ABSTRACT

JOHNSTON, SARAH ELLEN. Fluxes of Dissolved Organic Matter from Urban Catchments in the Neuse River Basin. (Under the direction of Dr. Christopher Osburn).

Urbanization and impervious surfaces can influence the transport and composition of organic matter (OM) during storm events. The Neuse River Basin has undergone extensive urbanization and land use change in the past few decades including the expansion of urban areas and increase in impervious surfaces, however the effects of these changes to OM source and quality are not well studied. Dissolved organic matter (DOM) is a water quality concern because during drinking water treatment, disinfection byproducts (DBPs) are formed from OM, including aromatic compounds. DBPs are potentially harmful and are therefore limited by the EPA. An understanding of how urbanization affects the mobilization of precursor material can help in establishment of effective monitoring programs. DOM sources and concentrations were evaluated in this study using optical analyses (absorbance and fluorescence) and biomarkers (lignin and stable carbon isotopes) at base flow and storm flow in small urban catchments within the Neuse River basin during the summer of 2014. Optical and lignin parameters were then related to each other to evaluate the potential for an optical proxy for lignin biogeochemical information. DOC concentration was related to discharge at the Neuse River site at Clayton, NC, but was found to be not significantly correlated at the Walnut Creek and Crabtree Creek sites. The differences in land use contribute to differences in DOM sources. An analysis including all sites indicated that there were significant differences in DOC, lignin phenol concentration, and carbon-normalized lignin yields during storm flow compared to base flow events. At both storm flow and base flow, the fluorescence results were dominated by terrestrially derived DOM. Subtle changes in quality of DOM
were observed during storm events, however lignin source did not change significantly. Additionally, there were significant relationships observed between lignin and optical parameters suggesting the presence of an optical proxy for lignin. Component 3 of the PARAFAC modeled fluorescence correlated with carbon-normalized lignin yield providing a potential optical proxy for lignin. Wetlands are likely an important contributor of DOM during storm events by providing a source of DOM during storm events from shallow groundwater as well as providing consistently wet soil that prevents drying out and a subsequent increase in labile DOM during storm events. The wetland area ranged from 0% of catchment area at PHC to 3.15% at WC; at CC and PHC storm events had lower molecular weight DOM compared to WC and NR. These changes in DOM quality, including spectral slope, specific UV absorption, and stable carbon isotope values, suggest that land use plays an important role in mobilizing DOM during storm events.
DEDICATION

To my family. Mom and dad, you give me the support I need to always strive to do my best and follow my passions. Adam, you remind me to constantly work toward my dreams and never give up. Jim, you shared my love of the natural world and taught me to laugh even in the worst of times; your joy and compassion will never be forgotten. Rebecca, you have always kept me grounded in truth and encourage me to be creative. I love you all.
I grew up in Oak Ridge, TN and received a Bachelor’s of Science degree from the University of Tennessee at Chattanooga in environmental geology and a minor in chemistry in 2012. After graduating, I spent 8 months working as a post-baccalaureate research intern at Oak Ridge National Laboratory in a metabolomics and organic synthesis lab. There I became interested in organic matter, particularly the lignin biomolecule, in aquatic ecosystems. After completion of a Master’s degree, I plan to pursue a PhD at Florida State University studying biogeochemistry.
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Thank you to the past and present members of the Osburn lab group.
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INTRODUCTION

Urbanization can alter the hydrologic flow paths within a watershed and create new pathways for material to enter streams and rivers (Booth and Jackson, 1997). Such changes in land use influence both the quantity and quality of organic matter (OM) entering a river through runoff (Hosen et al. 2014). Organic matter is ubiquitous in riverine systems and is critical for many biogeochemical processes; therefore, information about the source and changes to OM that occur with different land uses can indicate how changes to land use affect these processes (Findlay and Sinsabaugh, 2003). Information about source and quality of OM is evaluated in this study during base flow and storm flow events in the Neuse River Basin, NC through the use of optical measurements (absorbance, fluorescence) and biomarker analyses (stable carbon isotopes, lignin). The emphasis of this study is upon terrestrially derived OM, specifically plant material, as an indicator of the source and degradation of terrestrial DOM to investigate changes in quality and quantity of OM from runoff in urban catchments.

Urbanization can alter the lability and amount of OM being transported in runoff, which can have impacts on water quality and ecosystem health (Imberger et al. 2013). Small urban catchments are the focus of this study because they can be used to look at urban influences that affect the transport and quality of natural as well as anthropogenic OM from point and non-point sources. The urban landscape dramatically changes natural stream networks via channelization of streams (ostensibly to act as storm water runoff conveyances), removal of vegetative biomass, and the creation of impervious surfaces (roads, buildings,
etc. Impervious surfaces inhibit infiltration into the shallow groundwater and can also transport both natural OM and anthropogenic OM (e.g., oils, sewage, leaf litter, yard waste, and other potentially harmful pollutants) with negative impacts on stream water quality (Brabec et al. 2002).

One aspect of natural and anthropogenic OM is the formation of harmful disinfection byproducts (DBPs) during drinking water treatment. The chlorination and ozonation treatment processes cause humic substances to react and form potentially harmful halogenated organic compounds including trichloromethane and haloacetic acids (Reckhow et al. 1990; Leenheer and Croué, 2003). DBPs are regulated by the US Environmental Protection Agency (EPA). The main OM contributors to DBPs are thought to be aromatic carbon compounds such as lignin and highly aromatic natural organic matter such as humic and fulvic acids. Further, it is presently unknown whether or not DBP formation potential increases with storm events as a function of mobilizing more aromatic C. Thus, knowledge of the OM quality, specific to aromatic C, can provide information to allow treatment plants to better prepare for a potential increase in DBP-formation potential during storm events. The EPA sets limits on the concentration of both trihalomethane and haloacetic-acid compounds (Safe Drinking Water Act, 1974). Weishaar, et al. (2003) found that several organic compound groups react during the disinfection process to form DBPs, including phenolic compounds such as lignin. In 2008, Kraus et al. found that there is a relationship between trihalomethane formation and terrestrial organic matter. By investigating the source of DOM during storm events across a gradient of urban land uses, the effects of dilution on the pool of
natural organic matter can provide insights into how urban activities affect OM source and quality.

