Urbanization alters coastal plain stream carbon export and dissolved oxygen dynamics

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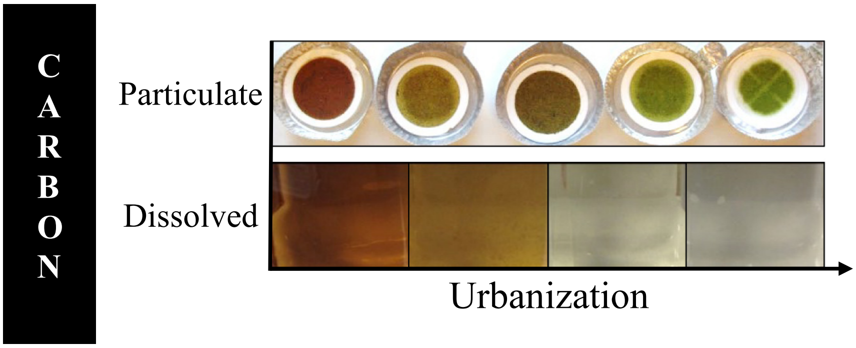
HIGHLIGHTS

- Urbanization reduced natural carbon stream exports and added diverse urban sources.
- Diel variation of dissolved oxygen was higher in urban streams.
- Conserving and restoring natural stream C sources may also improve water quality.

GRAPHICAL ABSTRACT



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ABSTRACT

Coastal plain streams in the southeastern United States supply carbon that supports important coastal ecosystems, but the effects of urbanization on carbon export from these streams have not been extensively studied. This study aimed to determine how urbanization changes coastal plain stream organic matter quality, rates of carbon export, and dissolved oxygen dynamics that have implications for stream ecosystem function. Organic matter quality, organic carbon export, and dissolved oxygen concentrations were measured for multiple years (2009 & 2013–2015) in North Carolina coastal plain streams that spanned a gradient of urbanization. Based on spectral characteristics, dissolved organic matter (DOM) quality appeared to shift from characteristic blackwater in minimally impacted streams to clear streamwater in urban streams due to large reductions in chromophoric DOM concentrations, aromaticity, and molecular weight. Differences in spectral indices and characteristics of dissolved organic carbon export suggest that urbanization reduced natural sources of DOM and provided various urban sources of DOM that were likely more bioavailable. Particulate organic matter in the urban streams was indicative of more labile autochthonous sources than that of the less impacted streams, and rates of particulate carbon export increased and shifted to higher flows with watershed impervious surface cover. Diel variation of dissolved oxygen increased with watershed impervious surface cover, indicating that urbanization and associated changes in carbon and nutrient cycling altered stream function. While the effects of urbanization on carbon export were similar to previous studies in other regions, the unique blackwater state of natural streams and receiving waters in the study area make them especially susceptible to negative ecological impacts from altered carbon and nutrient export. Management actions that conserve or restore natural carbon sources to the stream may help mitigate multiple negative effects of urbanization in southeastern US coastal plain streams.

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1. 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" (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., 2019; 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

