1002/hyp.11519

Hosen, J.D., McDonough, O.T., Febria, C.M., Palmer, M.A., 2014. Dissolved organic matter quality and bioavailability changes across an urbanization gradient in headwater streams. Environ. Sci. Technol. 48, 7817–7824. doi:10.1021/es501422z

Hounshell, A.G., Peierls, B.L., Osburn, C.L., Paerl, H.W., 2017. Stimulation of Phytoplankton Production by Anthropogenic Dissolved Organic Nitrogen in a Coastal Plain Estuary. Environ. Sci. Technol. 51, 13104–13112. doi:10.1021/acs.est.7b03538

Howarth, R.W., Billen, G., Swaney, D., Townsend, A., Jaworski, N., Lajtha, K., Downing, J.A., Elmgren, R., Caraco, N., Jordan, T., Berendse, F., Freney, J., Kudeyarov, V., Murdoch, P., Zhao-Liang, Z., 1996. Regional nitrogen budgets and riverine N & P fluxes for the drainages to the North Atlantic Ocean: Natural and human influences. Biogeochemistry 35, 75–139. doi:10.1007/BF02179825

Howarth, R.W., Marino, R., 2006. Nitrogen as the Limiting Nutrient for Eutrophication in Coastal Marine Ecosystems: Evolving Views of Three Decades. Limnol. Oceanogr. 51, 364–376.

Huang, W., Chen, R.F., 2009. Sources and transformations of chromophoric dissolved organic matter in the Neponset River Watershed. J. Geophys. Res. Biogeosciences 114, 0–05. doi:10.1029/2009JG000976

Hunt, W.F., Davis, A.P., Traver, R.G., 2012. Meeting Hydrologic and Water Quality Goals through Targeted Bioretention Design. J. Environ. Eng. 138, 698–707. doi:10.1061/(ASCE)EE.1943-7870.0000504

Hynes, R.K., Knowles, R., 1982. Effect of acetylene on autotrophic and heterotrophic nitrification. Can. J. Microbiol. 28, 334–340. doi:10.1139/m82-049

Hynes, R.K., Knowles, R., 1978. Inhibition by acetylene of ammonia oxidation in Nitrosomonas europaea. FEMS Microbiol. Lett. 4, 319–321. doi:10.1111/j.1574-6968.1978.tb02889.x

Imberger, S.J., Cook, P.L.M., Grace, M.R., Thompson, R.M., 2014. Tracing carbon sources in small urbanising streams: Catchment-scale stormwater drainage overwhelms the effects of reach-scale riparian vegetation. Freshw. Biol. 59, 168–186. doi:10.1111/fwb.12256

Iverson, G., Humphrey, C.P., O’Driscoll, M.A., Sanderford, C., Jernigan, J., Serozi, B., 2018. Nutrient exports from watersheds with varying septic system densities in the North Carolina Piedmont. J. Environ. Manage. 211, 206–217. doi:10.1016/j.jenvman.2018.01.063

Jahangir, M.M.R., Fenton, O., Mï¿½ller, C., Harrington, R., Johnston, P., Richards, K.G., 2017. In situ denitrification and DNRA rates in groundwater beneath an integrated constructed wetland. Water Res. 111, 254–264. doi:10.1016/j.watres.2017.01.015

Jawitz, J.W., Mitchell, J., 2011. Temporal inequality in catchment discharge and solute export. Water Resour. Res. 47. doi:10.1029/2010WR010197

Jayakaran, A.D., Libes, S.M., Hitchcock, D.R., Bell, N.L., Fuss, D., 2014. Flow, Organic, and Inorganic Sediment Yields from a Channelized Watershed in the South Carolina Lower

Coastal Plain. J. Am. Water Resour. Assoc. 50, 943–962. doi:10.1111/jawr.12148

Jefferson, A.J., Bell, C.D., Clinton, S.M., Mcmillan, S.K., 2015. Application of isotope hydrograph separation to understand contributions of stormwater control measures to urban headwater streams. Hydrol. Process. 29, 5290–5306. doi:10.1002/hyp.10680

Jefferson, A.J., Bhaskar, A.S., Hopkins, K.G., Fanelli, R., Avellaneda, P.M., McMillan, S.K., 2017. Stormwater management network effectiveness and implications for urban watershed function: a critical review. Hydrol. Process. 1–25. doi:10.1002/hyp.11347

Kalev, S., Duan, S., Toor, G.S., 2020. Enriched dissolved organic carbon export from a residential stormwater pond. Sci. Total Environ. 141773. doi:10.1016/j.scitotenv.2020.141773

Kana, T.M., Darkangelo, C., Hunt, M.D., Oldham, J.B., Bennett, G.E., Cornwell, J.C., 1994. Membrane Inlet Mass Spectrometer for Rapid High-Precision Determination of N2, O2, and Ar in Environmental Water Samples. Anal. Chem. 66, 4166–4170. doi:10.1021/ac00095a009

Kana, T.M., Sullivan, M.B., Cornwell, J.C., Groszkowski, K.M., 1998. Denitrification in estuarine sediments determined by membrane inlet mass spectrometry. Limnol. Oceanogr. 43, 334–339. doi:10.4319/lo.1998.43.2.0334

Kaushal, S.S., Belt, K.T., 2012. The urban watershed continuum: Evolving spatial and temporal dimensions. Urban Ecosyst. 15, 409–435. doi:10.1007/s11252-012-0226-7