The Neuse River basin has undergone rapid urbanization in the past decade, particularly in the so-called Triangle area (including Raleigh, Durham, and Chapel Hill) with a 46% population increase between 2000 and 2010 (US Census Bureau). The Neuse River flows into the Neuse River estuary (NRE), a system that has experienced increasing eutrophication as urbanization and agriculture expand and intensify throughout the river basin (Pearl et al. 2004). Understanding the fluxes of OM to the river is therefore important for assessing the potential to limit DBP precursors because the river basin also serves as a drinking water supply source for several communities through either surface water intake or groundwater extraction wells along with being a source of fishing and recreation in central and eastern North Carolina.

**Geochemical techniques for studying organic matter**

Bulk geochemical analyses used in this study include dissolved organic carbon (DOC) and carbon stable isotope (δ¹³C-DOC) analyses. Previous studies have correlated stream discharge to DOC concentration during storm flow events (McDowell and Likens, 1988; Buffam et al. 2001; Ward et al. 2012), particularly for forested watersheds. Carbon stable isotope analyses of bulk samples can be used to identify shifts in sources of DOC, particularly between major plant metabolic pathways (i.e. C₃ versus C₄ plants) and autochthonous versus allochthonous inputs. C₃ plants have more depleted isotope values (δ¹³C -26 to -30‰) compared to C₄ plants (δ¹³C -8 to -18‰) due to the differing efficiencies
in CO₂ fixation of the two plant groups. C₄ plants are dominated by grasses and include other monocot angiosperms such as corn (Bianchi and Canuel, 2011). Autochthonous inputs of carbon from bacteria and phytoplankton have been found to be more isotopically enriched in δ¹³C than allochthonous sources of organic carbon (Peterson et al. 1994; Bianchi and Canuel, 2011).

Optical measurements of DOM, including absorption and fluorescence spectroscopy are used to characterize the sources and quality of DOM. Chromophoric DOM (CDOM) is the light absorbing portion of DOM and its measurement can provide a non-destructive way to obtain both qualitative and quantitative information about DOM. CDOM is measured as a smooth curve that increases exponentially at lower wavelengths and can be described by the spectral slope (S). Spectral slope is used to distinguish between different sources of OM. Shallower spectral slopes are associated with more terrestrial OM and higher molecular weight, with steeper slopes indicating lower molecular weights (Helms, 2008). Absorption at wavelengths between 254 and 350 nm are frequently used when relating optical measurements to biomarker information (Spencer, et al. 2008; Osburn and Stedmon, 2011; Fichot and Benner, 2012). Relating optical measurements to biomarker information presents an opportunity to gain greater amounts of CDOM observations at larger spatial and temporal scales by providing a rapid, non-destructive sample analysis available in the laboratory, or as in-situ and-or as remotely sensed observations (Coble, 2007).

Along with absorbance spectroscopy, fluorescence spectroscopy is a commonly applied optical measurement that provides information about DOM type and origin (Mopper and
Schultz, 1993; Coble, 1996, 2007). Fluorescence is measured as a 3-dimensional excitation-emission matrix (EEM), and EEM fluorescence can be described as the fluorescence intensities at certain peaks, or by decomposing the data into excitation and emission loadings which can be visualized as EEMs using Parallel factor analysis (PARAFAC) (Stedmon and Bro, 2008; Coble, 2007).

Several relationships between optical measurements and biogeochemical information are frequently utilized in research and water quality monitoring. The specific ultraviolet (UV) absorption (SUVA) at 254 nm is proposed as a proxy for DOM aromaticity (Weishaar et al. 2003), and is currently used as a proxy for DBP formation during drinking water treatment. Several studies have found a correlation between optical measurements and lignin concentration using absorbance at 300 nm or 350 nm, or EEM components from PARAFAC models and lignin concentration (Hernes and Benner, 2003; Spencer et al. 2009; Osburn and Stedmon, 2011).

Lignin as a tracer of terrestrial DOM

Lignin is a complex macromolecule that is a major component of the cell walls of vascular plants, and constitutes a major portion of terrestrial organic matter (Hedges and Mann, 1979). Lignin is a distinct tracer of terrestrially derived OM, and due to its complex structure, geochemical information about plant material source and degradation can be derived from lignin analysis of DOM. Lignin phenols are measured from eight lignin oxidation products subdivided into 3 biochemical groups, vanillyl, syringyl, and cinnamyl phenols. Using the three groups of phenols, information about OM source can be evaluated
(Hedges and Ertel, 1982) with syringyl phenols being unique to angiosperm plant tissues, and cinnamyl phenols being unique to non-woody plant tissues. The vanillyl and syringyl groups are further divided into their functional groups, acids, aldehydes, and ketones; with increased degradation the aldehyde phenols are preferentially degraded compared to the acid or ketone phenols (Hedges et al. 1988). The carbon normalized lignin phenol yields gives insights into the amount of lignin contribution to the organic carbon pool; lignin contribution has previously been found to be a small fraction of the total DOM (Spencer et al. 2008; Osburn and Stedmon, 2011). Several studies have investigated the relationship between discharge, DOC, and lignin phenol concentrations at landscape scales within watersheds (Dalzell et al. 2005; Kraus et al. 2008; Hernes et al. 2008).

The combined use of these bulk optical and chemical measurements, and lignin biomarkers on samples collected at base flow and at storm flow during this study will provide multiple measurements of DOM source and quality in urban streams under variable hydrologic conditions. In addition to understanding how urbanization influences the concentration and quality of OM, the use of optical measurements as proxies for biogeochemical data will be investigated. This study aims to address (1) whether there are significant differences in DOM quality and sources during base flow and storm flow, (2) what effect land use has on DOM contribution to the Neuse River basin during storm events, and (3) whether there are any relationships between the optical properties and lignin content at both base flow and storm flow.
METHODS