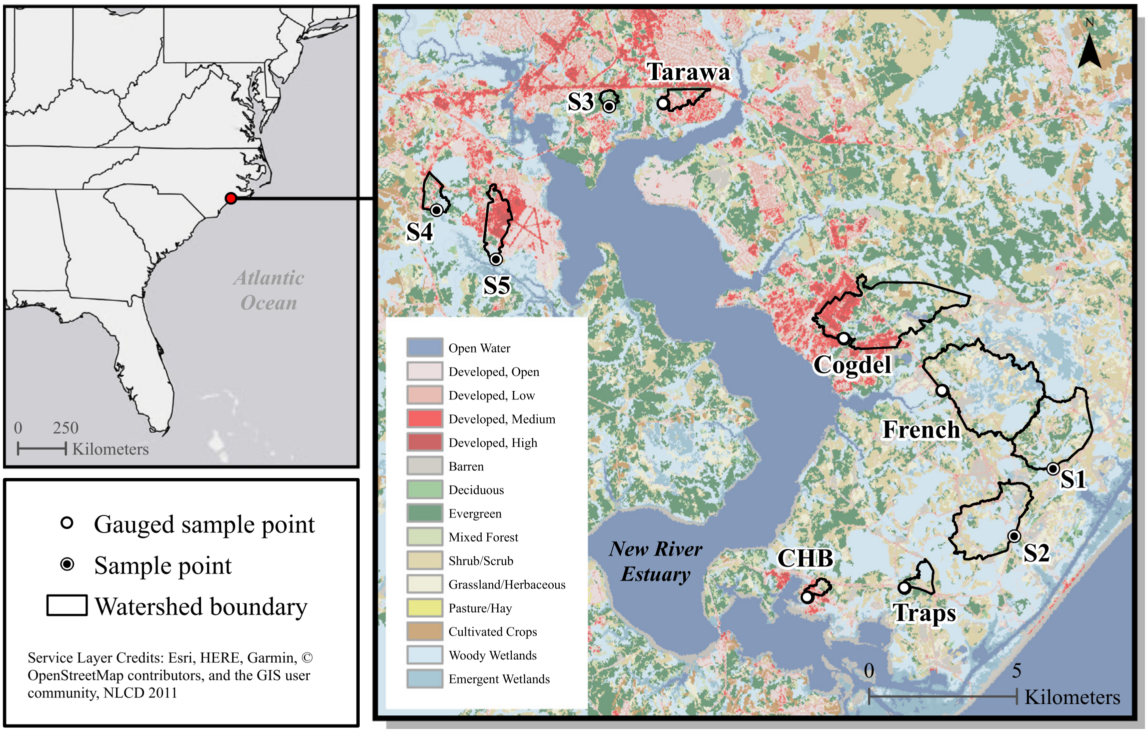

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Fig. 1. Map of study sites and watersheds on Marine Corps Base Camp Lejeune (MCBCL) near Jacksonville, NC. All ten streams were sampled for streamwater spectral analysis, and five streams were gauged for discharge and carbon export.

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.

2. Methods

2.1. Study sites

Ten streams on Marine Corps Base Camp Lejeune (MCBCL) located near Jacksonville, NC (Fig. 1) were selected for this study. The watersheds of these study streams ranged in ISC from 0.96% to 52.9% (Table 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 A1). 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 1). Additional land cover data is presented in Table A1.

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) (Fig. 1, Table A2). 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 A2). 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., 2017) 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 A2).

2.2. Stream export and DO concentrations

In the five gauged streams, water level and velocity were measured at 30 min intervals with a Teledyne ISCO water level and velocity sensor, and DO concentrations were measured at 30 min 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 h 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 h 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 30 min 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 A3). 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.

2.3. 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 h 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

Table 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).

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).

2.4. 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 h in a 90% acetone solution, and measuring the fluorescence of the solution with a Turner Designs Trilogy fluorometer (Welschmeyer, 1994).

2.5. 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).

3. Results

3.1. Stream carbon export and concentrations

3.1.1. 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 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 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 2). The export of suspended solids also increased with imperviousness (Table 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 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 2).

3.1.2. Timing of export

The timing of DOC and PC export varied by stream based on watershed size and watershed ISC (Fig. A1), but there were notable differences in the timing of DOC export relative to PC export based on

Table 2
Export and concentrations of C species and TSS. Letters indicate significant differences in stream concentrations based on Kruskal-Wallis and Dunn's tests.

Name	ISC (%)	Discharge (m yr^{-1})	Export (kg ha^{-1} yr^{-1})			% of total C export		Median concentrations (IQR) (mg/L)		
			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}

watershed ISC (Fig. 2, Fig. A1). 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 (Fig. 2a, Fig. A1). DOC C-Q slopes differed greatly between streams (Fig. 2b), but the variance in DOC concentrations relative to discharge was low ($CV_C/CV_Q < 0.5$, Fig. A2), showing that discharge generally controlled the timing of DOC export (i.e., chemostatic export regime). PC export was chemodynamic for all streams (i.e., $CV_C/CV_Q > 0.5$, Fig. A2), 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 (Fig. 2).