Kaushal, S.S., Delaney-Newcomb, K., Findlay, S.E.G., Newcomer, T.A., Duan, S., Pennino, M.J., Sivirichi, G.M., Sides-Raley, A.M., Walbridge, M.R., Belt, K.T., 2014. Longitudinal patterns in carbon and nitrogen fluxes and stream metabolism along an urban watershed continuum. Biogeochemistry 121, 23–44. doi:10.1007/s10533-014-9979-9

Kaushal, S.S., Gold, A.J., Bernal, S., Johnson, T.A.N., Addy, K., Burgin, A., Burns, D.A., Coble, A.A., Hood, E., Lu, Y.H., Mayer, P., Minor, E.C., Schroth, A.W., Vidon, P., Wilson, H., Xenopoulos, M.A., Doody, T., Galella, J.G., Goodling, P., Haviland, K., Haq, S., Wessel, B., Wood, K.L., Jaworski, N., Belt, K.T., 2018. Watershed ‘chemical cocktails’: forming novel elemental combinations in Anthropocene fresh waters. Biogeochemistry 141, 281–305. doi:10.1007/s10533-018-0502-6

Kaushal, S.S., Groffman, P.M., Band, L.E., Elliott, E.M., Shields, C.A., Kendall, C., 2011. Tracking nonpoint source nitrogen pollution in human-impacted watersheds. Environ. Sci. Technol. 45, 8225–8232. doi:10.1021/es200779e

Kessler, A.J., Roberts, K.L., Bissett, A., Cook, P.L.M., 2018. Biogeochemical controls on the relative importance of denitrification and dissimilatory nitrate reduction to ammonium in estuaries. Global Biogeochem. Cycles. doi:10.1029/2018GB005908

Klocker, C.A., Kaushal, S.S., Groffman, P.M., Mayer, P.M., Morgan, R.P., 2009. Nitrogen uptake and denitrification in restored and unrestored streams in urban Maryland, USA.

Aquat. Sci. 71, 411–424. doi:10.1007/s00027-009-0118-y

Koch, B.J., Febria, C.M., Gevrey, M., Wainger, L.A., Palmer, M.A., 2014. Nitrogen Removal by Stormwater Management Structures: A Data Synthesis. JAWRA J. Am. Water Resour. Assoc. 50, 1594–1607. doi:10.1111/jawr.12223

Kreiling, R.M., Richardson, W.B., Cavanaugh, J.C., Bartsch, L.A., 2011. Summer nitrate uptake and denitrification in an upper Mississippi River backwater lake: the role of rooted aquatic vegetation. Biogeochemistry 104, 309–324. doi:10.1007/s10533-010-9503-9

Lancaster, N.A., Bushey, J.T., Tobias, C.R., Song, B., Vadas, T.M., 2016. Impact of chloride on denitrification potential in roadside wetlands. Environ. Pollut. 212, 216–223. doi:10.1016/j.envpol.2016.01.068

Leech, D.M., Ensign, S.H., Piehler, M.F., 2016. Spatiotemporal patterns in the export of dissolved organic carbon and chromophoric dissolved organic matter from a coastal, blackwater river. Aquat. Sci. 78, 823–836. doi:10.1007/s00027-016-0474-3

Lehrter, J.C., 2006. Effects of land use and land cover, stream discharge, and interannual climate on the magnitude and timing of nitrogen, phosphorus, and organic carbon concentrations in three coastal plain watersheds. Water Environ. Res. 78, 2356–2368. doi:10.2175/106143006x102015

Lenhart, H.A., Hunt, W.F., Burchell, M.R., 2012. Harvestable Nitrogen Accumulation for Five Storm Water Wetland Plant Species: Trigger for Storm Water Control Measure Maintenance? J. Environ. Eng. 138, 972–978. doi:10.1061/(ASCE)EE.1943-7870.0000550

Lewis, W.M., 2002. Yield of nitrogen from disturbed minimally watersheds of the United States. Biogeochemistry 57, 375–385.

Lewitus, A.J., Brock, L.M., Burke, M.K., DeMattio, K.A., Wilde, S.B., 2008. Lagoonal stormwater detention ponds as promoters of harmful algal blooms and eutrophication along the South Carolina coast. Harmful Algae 8, 60–65. doi:10.1016/j.hal.2008.08.012

Lusk, Mary G, Toor, G.S., 2016. Biodegradability and Molecular Composition of Dissolved Organic Nitrogen in Urban Stormwater Runoff and Outflow Water from a Stormwater Retention Pond. Environ. Sci. Technol. 50, 3391–3398. doi:10.1021/acs.est.5b05714

Lusk, Mary G., Toor, G.S., 2016. Dissolved organic nitrogen in urban streams: Biodegradability and molecular composition studies. Water Res. 96, 225–235. doi:10.1016/j.watres.2016.03.060

Macek, C.L., Hale, R.L., Baxter, C. V., 2019. Dry Wetlands: Nutrient Dynamics in Ephemeral Constructed Stormwater Wetlands. Environ. Manage. doi:10.1007/s00267-019-01227-x

Mallin, M., Ensign, S., Wheeler, T., Mayes, D., 2002. Pollutant removal efficacy of three wet detention ponds. J. Environ. Qual. 31, 654–660.