Sample site description

The Neuse River basin is located in central North Carolina, beginning northwest of Durham, NC and becomes the Neuse River estuary (NRE) at New Bern, NC (Fig. 1). The Neuse River basin is dominated by several different land uses, including agriculture, urban, and forested land (Table 1). The river basin area is approximately 16,000 km² and includes two major cities near the sampling locations of this study, Raleigh and Durham, NC. In addition to sampling the Neuse River at Clayton, NC (35.6473°N, 78.4057°W), two additional locations were selected on tributaries to the Neuse River, Crabtree Creek (35.8211°N, 78.6341°W) and Walnut Creek (35.7493°N, 78.5345°W), both located within or near the Raleigh, NC metropolitan region (Fig. 2). The Crabtree Creek drainage basin includes a large recreational park and flows through several suburban neighborhoods before entering Raleigh. Walnut Creek originates in southwest Raleigh and flows past downtown before joining the Neuse River. Pigeon House Branch (35.7879°N, 78.6552°W), which flows through of urban Raleigh, was sampled only twice during the summer at storm flow. These samples were used as an urban end-member stream (97% urban land use). An additional sample from an unnamed stream in William B. Umstead State Park (35.8388°N, 78.7281°W) was added as a non-urban end-member, because Umstead Park is a recreational park in Raleigh that has very low urban impact (3% urban land use). Drainage areas at each of the sample locations were delineated using the Hydrology toolbox in ArcMap (v. 10.1) from the National Hydrography Dataset flow accumulation and direction rasters (30 m resolution).
Land use upstream of the sampling locations was determined using the delineated watershed and the National Land Cover Dataset raster for the Neuse River basin (NLCD, 2006). Land use categories were simplified into urban (including high, medium, and low intensities), forested (including deciduous, evergreen, and mixed forests), agricultural (including all croplands), water (includes all bodies of water, i.e. reservoirs, streams, rivers, and ponds), wetlands (herbaceous and woody), and other categories (herbaceous, barren, and unclassified), and percentage of land use for each catchment was calculated for each new category (Fig. 3).

Sample collection and preparation

During summer 2014 (May-September) surface water samples were collected from three locations in the Neuse River basin at base flow and storm flow, three additional sites were sampled infrequently for additional data. Sites were chosen based on the amount of urban activity surrounding them, ease of access, and proximity to a USGS gaging station (Fig. 1). The three sites were sampled 11 times total during base flow and storm flow conditions between May and September 2014. Base flow samples were collected when there had been negligible (less than 25 mm) of rain over a several day period. Storm flow samples were collected within 24 hours of a storm event; a storm event was defined as when there was over 0.25 in of rain in a 24-hour period and discharge exceeded the mean monthly discharge for the stream by about 20%. Within 24 hours of sample collection, sample water was filtered using a 0.22 µm pore size polyethersulfone filter (Millipore Sterivex or Whitman Polycap 36 TC) and stored at 4°C. Unused filters were flushed with ~500 mL acidified DI
water prior to introducing samples. Some filters were reused, and that case they were rinsed after each use by rinsing with 1 L of acidified DI water.

**Optical Analyses**

Absorbance of filtered samples was measured between 200 and 800 nm using a 1 cm quartz cuvette on a Cary 300 Bio UV-Visible spectrophotometer. Blank corrections were made by subtracting the absorbance of Milli-Q water from sample absorbance. Blank corrected absorbance measurements were converted to Napierian absorption coefficients using the following equation:

\[ a = 2.303A/l \quad (1) \]

where \( a \)=absorption coefficient \((m^{-1})\), \( A \)= absorbance, and \( l \)= pathlength \((m)\). CDOM absorption was quantified at 254 nm; the spectral slope ratio \((S_R)\) was calculated using the ratio of the spectral slope at 275 to 295 nm to the spectral slope at 350 to 400 nm (Helms et al. 2008).

Fluorescence emission spectra were measured on a Varian Eclipse spectrofluorometer using a 1 cm quartz cuvette, an excitation wavelength range between 225 to 500 nm at 5 nm increments, and an emission range of 300 and 600 nm at 2 nm increments. Excitation-emission matrices (EEMs) were generated by concatenating the 43 emission spectra recorded for each sample. Fluorescence EEMs were corrected for scattering by subtraction of a Milli-Q blank and instrument bias (Stedmon and Bro, 2008), fluorescence measurements were converted to quinine sulfate equivalents \((\text{ppb QSE})\) (Laewetz and Stedmond, 2009).

A parallel factor analysis (PARAFAC) model of the corrected EEM fluorescence data
for 36 sample EEMs was generated in Matlab (Mathworks Inc.) using the DOMFluor toolbox (Stedmon and Bro, 2008). PARAFAC decomposes multi-way data into excitation and emission loadings which can be related to chemical composition of fluorescent DOM. The number of PARAFAC components was validated using split half validation and random initialization to insure that the results corresponded to the least squares results rather than a local minimum within the dataset. Split half validation splits the data into two sets and generates model components for each half, the modeled components are considered robust when the two models are identical. Random initialization fits the model to random initial estimates. The fit of each model is compared to validate that the model is not caused by a local minimum. Outliers and an incorrect number of components can cause the validations to fail; removal of outliers or changing the number of components can improve model fit in this case. Two outliers were excluded from the PARAFAC model, one at Pigeon House Creek and the sample from Umstead Park Stream. These two samples had unique spectra, which was not surprising due both samples being end-members. Results were compared to the OpenFluor database and matched to spectra having a Tucker congruence exceeding 0.95 for excitation and emission of PARAFAC components.

Dissolved organic carbon (DOC) and carbon stable isotopes

DOC and carbon stable isotopes were measured for filtered samples using TOC wet chemical oxidation (OI 1010 TOC analyzer) coupled with an isotope ratio mass spectrometer (Thermo Delta V) (Osburn and St-Jean, 2007). Filtered samples were stored in 40 mL glass vials (pre-combusted at 500°C for at least 6 hours), acidified to pH 2 with 85% H₃PO₄ (Fisher
Scientific, certified ACS), and capped with teflon-lined septa. Samples were stored in the dark at 4°C prior to analysis. Samples were blank corrected using Millipore Milli-Q water and DOC concentration were calculated using a linear standard curve of caffeine standards of known concentration between 2 to 40 mg L$^{-1}$. $\delta^{13}$C values were calculated using the linear regression of $\delta^{13}$C values of sucrose and caffeine standards with known $\delta^{13}$C values in international units vpdb.