Though DOC export was chemostatic, all but one stream (Traps) had a significant relationship between discharge and DOC concentrations (Fig. 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 (Fig. 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 (Fig. A3).

3.2. Carbon quality

3.2.1. Relationship with ISC

Watershed ISC was significantly correlated with streamwater CDOM concentration (a_{350}) based on a negative logarithmic relationship (Fig. 3a, Table A4). Streamwater E_2:E_3 and S_r were both significantly correlated with watershed ISC as well, exhibiting positive relationships with ISC (Fig. 3b, c, Table A4). 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 (Fig. 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 Fig. 3, although the relationship between S_r and watershed ISC was not significant (Fig. A4). Both $SUVA_{254}$ and $SUVA_{350}$ were significantly correlated with watershed ISC based on negative logarithmic relationships (Fig. A4).

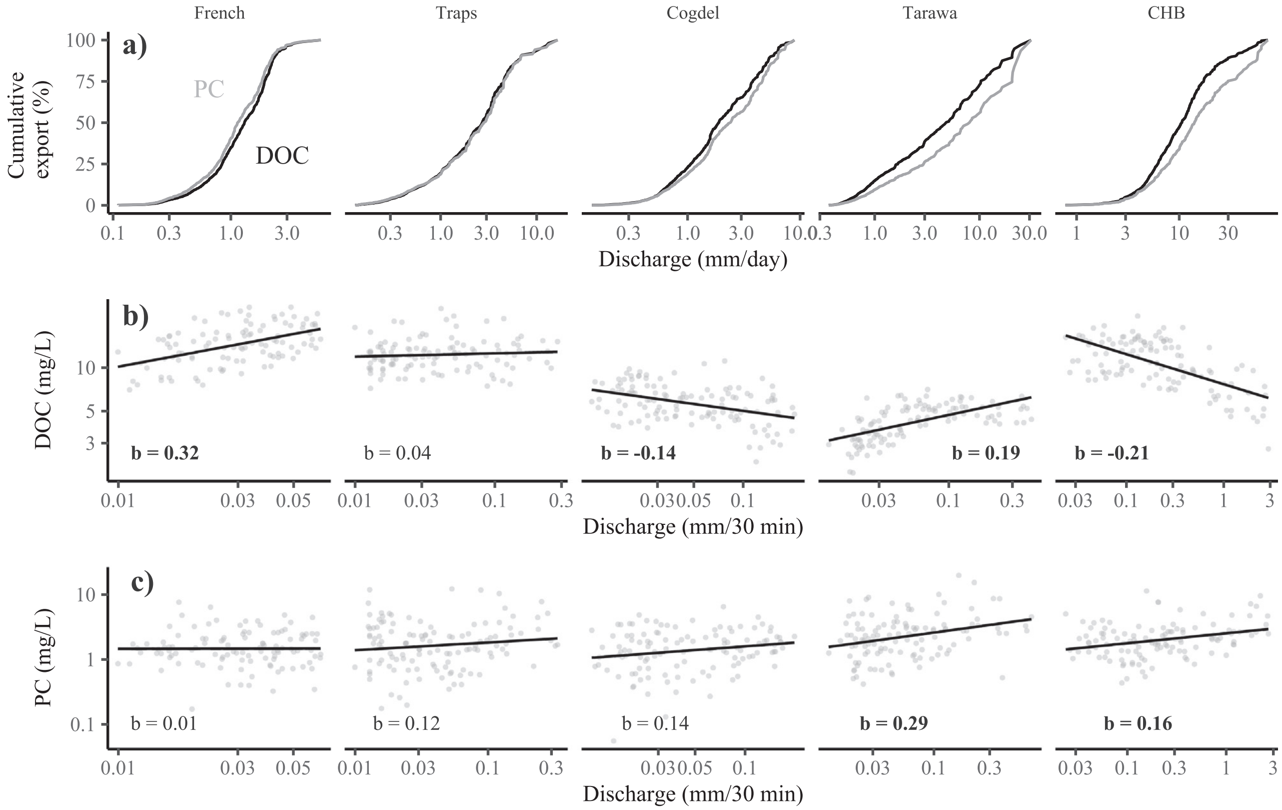