Mallin, M.A., Johnson, V.L., Ensign, S.H., 2009. Comparative impacts of stormwater runoff on water quality of an urban, a suburban, and a rural stream. Environ. Monit. Assess. 159, 475–491. doi:10.1007/s10661-008-0644-4

Mallin, M.A., Johnson, V.L., Ensign, S.H., MacPherson, T.A., 2006. Factors contributing to hypoxia in rivers, lakes, and streams. Limnol. Oceanogr. 51, 690–701. doi:10.4319/lo.2006.51.1_part_2.0690

Mallin, M.A., McIver, M.R., Ensign, S.H., Cahoon, L.B., 2004. PHOTOSYNTHETIC AND HETEROTROPHIC IMPACTS OF NUTRIENT LOADING TO BLACKWATER STREAMS. Ecol. Appl. 14, 823–838. doi:10.1890/02-5217

Markewich, H.W., Pavich, M.J., Buell, G.R., 1990. Contrasting soils and landscapes of the Piedmont and Coastal Plain, eastern United States. Geomorphology 3, 417–447. doi:10.1016/0169-555X(90)90015-I

McEnroe, N.A., Buttle, J.M., Marsalek, J., Pick, F.R., Xenopoulos, M.A., Frost, P.C., 2013. Thermal and chemical stratification of urban ponds: Are they "completely mixed reactors"? Urban Ecosyst. 16. doi:10.1007/s11252-012-0258-z

Mclaughlin, D.L., Kaplan, D.A., Cohen, M.J., 2013. Managing forests for increased regional water yield in the southeastern U.S. coastal plain. J. Am. Water Resour. Assoc. 49, 953–965. doi:10.1111/jawr.12073

McMillan, S.K., Piehler, M.F., Thompson, S.P., Paerl, H.W., 2010. Denitrification of Nitrogen Released from Senescing Algal Biomass in Coastal Agricultural Headwater Streams. J. Environ. Qual. 39, 274. doi:10.2134/jeq2008.0438

McPhillips, L., Walter, M.T., 2015. Hydrologic conditions drive denitrification and greenhouse gas emissions in stormwater detention basins. Ecol. Eng. 85, 67–75. doi:10.1016/j.ecoleng.2015.10.018

McPhillips, L.E., Matsler, A.M., 2018. Temporal Evolution of Green Stormwater Infrastructure Strategies in Three US Cities. Front. Built Environ. 4, 1–14. doi:10.3389/fbuil.2018.00026

Meierdiercks, K.L., Kolozsvary, M.B., Rhoads, K.P., Golden, M., McCloskey, N.F., 2017. The role of land surface versus drainage network characteristics in controlling water quality and quantity in a small urban watershed. Hydrol. Process. 31, 4384–4397. doi:10.1002/hyp.11367

Merriman, L.S., Moore, T.L.C., Wang, J.W., Osmond, D.L., Al-Rubaei, A.M., Smolek, A.P., Blecken, G.T., Viklander, M., Hunt, W.F., 2017. Evaluation of factors affecting soil carbon sequestration services of stormwater wet retention ponds in varying climate zones. Sci. Total Environ. 583, 133–141. doi:10.1016/j.scitotenv.2017.01.040

Messer, T.L., Burchell, M.R., Böhlke, J.K., Tobias, C.R., 2017. Tracking the fate of nitrate through pulse-flow wetlands: A mesocosm scale 15N enrichment tracer study. Ecol. Eng. 106, 597–608. doi:10.1016/j.ecoleng.2017.06.016

Messina, M.G., Conner, W.H., 1997. Southern Forested Wetlands: Ecology and Management 634.

Meyer, J.L., 1990. A Blackwater Perspective on Riverine Ecosystems. Bioscience 40, 643–651.

Meyer, J.L., Paul, M.J., Taulbee, W.K., 2005. Stream ecosystem function in urbanizing landscapes. J. North Am. Benthol. Soc. 24, 602–612. doi:10.1899/04-021.1

Moore, T.L.C., Hunt, W.F., 2012. Ecosystem service provision by stormwater wetlands and ponds - a means for evaluation? Water Res. 46, 6811–23. doi:10.1016/j.watres.2011.11.026

Moran, M.A., Sheldon, W.M., Zepp, R.G., 2000. Carbon loss and optical property changes during long-term photochemical and biological degradation of estuarine dissolved organic matter. Limnol. Oceanogr. 45, 1254–1264. doi:10.4319/lo.2000.45.6.1254

Morrissey, E.M., Jenkins, A.S., Brown, B.L., Franklin, R.B., 2013. Resource availability effects on nitrate-reducing microbial communities in a freshwater wetland. Wetlands 33, 301–310. doi:10.1007/s13157-013-0384-2

Morse, N.R., McPhillips, L.E., Shapleigh, J.P., Walter, M.T., 2017. The role of denitrification in stormwater detention basin treatment of nitrogen. Environ. Sci. Technol. acs.est.7b01813. doi:10.1021/acs.est.7b01813

Morse, N.R., Payne, E.G.I., Henry, R., Hatt, B.E., Chandrasena, G., Shapleigh, J.P., Louis, P., Cook, M., Coutts, S., Hathaway, J., Walter, M.T., Mccarthy, D., 2018. Plant-microbe interactions drive denitrification rates, dissolved nitrogen removal, and the abundance of denitrification genes in stormwater control measures. Environ. Sci. Technol. doi:10.1021/acs.est.8b02133