$Lignin Analysis$

Lignin phenols oxidation products were used as a marker for terrestrial plant material. 1 L of 0.2 µm filtrate was acidified to pH 2 using 85% H$_3$PO$_4$, approximately 2% volume or 20 mL of methanol (HPLC grade) was added to the sample to improve extraction efficiency (Spencer et al. 2010). Samples were extracted onto C$_{18}$ resin (10 g, unbonded, Thermo HyperSep C$_{18}$ and Agilent BondElut C$_{18}$) following Louchouarn et al (2000) and eluted using 40 mL HPLC grade methanol into combusted glass vials and dried in a Zymark Turbovap using 10-12 psi N$_2$(Airgas PP300) at 60°C. Dried samples were redissolved in 3.5 mL 2N NaOH and transferred to 7 mL Teflon reaction vessels containing 500 mg cupric oxide, 50 mg ferrous ammonium sulfate, and 15 mg glucose for microwave assisted hydrolysis. Ferrous ammonium sulfate was added to remove excess oxygen from the reaction and glucose prevents over-oxidation of low carbon samples. The reaction vessels were sparged for 15 minutes with N$_2$ to remove oxygen, capped, and microwaved at 150°C for 90 minutes (Louchouarn et al. 2001). A blank was included in all microwave reactions containing 2N NaOH, cupric oxide, ferrous ammonium sulfate, and glucose. Lignin concentrations in all
blanks were below instrument detection limits. Following oxidation, samples were acidified to pH 1 and trans-cinnamic acid was added as a recovery and internal standard. Acidified samples were extracted in ethyl acetate (ACS grade), dried with sodium sulfate (ACS grade), and dried in a Zymark TurboVap using the same settings as the C18 extracts. Dried extracts were redissolved in 400 µL pyridine (HPLC grade). A 50 µL aliquot of the dissolved sample was derivatized with 100 µL BSTFA at 60°C for 10 min prior to GC-MS analysis. A Varian 431-GC (VF5-MS column, 30 m x 0.25 mm i.d., Varian) and MS-210 in MS/MS mode were used for quantification following Louchouarn et al. (2010). A five point calibration curve and internal standard was used to quantify lignin oxidation products. Standards contained vanillin (VAL), vanillic acid (VAD), acetovanillone (VON), syringaldehyde (SAL), syringic acid (SAD), acetylsyringone (SON), p-coumaric acid (CAD), and ferulic acid (FAD) at known concentrations. T-cinnamic acid was used as a recovery and internal standard because it is not found in plant material so should not be present in any samples.

Lignin phenol concentration (Σ8) was quantified using the sum of the eight phenols (VAL, VAD, VON, SAL, SAD, SON, CAD, and FAD). Σ8 was normalized to DOC concentration to calculate lignin yields for each sample. C:V and S:V ratios were computed as ratios of the sum of the groups of phenols; cinnamyl phenols (CAD and FAD), vanillyl phenols (VAL, VAD, and VON), and syringyl phenols (SAL, SAD, and SON) and were used as indicators of vascular plant type. The acid:aldehyde ratio is used as an indicator of degradation, however due to peroxide contamination of the ethyl acetate used during the liquid-liquid extraction the values are not accurate. This contamination did not affect the
remaining lignin quantifications (Appendix 2).

Statistical Analysis

All statistical analyses were performed using Excel 2011 and Matlab v.R2013a (Mathworks Inc.) at a 95% confidence interval unless otherwise noted. One-way analysis of variance (ANOVA) was used to examine effects of discharge on chemical variables.

RESULTS

Dissolved organic carbon and carbon stable isotope ratios

During the sample period there were several large storms in the Neuse River Basin, and discharge ranged between base flow and flood stage at the three sites. The largest storm occurred on 16 July 2014 when it rained 51.8 mm in a 24 hour period, prior to the first sample collection, 108 mm of rain fell in the Raleigh area causing flooding at the Neuse River near Clayton, NC and increased discharge that persisted through the first sample collection. The storm hydrograph at Walnut Creek and Crabtree Creek responded rapidly to rain events and returned to base flow more quickly than the Neuse River (Fig. 5). Flood conditions were observed at all sites during the sampling period following large storm events, particularly at Walnut Creek where wetland flooding was observed several times. Discharge and stage data are presented for each sample from the Neuse River in Table 2, all other data are in Appendix 1; stage was used in place of discharge at Crabtree Creek at Anderson Road due to the lack of USGS discharge data collected at that site. Data were analyzed at Crabtree Creek by using either the stream stage or the discharge at a station downstream that had a
strong correlation with stage measured at the sample site ($r^2=0.95$).

DOC concentrations ranged from 1.42 mg L$^{-1}$ to 48.6 mg L$^{-1}$ (median 6.05 mg L$^{-1}$) for all sample sites during the study period. At the three main sites of the study – Neuse River (NR), Walnut Creek (WC), and Crabtree Creek (CC) – DOC concentrations ranged from 3.59 mg L$^{-1}$ to 8.31 mg L$^{-1}$ (median 6.07 mg L$^{-1}$) (Fig. 4). The highest and lowest DOC concentrations were observed at Pigeon House Creek (PHC) and the William B. Umstead State Park stream (UPS), respectively. A positive relationship between discharge and DOC was observed at the Neuse River ($r^2=0.75$, p <0.05) and Walnut Creek ($r^2=0.34$, p >0.05), however at CC a weakly negative correlation between DOC concentration and discharge was observed ($r^2=0.16$, p<0.05) (Table 3).

Carbon stable isotope values of DOM ($\delta^{13}$C-DOM) are used to distinguish between autochthonous and allochthonous sources of OM and the photosynthetic pathways of plant sources ($C_3$ versus $C_4$) (Peterson and Fry, 1987). The $\delta^{13}$C values for all sample locations varied between -22.88‰ to -28.02‰, with a median value of -26.06‰, which is typical of terrestrial, $C_3$ plant sources. The median $\delta^{13}$C-DOM at the NR, WC, and CC were all very similar and within similar ranges of values (Fig. 6). The Neuse River and Walnut Creek both had outliers at very high discharge events indicating a possible shift in OM source during large storm events. At PHC the $\delta^{13}$C-DOM values were more enriched compared to what was observed at the main stations suggesting that there is more contribution from $C_4$ plants at the urban end-member. UPS was close to the average for all samples collected at base flow (-26.02‰).
Absorbance and fluorescence of DOM

CDOM absorption at 254 nm had a weak positive relationship with discharge at the NR and WC; however, at CC there was a negative correlation (Table 3). There was a weak correlation between spectral slope (S) and discharge across all three sample locations ($r^2=0.28$, $p < 0.05$, n=37); this relationship is prominent in CC where there is positive correlation between stage and S ($r^2=0.68$, $p < 0.05$, n=11). Specific UV absorbance (SUVA$_{254}$) is used as a proxy for DOC aromaticity (Weishaar et al. 2003) and was calculated by dividing the decadal absorbance at 254 nm by the DOC concentration. SUVA$_{254}$ values ranged between 0.84 to 4.5 L mg C$^{-1}$ m$^{-1}$ with the lowest value at PHC during a large discharge event.