Fig. 2. a) Cumulative export of DOC and PC across values of discharge. **b)** Relationships between DOC and discharge, and **c)** PC and discharge. Overall slopes of the C-Q relationships are presented as b, with bold values indicating significant C-Q relationships ($\alpha = 0.05$).

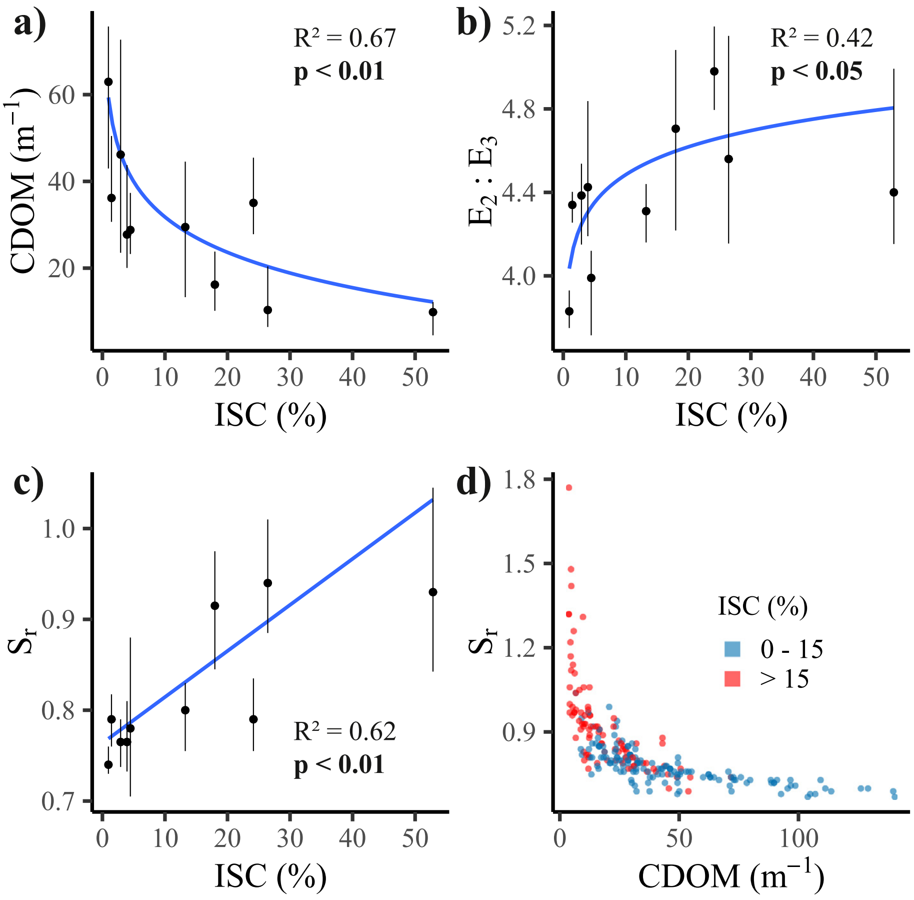

Fig. 3. a) Concentrations of CDOM (a_{350}), **b)** E_2:E_3 (a_{254}:a_{350}), and **c)** spectral slope ratios (S_r) in streamwater samples from ten streams across a range of watershed ISC. Points indicate median values and error bars show the 25th and 75th percentiles. **d)** Relationship between CDOM 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 (Fig. 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 (Fig. 4). While not shown in the NMDS, the more developed streams also had lower relative values of CDOM to DOC ($SUVA_{350}$).

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 (Fig. 5a, Table A5). 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 (Fig. 5b, Table A5). C:N decreased as chl-*a* increased based on a log-log relationship, and this relationship was significant but highly variable (Fig. A6).