Mosier, A.R., 1980. Acetylene inhibition of ammonium oxidation in soil. Soil Biol. Biochem. 12, 443–444. doi:10.1016/0038-0717(80)90023-1

Mulholland, P.J., Kuenzler, E.J., 1979. Organic carbon export from upland and forested wetland watersheds. Limnol. Oceanogr. 24, 960–966. doi:10.4319/lo.1979.24.5.0960

Musolff, A., Fleckenstein, J.H., Rao, P.S.C., Jawitz, J.W., 2017. Emergent archetype patterns of coupled hydrologic and biogeochemical responses in catchments. Geophys. Res. Lett. 44, 4143–4151. doi:10.1002/2017GL072630

Musolff, A., Schmidt, C., Selle, B., Fleckenstein, J.H., 2015. Catchment controls on solute export. Adv. Water Resour. 86, 133–146. doi:10.1016/j.advwatres.2015.09.026

Nathan, R.J., McMahon, T.A., 1990. Evaluation of automated techniques for base flow and recession analyses. Water Resour. Res. 26, 1465–1473. doi:10.1029/WR026i007p01465

National Research Council, 2009. Urban Stormwater Management in the United States. National Academies Press, Washington, D.C. doi:10.17226/12465

Newcomer Johnson, T.A., Kaushal, S.S., Mayer, P.M., Grese, M.M., 2014. Effects of stormwater management and stream restoration on watershed nitrogen retention. Biogeochemistry 121, 81–106. doi:10.1007/s10533-014-9999-5

Newcomer Johnson, T.A., Kaushal, S.S., Mayer, P.M., Smith, R.M., Sivirichi, G.M., 2016. Nutrient Retention in Restored Streams and Rivers : A Global Review and Synthesis. Water 8, 1–28. doi:10.3390/w8040116

Newcomer, T.A., Kaushal, S.S., Mayer, P.M., Shields, A.R., Canuel, E.A., Groffman, P.M., Gold, A.J., 2012. Influence of natural and novel organic carbon sources on denitrification in forest, degraded urban, and restored streams. Ecol. Monogr. 82, 449–466. doi:10.1890/12-0458.1

Newell, S.E., McCarthy, M.J., Gardner, W.S., Fulweiler, R.W., 2016a. Sediment Nitrogen Fixation: a Call for Re-evaluating Coastal N Budgets. Estuaries and Coasts. doi:10.1007/s12237-016-0116-y

Newell, S.E., Pritchard, K., Foster, S., Fulweiler, R., 2016b. Molecular evidence for sediment nitrogen fixation in a temperate New England estuary. PeerJ 4, e1615. doi:10.7717/peerj.1615

Nixon, S.W., Ammerman, J.W., Atkinson, L.P., Berounsky, V.M., Billen, G., Boicourt, W.C., Boynton, W.R., Church, T.M., Ditoro, D.M., Elmgren, R., Garber, J.H., Giblin, a E., Jahnke, R. a, Owens, N.J.P., Pilson, M.E.Q., Seitzinger, S.P., 1996. The fate of nitrogen and phosphorus at the land sea margin of the North Atlantic Ocean. Biogeochemistry 35, 141–180. doi:10.1007/BF02179826

Nogaro, G., Burgin, A.J., 2014. Influence of bioturbation on denitrification and dissimilatory nitrate reduction to ammonium (DNRA) in freshwater sediments. Biogeochemistry 120, 279–294. doi:10.1007/s10533-014-9995-9

Norton, R.A., Harrison, J.A., Kent Keller, C., Moffett, K.B., 2017. Effects of storm size and frequency on nitrogen retention, denitrification, and N2O production in bioretention swale mesocosms. Biogeochemistry 134, 353–370. doi:10.1007/s10533-017-0365-2

O'Brien, J.M., Hamilton, S.K., Podzikowski, L., Ostrom, N., 2012. The fate of assimilated nitrogen in streams: An in situ benthic chamber study. Freshw. Biol. 57, 1113–1125. doi:10.1111/j.1365-2427.2012.02770.x

O'Driscoll, M., Clinton, S., Jefferson, A., Manda, A., McMillan, S., 2010. Urbanization Effects on Watershed Hydrology and In-Stream Processes in the Southern United States. Water 2, 605–648. doi:10.3390/w2030605

Oksanen, J., Blanchet, F.G., Friendly, M., Kindt, R., Legendre, P., McGlinn, D., Minchin, P.R., O'Hara, R.B., Simpson, G.L., Solymos, P., Stevens, M.H.H., Szoecs, E., Wagner, H., 2019. vegan: Community Ecology Package.

Outcalt, K.W., Sheffield, R.M., 1996. The longleaf pine forest: trends and current conditions, Resource Bulletin SRS-9, U.S. Department of Agriculture, Forest Service, Southern Research Station, Asheville, NC. Outcalt, K.W., Wade, D.D.

Page, J.L., Winston, R.J., Asce, M., Mayes, D.B., Perrin, C.A., Hunt Iii, W.F., Wre, D., Hunt, W.F., 2015. Retrofitting Residential Streets with Stormwater Control Measures over Sandy Soils for Water Quality Improvement at the Catchment Scale. J. Environ. Eng. 141, 04014076.