A three-component PARAFAC model was fit to the data, the components correspond to terrestrially derived DOM (Table 5). Component EEMs and excitation and emission loadings are shown in figure 7. The OpenFluor database is a compilation of previously published fluorescent components generated by PARAFAC models fit to a variety of natural and anthropogenic aquatic ecosystems. The excitation and emission spectra for each of the components were matched to 18 datasets in the OpenFluor database at a minimum similarity score of 0.95 using Tucker’s Congruency Coefficient (Stedmon and Bro, 2008) from 9 publications. Components 1 and 2 were matched with OpenFluor spectra, however C3 did not return any spectral matches. C1 was most closely matched terrestrial OM from two water treatment locations (Murphy et al. 2011; Shutova et al. 2014) and a component from the Baltic Sea suggested to be the product of photodegradation (Stedmon et al. 2007).
Component 2 was matched with terrestrially derived humic OM from streams, a lake, and an estuary DOM in Denmark (Søndergaard et al. 2003) and a Neuse River Estuary component corresponding to possible degradation that was novel to the study (Osburn et al. 2012). Three results from OpenFluor matched C1 and C2, the two water treatment studies (Murphy et al. 2011; Shutova et al. 2014) and humic substances from streams, a lake, and an estuary in Denmark (Søndergaard et al. 2003). Component 3 did not match spectra in the OpenFluor dataset with a similarity score greater than 0.95. The maximum excitation and emission wavelengths of C3 were similar to the maxima wavelengths from component 3 in Osburn et al. (2012) related to photolabile terrestrial humic acid from agriculturally influenced streams and estuaries. However, there are greater peak intensities and the peak excitation maxima are at higher wavelengths. C3 also contributed the lowest amount to the total DOM fluorescence (F$_{\text{max}}$ range 12.4-20.1%) with the minimum and maximum occurring at NR during storm flow and base flow, respectively. During storm events there was significantly less C3 contribution during storm events.

**Lignin phenol concentrations and ratios**

The sum of the eight lignin phenol concentrations (vanillyls, syringyls, and cinnamyls, Σ8) ranged from 11.57 µg L$^{-1}$ to 63.07 µg L$^{-1}$, with the maximum observed value at Pigeon House Creek (63.07 µg L$^{-1}$). The largest variability in lignin concentration was observed at Walnut Creek where values ranged from 12.32 to 62.66 µg L$^{-1}$ (Fig. 8). There was a positive trend in Σ8 and discharge with the strongest correlation observed at the Neuse River ($R^2=0.64$) (Table 3). There was no observed relationship between discharge and Σ8 at
Crabtree Creek and a weak correlation at Walnut Creek ($R^2=0.46$). Walnut Creek had two distinct data trends in lignin concentrations at high discharge events (Fig. 8). The carbon normalized lignin phenol yields ($\Lambda_8$, mg (100 mg OC)$^{-1}$) calculated for Walnut Creek showed a similar pattern at the highest discharge events (Fig. 9). The $\Sigma_8$ at NR, WC, and CC and $\Lambda_8$ at NR and WC were significantly different ($\Sigma_8 p < 0.01$; $\Lambda_8 p < 0.05$) at storm flow versus base flow, similar to the relationship seen in DOC concentration.

As a terrestrial plant biomarker, lignin phenol ratios can provide source information; therefore the ratios of cinnamyl to vanillyl (C/V) and syringyl to vanillyl (S/V) were evaluated against discharge. Vanillyl phenols are ubiquitous in all terrestrial plants while syringyl phenols are only present in angiosperms and cinnamyl phenols are indicative of non-woody plant tissues. Using the ratio of the phenols the sources and changes in plant material source can be identified. At all sample sites non-woody angiosperm plant tissue was present (Fig. 10). Both ratios changed very little with discharge, particularly at WC and CC where there was almost no variation in S/V ratios with discharge. Similarly, NR had higher variability in S/V and C/V ratios that was not related to discharge. High C/V values, within the range of non-woody angiosperm tissue, observed at all sample locations indicate that there is a relative importance of grasses and leaves to the DOM in these samples. The highest non-woody angiosperm tissue proportion was observed at UPS during base flow; however only one sample was collected from this site so source information over a range of discharge events is not available. The increase in lignin concentration at WC with discharge does not correspond to a change in S/V or C/V ratios indicating that the source of the lignin stays the
same while concentration increases. The use of the lignin phenol vegetative index further
corroborates the observation at WC that source does not change significantly with increasing
discharge.

The lignin phenol vegetation index (LPVI) is a numerical approximation of plant
source (Tareq et al. 2004), the use of the LPVI can differentiate between the plant tissue
sources that might not be obvious in the traditional C/V: S/V biplot.

\[ LPVI = \left[ \frac{S(S+1)}{(S+1)(V+1)} \times \frac{C(C+1)}{(C+1)(V+1)} \right] \]  

where LPVI is calculated using percent syringlys (S), vanillyls (V), and cinnamyls (C) of the
total carbon-noramlized lignin yield ($\Lambda_8$). The ranges of values separate gynmosperm and
angiosperm plant tissue because gymnosperms woods do not produce either S or C phenols
(LPVI=1) while angiosperm woods produce S phenols (LPVI 67 to 415). Non-woody tissue
contains C phenols, which allows separation between non-woody angiosperm (LPVI 378-
2782) and gymnosperm tissues (LPVI 12 to 27) (Table 4).

The results of applying the LPVI indicate that lignin sources are both woody and non-
woody angiosperms. Dissolved lignin in CC had the most source variation (Table 4) with
five samples falling within the range of woody angiosperm tissue, while the other two main
sites (NR, WC) had values characteristic of non-woody angiosperm tissues.

Acid/aldehyde ratios of vanillyl and syringyl phenols are indicators of degradation of
lignin phenols (Hedges et al. 1988). The (Ad:Al), ratios observed during this study are higher
than most previously published data, and the source of high ratios was attributed to peroxide
contamination of ethyl acetate during the liquid-liquid extraction process. A Baeyer-Villager
type oxidation of aldehydes (i.e. vanillin) to carboxylic acids (i.e. vanillic acid) occurred, oxidizing most vanillin and syringaldehyde to their corresponding carboxylic acid LOPs (reaction described in Appendix 2). Due to this reaction the ratios are not comparable to other studies and cannot be used to assess degradation, however stoichiometric relationships allow the quantification of C/V and S/V ratios as well as total lignin phenols. The presence of the oxidation reaction in the ethyl acetate extraction was further tested by insuring there was no significant difference between the microwave and oven oxidation methods (Appendix 2). If there were superoxidation occurring during the cupric oxide oxidation step it would be associated with low carbon samples (OC < 2 mg; Louchouarn, 2000).