3.2.2. 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 (Fig. 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

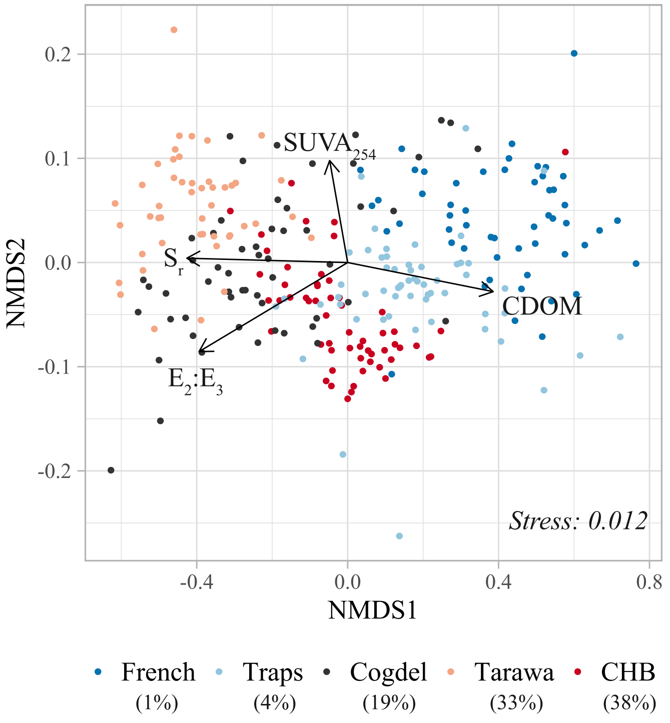

Fig. 4. NMDS ordination of spectral indices from five gauged streams across a gradient of watershed ISC.

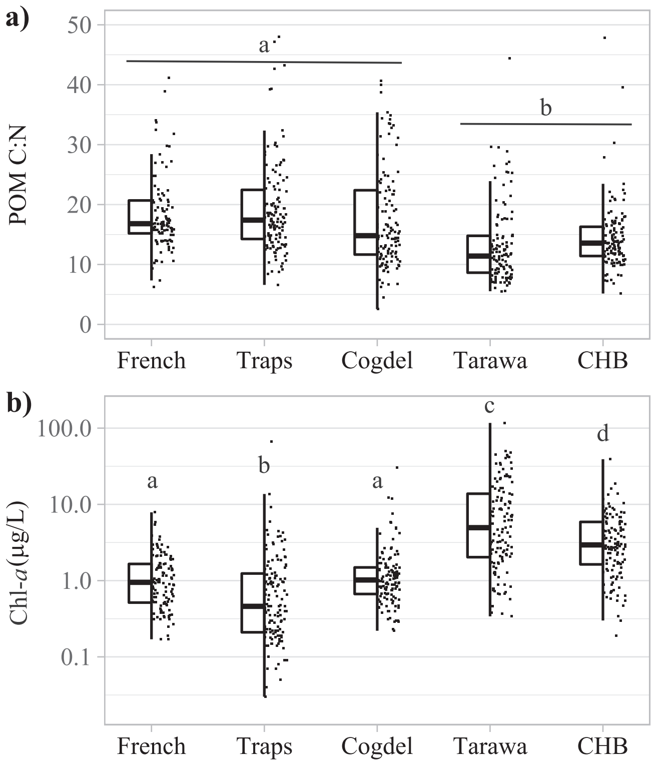

Fig. 5. **a**) Boxplot of particulate C:N and **b**) chl-*a* concentrations (log-scale) for each watershed. Letters indicated significant differences based on a Kruskal-Wallis and Dunn's post-hoc test with Bonferroni adjustments ($\alpha = 0.05$).

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.

3.3. Dissolved oxygen concentrations

Dissolved oxygen concentrations were significantly different between study streams, but the concentrations did not correspond with watershed ISC (Table A6). 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 (Fig. 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 (Fig. 7b), and this can be visualized by comparing the average diel pattern of DO concentrations (Fig. 7c).