Parr, T.B., Cronan, C.S., Ohno, T., Findlay, S.E.G., Smith, S.M.C., Simon, K.S., 2015. Urbanization changes the composition and bioavailability of dissolved organic matter in headwater streams. Limnol. Oceanogr. 60, 885–900. doi:10.1002/lno.10060

Passeport, E., Vidon, P., Forshay, K.J., Harris, L., Kaushal, S.S., Kellogg, D.Q., Lazar, J., Mayer, P., Stander, E.K., 2013. Ecological engineering practices for the reduction of excess nitrogen in human-influenced landscapes: a guide for watershed managers. Environ. Manage. 51, 392–413. doi:10.1007/s00267-012-9970-y

Paul, M.J., Meyer, J.L., 2001. STREAMS IN THE URBAN LANDSCAPE. Annu. Rev. Ecol. Syst. 32, 333–365. doi:10.1146/annurev.ecolsys.32.081501.114040

Payne, E.G.I., Fletcher, T.D., Russell, D.G., Grace, M.R., Cavagnaro, T.R., Evrard, V., Deletic, A., Hatt, B.E., Cook, P.L.M.M., 2014. Temporary Storage or Permanent Removal? The Division of Nitrogen between Biotic Assimilation and Denitrification in Stormwater Biofiltration Systems. PLoS One 9. doi:10.1371/journal.pone.0090890

Peacock, M., Audet, J., Jordan, S., Smeds, J., Wallin, M.B., 2019. Greenhouse gas emissions from urban ponds are driven by nutrient status and hydrology. Ecosphere 10, e02643. doi:10.1002/ecs2.2643

Pellerin, B.A., Kaushal, S.S., McDowell, W.H., 2006. Does Anthropogenic Nitrogen Enrichment Increase Organic Nitrogen Concentrations in Runoff from Forested and Human-dominated Watersheds? Ecosystems 9, 852–864. doi:10.1007/s10021-006-0076-3

Pellerin, B.A., Wollheim, W.M., Hopkinson, C.S., McDowell, W.H., Williams, M.R., Vörösmarty, C.J., Daley, M.L., 2004. Role of wetlands and developed land use on dissolved organic nitrogen concentrations and DON/TDN in northeastern U.S. rivers and streams. Limnol. Oceanogr. 49, 910–918. doi:10.4319/lo.2004.49.4.0910

Pennino, M.J., Kaushal, S.S., Mayer, P.M., Utz, R.M., Cooper, C.A., 2016. Stream restoration and sewers impact sources and fluxes of water, carbon, and nutrients in urban watersheds. Hydrol. Earth Syst. Sci. doi:10.5194/hess-20-3419-2016

Petrone, K.C., 2010. Catchment export of carbon, nitrogen, and phosphorus across an agro-urban land use gradient, Swan-Canning River system, southwestern Australia. J. Geophys. Res. 115, G01016. doi:10.1029/2009JG001051

Petrone, K.C., Fellman, J.B., Hood, E., Donn, M.J., Grierson, P.F., 2011. The origin and function of dissolved organic matter in agro-urban coastal streams. J. Geophys. Res. Biogeosciences

116, 1028. doi:10.1029/2010JG001537

Petrone, K.C., Richards, J.S., Grierson, P.F., 2009. Bioavailability and composition of dissolved organic carbon and nitrogen in a near coastal catchment of south-western Australia. Biogeochemistry 92, 27–40. doi:10.1007/s10533-008-9238-z

Peuravuori, J., Pihlaja, K., 1997. Molecular size distribution and spectroscopic properties of aquatic humic substances. Anal. Chim. Acta 337, 133–149. doi:10.1016/S0003-2670(96)00412-6

Piehler, M.F., Smyth, A.R., 2011. Habitat-specific distinctions in estuarine denitrification affect both ecosystem function and services. Ecosphere 2, art12. doi:10.1890/ES10-00082.1

Pisani, O., Bosch, D.D., Coffin, A.W., Endale, D.M., Liebert, D., Strickland, T.C., 2020. Riparian land cover and hydrology influence stream dissolved organic matter composition in an agricultural watershed. Sci. Total Environ. 717. doi:10.1016/j.scitotenv.2020.137165

Price, K., 2011. Effects of watershed topography, soils, land use, and climate on baseflow hydrology in humid regions: A review. Prog. Phys. Geogr. 35, 465–492. doi:10.1177/0309133311402714

R Core Team, 2020. R: A Language and Environment for Statistical Computing.

Rahman, M.M., Roberts, K.L., Warry, F., Grace, M.R., Cook, P.L.M., 2019. Factors controlling dissimilatory nitrate reduction processes in constructed stormwater urban wetlands. Biogeochemistry 142. doi:10.1007/s10533-019-00541-0

Rao, A.M.F., Charette, M.A., 2012. Benthic Nitrogen Fixation in an Eutrophic Estuary Affected by Groundwater Discharge. J. Coast. Res. 280, 477–485. doi:10.2112/JCOASTRES-D-11-00057.1

Reed, M.L., DiTullio, G.R., Kacenas, S.E., Greenfield, D.I., 2015. Effects of nitrogen and dissolved organic carbon on microplankton abundances in four coastal South Carolina (USA) systems. Aquat. Microb. Ecol. 76, 1–14. doi:10.3354/ame01764

Reed, M.L., Pinckney, J.L., Keppler, C.J., Brock, L.M., Hogan, S.B., Greenfield, D.I., 2016. The influence of nitrogen and phosphorus on phytoplankton growth and assemblage composition in four coastal, southeastern USA systems. Estuar. Coast. Shelf Sci. 177, 71–82. doi:10.1016/j.ecss.2016.05.002