**Relationship between lignin and optical properties**

Several lignin parameters were significantly correlated to CDOM optical measurements (Table 6); all sites were analyzed together for optical relationships. Σ8 was most correlated with \( a_{254} \) \((r^2=0.46, p < 0.05)\); the carbon normalized lignin concentration was also weakly positively correlated to \( SUVA_{254} \) \((r^2=0.17, p < 0.05)\). There was a weak relationship between the three lignin source parameters, S:V, C:V, and LPVI, and \( SUVA_{254} \). NR was also significantly correlated with \( S_R \) \((r^2=0.37, p < 0.05)\), however this relationship was not present at the tributary sites, WC and CC.

The fluorescence data percent contribution to fluorescence maxima were compared to lignin parameters. Component 3 was unidentified by OpenFluor, but was significantly correlated to carbon-normalized lignin yield at NR and WC. The relationship was positive at NR and a negative correlation at WC, this could be due to different stream sizes and land
uses at the two sites. CC did not have a significant relationship between \( \%C3 \) and \( \Lambda_8 \). This suggests that C3 could be modeling a terrestrial DOM source that relates to lignin contribution that could be dependent on land use and DOM source. The other lignin parameters were not significantly correlated to model components.

To better understand the relationship between lignin and fluorescence data, a larger sample size with additional PARAFAC components is needed. NR is the main river whereas the other sample sites were at lower order tributaries; stream order could influence the ability to relate lignin and optical properties at the lower order streams. Previously, most optical proxy studies have been conducted on large fluvial systems or in estuaries (Hernes et al. 2003; Spencer et al. 2009; Osburn and Stedmon, 2011).

**DOM trends with discharge**

The DOC, SUVA\(_{254} \), and lignin phenol data were grouped by percentage of monthly mean discharge. The samples collected below the median percentage of discharge (108% average stage- base flow) were compared with the samples collected above 125% of the average discharge (storm flow). Data was analyzed using ANOVA; UPS and PHC were excluded from the analysis due to being outliers. DOC concentrations of samples collected at base flow and storm flow were compared and were not significantly different (\( p < 0.05 \)). \( \Sigma_8 \) increased significantly during storm events while \( \Lambda_8 \) did not differ significantly indicating that during storm events there was an increase in lignin but not a significant corresponding increase in carbon-normalized lignin yields. However, there was a significant decrease in SUVA\(_{254} \) during storm events, suggesting a decrease in aromaticity of DOM during high
discharge events. The time interval for discharge between storm events was significantly correlated to a decrease in SUVA_{254} at CC.

The time interval between storm events also was evaluated using daily precipitation data from the National Weather Service at the Raleigh-Durham International Airport. Precipitation can vary widely throughout the NRB causing some variability in the actual precipitation falling at sites several miles from the airport. The time between storms was defined using the same criteria outlined for defining storm events (discharge greater than 120% of the mean discharge, and generally greater than 25 mm of rain in a 24-hour period). NR and WC did not have a significant relationship between time interval between storm events and DOM aromaticity.

DISCUSSION

DOC and lignin phenol content

The increase in DOC concentrations with increased discharge at two of the main sites, NR and WC, provides evidence that there was a flux of terrestrial OM into the systems during rain events. This trend of increased DOC concentration with discharge has previously been reported (McDowell and Likens, 1988; Buffam et al. 2001; Ward et al. 2012) including in urban watersheds (Hook and Yeakley, 2005). At base flow, the concentrations at these two sites of DOC, Σ_8, and Λ_8 were significantly lower than the values at storm flow suggesting a large portion of organic matter is mobilized during storm events (Table 3). The two samples collected from PHC collected during storm events but were not included in the statistical analyses of storm flow and base flow because no base flow samples were available.
However, the PHC samples were collected at different locations on the stream hydrograph; the sample collected at the peak discharge contained over 10 times the amount of DOC compared to the sample collected during the falling limb of the hydrograph. This suggests that at the peak of discharge there is also a peak in DOM being transported within the small urban stream.

When including carbon-normalized lignin yields in the analysis of storm flow samples at PHC there was a notable decrease in $\Lambda_8$ during the high discharge event ($\Lambda_8=0.12$), while the sample collected at the falling limb of the hydrograph has a $\Lambda_8$ value ($\Lambda_8=0.53$) only slightly higher than the mean of the sample set ($\Lambda_8=0.46$). This relationship was not examined in the other systems because all samples at the three main sites were collected during the falling limb of the hydrograph, however the storm flow samples did not have significant differences in DOC, $\Sigma_8$, and $\Lambda_8$ between samples collected above and below 180% of the average discharge. More samples at storm flow are likely needed to determine if there is a peak location on the stream hydrograph where the most DOM is being mobilized (Moatar et al. 2013). For example, at CC, a slight negative correlation was found between DOC concentration and discharge suggesting that a decrease of DOM being transported during storm events in the CC watershed (Table 3).

Several factors could be controlling the transport of DOM during storm events, including runoff from impervious surfaces and vertical infiltration into the soil mobilizing organic matter into the streams. Sickman et al. (2007) suggest that impervious surfaces could allow more organic material to accumulate on the surfaces between storm events before
being flushed in to the streams. Trends in DOC concentrations observed at NR and WC support their finding of increased mobilization of DOC during storm events. The slight negative relationship between discharge and DOC concentration at CC, however, does not support this claim and suggests that there is a limited mobilization of DOM during storm events whereas the other two main sites had additions of DOM with increased discharge. A decrease in DOM could be due to the extensive paved surfaces, intense urban development, and lack of wetlands in the Crabtree Creek catchment or a dilution effect where DOC does increase but not to the extent that discharge does. Wetlands at NR and WC could be contributing large amounts of DOM during storm events because the water table is close to the surface and during storm events could be mobilizing more DOM from both the organic rich wetlands and the shallow groundwater.