4. 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.

4.1. 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 (Figs. 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 (Fig. 3), patterns of both DOC and CDOM enrichment with stream discharge (Fig. 4, Fig. 6a), and a significant relationship between % ISC and % wetland land cover in the study watersheds ($R^2 = 0.78$, $p < 0.01$, Table A1) 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

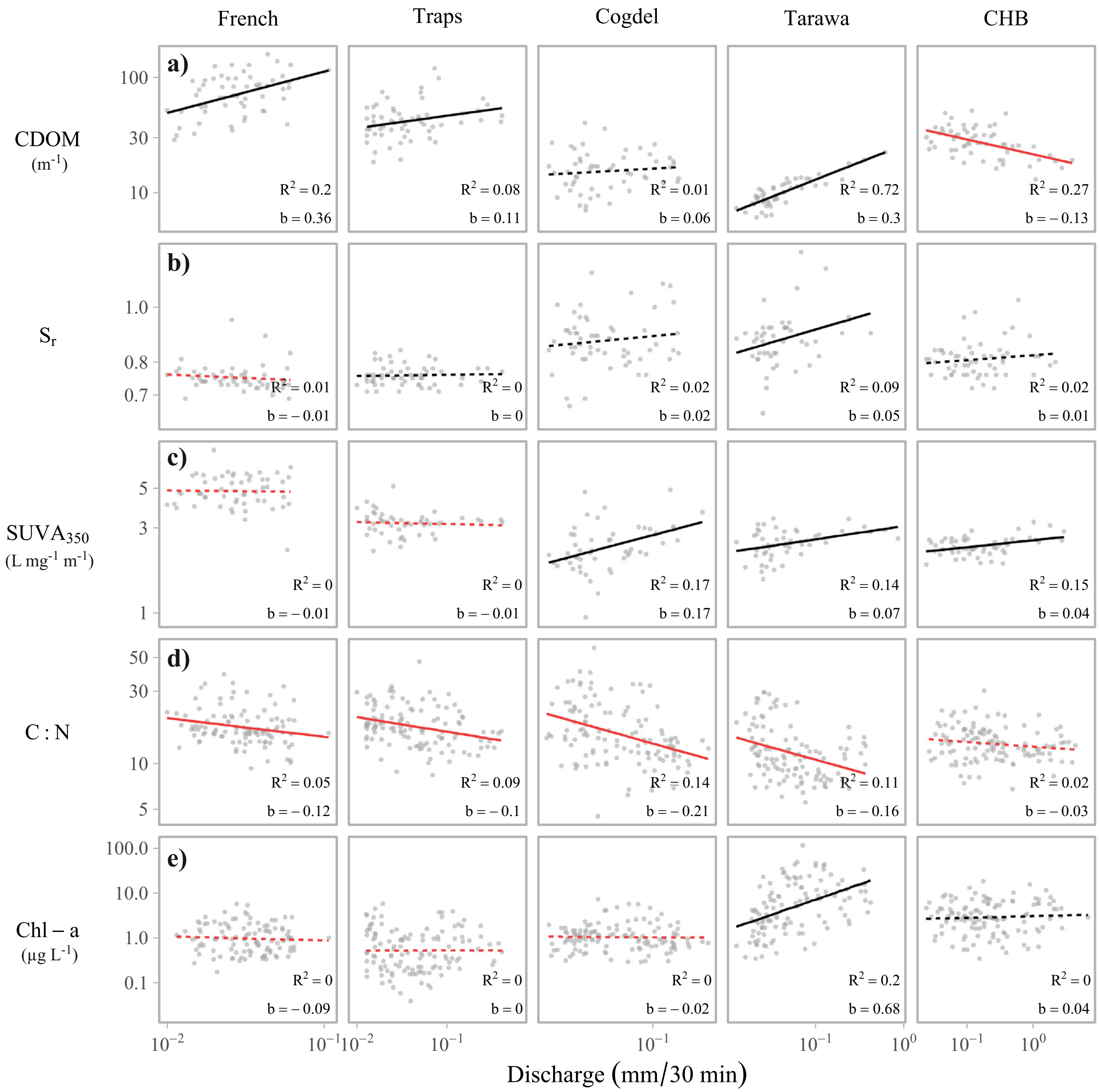

Fig. 6. a–c) The relationship between DOM spectral metrics and discharge. **d & e)** The relationship between POM quality indices and discharge. Regression lines indicate if the slope (b) is positive (black) or negative (red) and significant (full line, $\alpha = 0.05$) or not significant (dashed line).

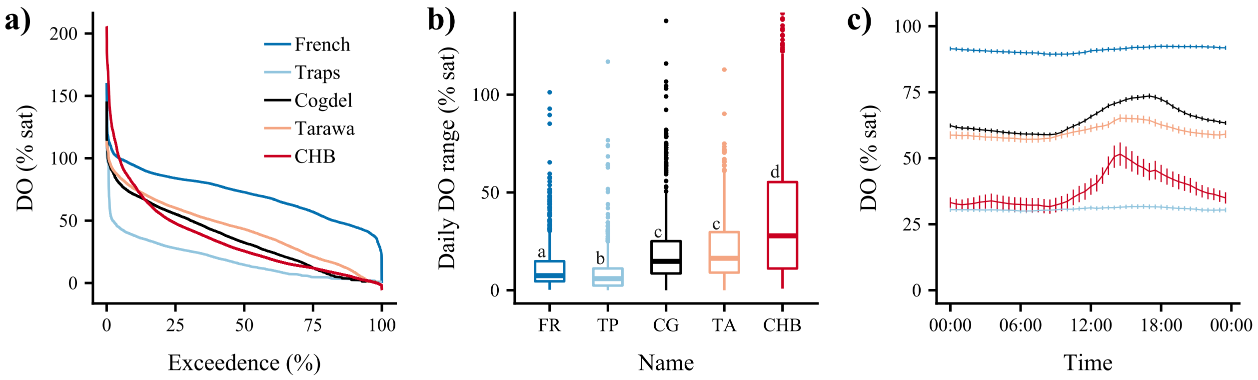

Fig. 7. a) Exceedance plot of dissolved oxygen. **b)** Daily DO range for each stream with letters indicating significant differences based on a Kruskal-Wallis and Dunn's post-hoc test with Bonferroni adjustments ($\alpha = 0.05$). **c)** Average diel pattern of DO during baseflow over study period (bars indicate SE).

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 and 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., 2019).

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 (Fig. 4) suggest that natural sources of DOM were present but diminished (Fig. 4, Fig. 6). The Tarawa stream, fed primarily by stormwater ponds that are flushed during storm events, exhibited a distinct autochthonous DOM signature (Fig. 4) that increased with discharge (Fig. 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 (Figs. 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).

4.2. 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 (Fig. 5, Table 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 (Fig. 2, Fig. A1), 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 A2), 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., 2019, 2017), 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., 2019, 2017). Nutrient availability (NO_x & NH_4 concentrations) increased with watershed ISC in the same five gauged streams during the same period (Gold et al., 2019), 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.

4.3. Changing DO dynamics with urbanization

Diel variation of DO was greater in streams with higher watershed ISC (Fig. 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., 2019). 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 A6). 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 suggest that this factor alone may not be a good indicator of stream health in these coastal plain streams.

4.4. 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., 2019) 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 excitation-emission 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., 2019). 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.

5. 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.

CRediT authorship contribution statement

Adam C. Gold: Data curation, Formal analysis, Visualization, Writing - original draft.**Suzanne P. Thompson:**Conceptualization, Data curation, Investigation, Methodology, Writing - review & editing.**Caitlin L. Magel:** Data curation, Investigation, Writing - review & editing.**Michael F. Piehler:**Conceptualization, Methodology, Writing - review & editing.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.scitotenv.2020.141132.

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