Reisinger, A.J., Doody, T.R., Groffman, P.M., Kaushal, S.S., Rosi, E.J., 2019. Seeing the light: Urban stream restoration affects stream metabolism and nitrate uptake via changes in canopy cover. Ecol. Appl. e01941. doi:10.1002/eap.1941

Reisinger, A.J., Groffman, P.M., Rosi-Marshall, E.J., 2016. Nitrogen cycling process rates across urban ecosystems. FEMS Microbiol. Ecol. 92, fiw198. doi:10.1093/femsec/fiw198

Rivers, E., McMillan, S., Bell, C., Clinton, S., 2018. Effects of Urban Stormwater Control

Measures on Denitrification in Receiving Streams. Water 10, 1582. doi:10.3390/w10111582

Rosenzweig, B.R., Smith, J.A., Baeck, M.L., Jaffé, P.R., 2011. Monitoring Nitrogen Loading and Retention in an Urban Stormwater Detention Pond. J. Environ. Qual. 40, 598. doi:10.2134/jeq2010.0300

Rysgaard, S., Risgaard-Petersen, N., Niels Peter, S., Kim, J., Lars Peter, N., 1994. Oxygen regulation of nitrification and denitrification in sediments. Limnol. Oceanogr. 39, 1643–1652. doi:10.4319/lo.1994.39.7.1643

Sanger, D., Blair, A., DiDonato, G., Washburn, T., Jones, S., Riekerk, G., Wirth, E., Stewart, J., White, D., Vandiver, L., Holland, A.F., 2013. Impacts of Coastal Development on the Ecology of Tidal Creek Ecosystems of the US Southeast Including Consequences to Humans. Estuaries and Coasts 38, 49–66. doi:10.1007/s12237-013-9635-y

Schlesinger, W.H., 2009. On the fate of anthropogenic nitrogen. Proc. Natl. Acad. Sci. 106, 203–208. doi:10.1073/pnas.0810193105

Schroer, W.F., Benitez-Nelson, C.R., Smith, E.M., Ziolkowski, L.A., 2018. Drivers of Sediment Accumulation and Nutrient Burial in Coastal Stormwater Detention Ponds, South Carolina, USA. Ecosystems. doi:10.1007/s10021-017-0207-z

Scott, J.T., McCarthy, M.J., Gardner, W.S., Doyle, R.D., 2008. Denitrification, dissimilatory nitrate reduction to ammonium, and nitrogen fixation along a nitrate concentration gradient in a created freshwater wetland. Biogeochemistry 87, 99–111. doi:10.1007/s10533-007-9171-6

Seitzinger, S., Harrison, J.A., Böhlke, J.K., Bouwman, A.F., Lowrance, R., Peterson, B., Tobias, C., Drecht, G. Van, 2006. DENITRIFICATION ACROSS LANDSCAPES AND WATERSCAPES: A SYNTHESIS. Ecol. Appl. 16, 2064–2090. doi:10.1890/1051-0761(2006)016[2064:DALAWA]2.0.CO;2

Seitzinger, S.P., 1988. Denitrification in freshwater and coastal marine ecosystems: Ecological and geochemical significance. Limnol. Oceanogr. 33, 702–724. doi:10.4319/lo.1988.33.4_part_2.0702

Seitzinger, S.P., Nielsen, L.P., Caffrey, J., Christensen, P.B., 1993. Denitrification measurements in aquatic sediments: A comparison of three methods. Biogeochemistry 23, 147–167. doi:10.1007/BF00023750

Seitzinger, S.P., Sanders, R.W., Styles, Renée, Styles, Renee, 2010. Bioavailability of DON from natural and anthropogenic sources to estuarine plankton. Limnology 47, 353–366.

Shields, C.A., Band, L.E., Law, N., Groffman, P.M., Kaushal, S.S., Savvas, K., Fisher, G.T., Belt, K.T., 2008. Streamflow distribution of non-point source nitrogen export from urban-rural catchments in the Chesapeake Bay watershed. Water Resour. Res. doi:10.1029/2007WR006360

Slone, L.A., McCarthy, M.J., Myers, J.A., Hammerschmidt, C.R., Newell, S.E., 2018. River sediment nitrogen removal and recycling within an agricultural Midwestern USA watershed. Freshw. Sci. 37, 1–12. doi:10.1086/696610

Smith, C.J., Dong, L.F., Wilson, J., Stott, A., Osborn, A.M., Nedwell, D.B., 2015. Seasonal variation in denitrification and dissimilatory nitrate reduction to ammonia process rates and corresponding key functional genes along an estuarine nitrate gradient. Front. Microbiol. 6, 1–11. doi:10.3389/fmicb.2015.00542

Smith, R.M., Kaushal, S.S., 2015. Carbon cycle of an urban watershed: exports, sources, and metabolism. Biogeochemistry 126, 173–195. doi:10.1007/s10533-015-0151-y

Smucker, N.J., Detenbeck, N.E., Morrison, A.C., 2013. Diatom responses to watershed development and potential moderating effects of near-stream forest and wetland cover. Freshw. Sci. 32, 230–249. doi:10.1899/11-171.1

Soil Survey Staff, 2015. Web Soil Survey.