Lignin represented a small fraction of DOC, similar to values reported in previous studies of DOM in several systems including the San Joaquin-Sacramento River Delta (Hernes et al. 2008; Kraus et al. 2008) and at the Congo River (Spencer et al. 2009). The carbon-normalized lignin yield ($\Lambda_8$) is a measure of the relative contribution of vascular plant material to the total amount of DOM. Only small changes in $\Lambda_8$ were observed in relation to discharge except at Walnut Creek, where there were high $\Lambda_8$ values during the three highest discharge events. At high discharge, however, there was significantly more relative lignin contribution than at base flow. These differences in lignin contribution could be due to several influences including wetland flooding observed during sampling dates following large rain events. Wetlands account for approximately 3% of the land area in the Walnut
Creek watershed, while the highest proportion of impervious surfaces at the three sample sites occurs within the Walnut Creek catchment. The concentrations of the sum of the eight lignin phenols ($\Sigma_8$) and carbon-normalized lignin yields ($\Lambda_8$) were similar to previously reported averages in other river systems, including the Yukon River (Spencer et al. 2008), the Mississippi River (Hernes and Benner, 2003), and wetlands of the Sacramento-San Joaquin River Delta (Eckard et al. 2007). At PHC, where land use is 98% urban, $\Lambda_8$ was very low at peak discharge ($\Lambda_8=0.13 \text{ mg}(100 \text{ mg OC})^{-1}$) indicating that vascular plant inputs are less important relative to other sources of DOM. Similarly, the SUVA$_{254}$ (0.84 L mg$^{-1}$ m$^{-1}$) value for this sample indicates that there is less aromaticity of DOM compared to the average for all sample sites.

**Lignin source description**

Lignin source information was evaluated in this study to determine whether there were shifts in DOM source during storm events compared to base flow. C:V and S:V ratios and LPVI provide qualitative and quantitative means to understand source changes in lignin. Most samples in this study were found to be within the range of non-woody angiosperms (Fig. 8) while a few select sites were also in the range of woody angiosperms when applying the LPVI (Table 4). Hernes et al. (2008) also found that there was little change to the C:V and S:V ratios with flow within the Willow Slough watershed which was also dominated by non-woody angiosperms. The biplot of C:V and S:V ratios shows that there is a trend in the lignin source at NR, but this trend is not related to changes in discharge. Variations not related to discharge or tributary type have been previously reported by Spencer et al. (2008)
in the Yukon River Basin. The highest C:V and S:V ratios and LPVI values were observed at UPS (1.17, 1.40, 2173 respectively), yet this stream also has the least variation in land use (98% non-urban land use) being nearly entirely forested. At PHC during peak discharge, high values of C:V, S:V, and LPVI also were measured (1.01, 1.37, 1738 respectively). By contrast to UPS, land cover in PHC is 98% developed (i.e., urban) and 2% forested, and much of the water is transported storm water conveyances built by the City of Raleigh. Extensive coverage of urban lawns, including trees and grasses, in this stream’s catchment, and its largely urban land cover, could explain these higher values.

**Stable carbon isotopes and land use**

Carbon isotopes of dissolved organic matter (δ¹³C-DOM) were within the range of C₃ plants at NR, WC, and CC (median -26.07‰) (Fig. 6), which is expected due to the prevalence of the C₃ vegetation in the study area. PHC had more isotopically enriched δ¹³C-DOM values (median -23.85‰) indicating that the source of DOM in the urban end-member catchment is more dominated by C₄ plants (i.e. grasses and corn). PHC is mainly used as a storm water conveyance stream and is highly urbanized; this high level of urbanization might have a larger influence on stable isotope values from sewage that is typically more enriched in δ¹³C (Peterson and Fry, 1987). There was very little variation in the median δ¹³C-DOM values measured at NR, WC, and CC; this could be due to similar land cover in all catchments. NR contains more agricultural land use than the other catchments in this study, and the dominant crops are hay/pasture, tobacco, and corn, it was expected that the presence of corn would increase the δ¹³C-DOM values because corn plants utilize the C₄
photosynthetic pathway which generally leads to more enriched $\delta^{13}C$ values, but this was not observed in the NR catchment.

**CDOM in urban catchments**

CDOM measurements can provide useful information about source and aromaticity of DOM (Weishaar et al. 2003). The aromaticity can be evaluated as it relates to DBP formation. Though DBPs were not measured in this study, relationships formed in previous studies between CDOM, lignin, and DBPs were used to evaluate whether storm events are mobilizing material that is potentially more problematic for drinking water treatment (Kraus et al. 2008; Weishaar et al. 2003; Hua et al. 2014). In CC there is a strong relationship between spectral slope (S) and stage ($R^2=0.68, p < 0.01, n=11$) indicating that with increased discharge lower molecular weight DOM is mobilized. Low molecular weight DOM is typically present in autochthonous DOM suggesting that there is mobilization of bacterially derived DOM during storm events (Helms et al. 2008). This relationship could also be caused by leaky sewer systems delivering sewage to the creek during storm events, which would be enriched in bacterially derived DOM (Hosen et al. 2014). Another possibility is leaching from solid waste falling into the stream, which has been shown to promote microbial degradation and production of DOM in groundwater (Lu et al. 2009; He et al. 2011; He et al. 2014). NR is the only site that has a landfill within the watershed so this process is not likely to significantly impact the other sample sites; leachates are produced slowly and would be relatively older DOM when entering the groundwater. There was a weak relationship between S and discharge at NR as well, indicating that there might be an addition of lower
molecular weight DOM during storm events similar to CC.

There are some caveats involved in using S over the entire wavelength range (Helms et al. 2008) including the lack of standardization and the effects of dilution, among others. Additionally, Helms et al. (2008) found that the use of S over narrow wavelength ranges (275-295 nm and 350-400 nm, respectively) better represents changes in spectral slope for understanding source and transformations of DOM. Using $S_{275-295}$ and $S_{350-400}$ indicates that the relationship of lower molecular weights measured at CC were also observed over narrow wavelength regions. At NR there was not a significant relationship between $S_{275-295}$ and discharge, but there was a significant increase in $S_{350-400}$ with increased discharge ($r^2=0.46$, $p < 0.05$, $n=11$). At WC, however, there were no significant trends between discharge and spectral slope data.

PARAFAC modeled fluorescence spectra suggested that there was a dominance of terrestrially derived humic DOM contributing to the total DOM in the samples. Components 1 and 2 were both matched to components in the OpenFluor database that corresponded to ubiquitous humic substances (Murphy et al. 2011; Shutova et al. 2014; Søndergaard et al. 2003) and possible degradation products of humic substances (Stedmon et al. 2007). Component 3 did not match any spectra in the OpenFluor database and possibly was unique to this study.