Sønderup, M.J., Egemose, S., Hansen, A.S., Grudinina, A., Madsen, M.H., Flindt, M.R., 2016. Factors affecting retention of nutrients and organic matter in stormwater ponds. Ecohydrology 9, 796–806. doi:10.1002/eco.1683

Song, B., Lisa, J.A., Tobias, C.R., 2014. Linking DNRA community structure and activity in a shallow lagoonal estuarine system. Front. Microbiol. 5, 460. doi:10.3389/fmicb.2014.00460

Song, K., Winters, C., Xenopoulos, M.A., Marsalek, J., Frost, P.C., 2017. Phosphorus cycling in urban aquatic ecosystems: connecting biological processes and water chemistry to sediment P fractions in urban stormwater management ponds. Biogeochemistry 132, 203–212. doi:10.1007/s10533-017-0293-1

Song, K., Xenopoulos, M.A., Buttle, J.M., Marsalek, J., Wagner, N.D., Pick, F.R., Frost, P.C., 2013. Thermal stratification patterns in urban ponds and their relationships with vertical nutrient gradients. J. Environ. Manage. 127, 317–323. doi:10.1016/j.jenvman.2013.05.052

Spencer, R.G.M., Aiken, G.R., Dornblaser, M.M., Butler, K.D., Holmes, R.M., Fiske, G., Mann, P.J., Stubbins, A., 2013. Chromophoric dissolved organic matter export from U.S. rivers. Geophys. Res. Lett. 40, 1575–1579. doi:10.1002/grl.50357

Stanley, E.H., Maxted, J.T., 2008. Changes in the dissolved nitrogen pool across land cover gradients in wisconsin streams. Ecol. Appl. 18, 1579–1590. doi:10.1890/07-1379.1

Stanley, E.H., Powers, S.M., Lottig, N.R., Buffam, I., Crawford, J.T., 2012. Contemporary changes in dissolved organic carbon (DOC) in human-dominated rivers: Is there a role for DOC management? Freshw. Biol. 57, 26–42. doi:10.1111/j.1365-2427.2011.02613.x

Stranko, S.A., Hilderbrand, R.H., Palmer, M.A., 2012. Comparing the Fish and Benthic Macroinvertebrate Diversity of Restored Urban Streams to Reference Streams. Restor. Ecol. 20, 747–755. doi:10.1111/j.1526-100X.2011.00824.x

Sun, G., McNulty, S.G., Amatya, D.M., Skaggs, R.W., Swift, L.W., Shepard, J.P., Riekerk, H., 2002. A comparison of the watershed hydrology of coastal forested wetlands and the mountainous uplands in the Southern US. J. Hydrol. 263, 92–104. doi:10.1016/S0022-1694(02)00064-1

Sun, G., Noormets, A., Gavazzi, M.J., McNulty, S.G., Chen, J., Domec, J.C., King, J.S., Amatya, D.M., Skaggs, R.W., 2010. Energy and water balance of two contrasting loblolly pine plantations on the lower coastal plain of North Carolina, USA. For. Ecol. Manage. 259, 1299–1310. doi:10.1016/j.foreco.2009.09.016

Taguchi, V.J., Olsen, T.A., Natarajan, P., Janke, B.D., Gulliver, J.S., Finlay, J.C., Stefan, H.G., 2019. Internal Loading in Stormwater Ponds as a Phosphorus Source to Downstream Waters. Submitted. doi:10.1002/lol2.10155

Tank, J.L., Martí, E., Riis, T., von Schiller, D., Reisinger, A.J., Dodds, W.K., Whiles, M.R., Ashkenas, L.R., Bowden, W.B., Collins, S.M., Crenshaw, C.L., Crowl, T.A., Griffiths, N.A., Grimm, N.B., Hamilton, S.K., Johnson, S.L., McDowell, W.H., Norman, B.M., Rosi, E.J., Simon, K.S., Thomas, S.A., Webster, J.R., 2018. Partitioning assimilatory nitrogen uptake in streams: an analysis of stable isotope tracer additions across continents. Ecol. Monogr. 88, 120–138. doi:10.1002/ecm.1280

Textor, S.R., Guillemette, F., Zito, P.A., Spencer, R.G.M., 2018. An Assessment of Dissolved Organic Carbon Biodegradability and Priming in Blackwater Systems. J. Geophys. Res. Biogeosciences 123, 2998–3015. doi:10.1029/2018JG004470

Thompson, S., Piehler, M., Paerl, H., 2000. Denitrification in an estuarine headwater creek within an agricultural watershed. J. Environ. Qual. 29, 1914–1923.

Thompson, S.E., Basu, N.B., Lascurain, J., Aubeneau, A., Rao, P.S.C., 2011. Relative dominance of hydrologic versus biogeochemical factors on solute export across impact gradients. Water Resour. Res. 47, 1–20. doi:10.1029/2010WR009605

Tillinghast, E.D., Hunt, W.F., Jennings, G.D., 2011. Stormwater control measure (SCM) design standards to limit stream erosion for Piedmont North Carolina. J. Hydrol. 411, 185–196. doi:10.1016/j.jhydrol.2011.09.027

Toet, C., Hvitved-Jacobsen, T., Tousef, Y.A., 1990. Pollutant removal and eutrophication in urban runoff detention ponds 22, 1990.

Tufford, D.L., Samarghitan, C.L., McKellar, H.N., Porter, D.E., Hussey, J.R., 2003. IMPACTS OF URBANIZATION ON NUTRIENT CONCENTRATIONS IN SMALL SOUTHEASTERN COASTAL STREAMS. J. Am. Water Resour. Assoc. 39, 301–312. doi:10.1111/j.1752-1688.2003.tb04385.x

Utz, R.M., Eshleman, K.N., Hilderbrand, R.H., 2011. Variation in physicochemical responses to urbanization in streams between two Mid-Atlantic physiographic regions. Ecol. Appl. 21, 402–415. doi:10.1890/09-1786.1

Utz, R.M., Hopkins, K.G., Beesley, L., Booth, D.B., Hawley, R.J., Baker, M.E., Freeman, M.C., L. Jones, K., 2016. Ecological resistance in urban streams: the role of natural and legacy attributes. Freshw. Sci. 35, 380–397. doi:10.1086/684839

Van Meter, K.J., Basu, N.B., 2015. Catchment legacies and time lags: A parsimonious watershed model to predict the effects of legacy storage on nitrogen export. PLoS One 10, 1–22. doi:10.1371/journal.pone.0125971

Vietz, G.J., Walsh, C.J., Fletcher, T.D., 2015. Urban hydrogeomorphology and the urban stream syndrome: Treating the symptoms and causes of geomorphic change. Prog. Phys. Geogr. 40, 480–492. doi:10.1177/0309133315605048

Von Korff, B.H., Piehler, M.F., Ensign, S.H., 2014. Comparison of Denitrification Between River Channels and Their Adjoining Tidal Freshwater Wetlands. Wetlands 34, 1047–1060. doi:10.1007/s13157-014-0545-y

Wahl, M.H., McKellar, H.N., Williams, T.M., 1997. Patterns of nutrient loading in forested and urbanized coastal streams. J. Exp. Mar. Bio. Ecol. 213, 111–131. doi:10.1016/S0022-0981(97)00012-9

Waller, L.J., Evanylo, G.K., Krometis, L.-A.H., Strickland, M., Wynn-Thompson, T.M., Badgley, B.D., 2018. Engineered and Environmental Controls of Microbial Denitrification in Established Bioretention Cells. Environ. Sci. Technol. acs.est.7b06704. doi:10.1021/acs.est.7b06704

Walsh, C.J., Roy, A.H., Feminella, J.W., Cottingham, P.D., Groffman, P.M., Morgan, R.P., 2005. The urban stream syndrome: current knowledge and the search for a cure. J. North Am. Benthol. Soc. 24, 706. doi:10.1899/0887-3593(2005)024\[0706:TUSSCK\]2.0.CO;2

Walter, H.M., Keeney, D.R., Fillery, I.R., 1979. Inhibition of Nitrification by Acetylene. Soil Sci. Soc. Am. J. 43, 195–196. doi:10.2136/sssaj1979.03615995004300010038x

Wear, E.K., Koepfler, E.T., Smith, E.M., 2014. Spatiotemporal Variability in Dissolved Organic Matter Composition is More Strongly Related to Bacterioplankton Community Composition than to Metabolic Capability in a Blackwater Estuarine System. Estuaries and Coasts 37, 119–133. doi:10.1007/s12237-013-9651-y

Weishaar, J.L., Aiken, G.R., Bergamaschi, B.A., Fram, M.S., Fujii, R., Mopper, K., 2003. Evaluation of specific ultraviolet absorbance as an indicator of the chemical composition and reactivity of dissolved organic carbon. Environ. Sci. Technol. 37, 4702–4708. doi:10.1021/es030360x

Welschmeyer, N.A., 1994. Fluorometric Analysis of Chlorophyll a in the Presence of Chlorophyll b and Pheopigments. Limnol. Oceanogr. 39, 1985–1992.

Wetzel, R.G., 2001. Limnology: Lake and River Ecosystems, 3rd ed. Academic Press, San Diego, CA.

Williams, C.J., Frost, P.C., Morales-Williams, A.M., Larson, J.H., Richardson, W.B., Chiandet, A.S., Xenopoulos, M.A., 2016. Human activities cause distinct dissolved organic matter composition across freshwater ecosystems. Glob. Chang. Biol. 22, 613–626. doi:10.1111/gcb.13094

Williams, C.J., Frost, P.C., Xenopoulos, M.A., 2013. Beyond best management practices: Pelagic biogeochemical dynamics in urban stormwater ponds. Ecol. Appl. 23, 1384–1395. doi:10.1890/12-0825.1

Withers, P.J.A., Jarvie, H.P., 2008. Delivery and cycling of phosphorus in rivers: A review. Sci. Total Environ. 400, 379–395. doi:10.1016/j.scitotenv.2008.08.002

Yarbro, L.A., Kuenzler, E.J., Mulholland, P.J., Sniffen, R.P., 1984. Effects of stream channelization on exports of nitrogen and phosphorus from north Carolina coastal plain watersheds. Environ. Manage. 8, 151–160. doi:10.1007/BF01866936

Zhou, Y., Zhou, L., Zhang, Y., Garcia, J., Souza, D., Podgorski, D.C., Spencer, R.G.M., Jeppesen, E., Davidson, T.A., 2019. Autochthonous dissolved organic matter potentially fuels methane ebullition from experimental lakes *. Water Res. 166, 115048. doi:10.1016/j.watres.2019.115048

Zhu, W.-X., Dillard, N.D., Grimm, N.B., 2004. Urban nitrogen biogeochemistry: status and processes in green retention basins. Biogeochemistry 71, 177–196. doi:10.1007/s10533-004-9683-2