The limited information provided by PARAFAC analysis could be due to the relatively small number of samples used to model fluorescence ($N=36$). PARAFAC modeling of fluorescence is most useful when sufficient numbers of observations are taken for a system to
best capture its variability. The use of samples only collected during the summer months may not fully represent the annual seasonal variability of the study streams. Moreover, each stream could have been studied in more detail. This would have allowed perhaps identification of a larger number of components across the several study sites.

For example, the novelty of C3 could be an important marker for unique fluorescence exported from urbanized catchments. The excitation and emission wavelengths match a novel component found in the study of the Neuse River Estuary (Osburn et al. 2012); however the peak intensities and loadings were not similar. This peak could be related to the peak found in DOM and particulate OM in the Neuse River Estuary but seasonal constraints might limit the comparability of the two PARAFAC modeled components. The relationship between %C3 of the fluorescence maximum and lignin contribution suggest that C3 is related to allochthonous DOM contribution and that it could represent an optical proxy for lignin contribution. Differences in the trends between NR and WC could be related to urban land use with WC being more heavily influenced by anthropogenic waste compared to NR where anthropogenic DOM could be more diluted than surface water in the small tributaries.

**DOM source during storm events**

The relationship between DBP formation potential and DOM aromaticity has been previously reported by Weishaar et al. (2003) who related SUVA\textsubscript{254} the formation of DBPs with aromatic compounds. Additionally, Kraus et al. (2008) related halo-acetic acid formation potential to DOM aromaticity in the Sacramento-San Joaquin River Delta area. Using these relationships, the potential sources of DBPs in Neuse River Basin stream waters
can be investigated. PHC is the urban end member in this study and has the lowest carbon-normalized lignin yield and SUVA$_{254}$ indicating that the DOM from this site at peak discharge had the lowest aromaticity amongst the streams studied. Sources of allochthonous DOM do not change significantly during storm events based on data from lignin sources, however there is an increase in the amount of DOM being mobilized at NR and WC. Wetlands do not have a distinguishable impact on lignin sources during storm events.

Lower molecular weight DOM increased during storm events at CC, this increase indicates that autochthonous DOM is an important source of DOM being mobilized in this watershed. Inamdar et al (2011) found that DOM source was dependent on rainfall intensity with short duration, heavy rainfall storms typical of summer storms in NC mobilizing more aromatic DOM compared to long duration storms. A relationship between the time interval between rainfall events has also been shown to increase the labile fraction of DOM (Borken and Matzner, 2009). At CC, where wetlands account for 1.76% of the catchment area, dry periods between rain events could allow more drying of soil and the subsequent increase in low molecular weight DOM being mobilized when the soil is wetted. In contrast, at WC wetlands are 3.15% of the catchment area. The soil may retain moisture at WC compared to CC limiting the drying and wetting effect Borken and Matzner (2009) suggest. The PHC watershed contains no wetlands, the sample collected 9-July-14 contained relatively lower molecular weight, less aromatic DOM compared to the other sample sites. This relationship suggests that increased soil dryness could increase the mobilization of more fresh, labile DOM. Time interval between rain events was did not significantly correlate with spectral
slope at any site, however at CC there was a decrease in SUVA$_{254}$ with increased time interval between rain events. The presence of wetlands within watersheds might have a large impact on the sources of DOM being mobilized, particularly when there are long dry periods between storms. Frequent small rain events where precipitation was below approximately 10 mm in a 24-hour period were not considered storm events, however these rain events could wet soil enough to mobilize labile DOM. The interactivity between land use, runoff, time interval between rain events and groundwater in the region could cause differences in DOM dynamics of streams in geographically close proximity.

CONCLUSIONS

This study demonstrated that there are several factors that influence DOM concentration and quality in urban catchments within the Neuse River basin. The major conclusions of this study are:

1. Differences in concentration of DOM are present at all sites with increased discharge, however the relationship was only significant at NR.

2. The differences in concentration and discharge at CC do not support the hypothesis that there are increased DOC concentrations during storm events; this is likely attributable to high impact urban land use and lack of wetlands present in the CC catchment.

3. DOM quality changes significantly during storm events at NR and CC with lower molecular weight, more terrestrially derived OM being mobilized during high discharge events.
4. Lignin phenol sources do not change significantly after storm events suggesting that the source of lignin does not change despite discharge increasing. The lignin composition was predominantly from non-woody and woody angiosperm tissue, which was expected because the Neuse river basin, including its sub-catchments, is dominated by angiosperm trees and grasses.

5. Weak relationships between lignin parameters and optical properties suggest that lignin does contribute to CDOM, and that there is a possible optical proxy. More samples at each site could improve our understanding of this relationship.

6. Where significant correlations were observed at NR, but not at WC or CC, it suggests that small catchments with complex land use might contribute to variations in DOM concentration and quality.

FUTURE DIRECTIONS

This study was an initial investigation of optical properties and lignin composition in urban catchments in the Neuse River basin and has implications for understanding DOM transport during storm events and how it relates to water quality. Where surface water is treated for drinking water, the formation of DBPs during chlorination can negatively impact drinking water quality. Aromatic DOM, such as lignin, has been related to DBP formation, therefore understanding how DOM is being mobilized during storm events will help inform municipalities about when excessive DBP formation might occur. This study suggested that during storm events significantly more DOM including lignin is mobilized and could enhance the formation of DBPs. In future studies the analysis of DBP formation potential and
the influence of land use over a larger range of urbanized watersheds would provide a better understanding of when DBPs are most likely to negatively impact drinking water.

The results of the PARAFAC model suggest that there is a dominance of terrestrially derived organic matter contributing to DOM in the Neuse River. The component 3 results were novel to this study and did not match with any previously reported fluorescence spectra in fluorescence intensities. Sampling was limited to May through September, which eliminated possible seasonal effects to DOM. The addition of samples collected at base flow and storm flow throughout the year would provide a more robust PARAFAC model fit of the fluorescence data and potential to isolate an urban signature that has been previously reported in the Neuse River basin by Handsel (2015).
### TABLES AND FIGURES

**Table 1.** Watershed area and land use percentage data for the drainage area above each sample location.

<table>
<thead>
<tr>
<th>Site</th>
<th>Watershed area (km²)</th>
<th>Urban-High*</th>
<th>Urban-Medium**</th>
<th>Urban-Low***</th>
<th>Agriculture</th>
<th>Forest</th>
<th>Water</th>
<th>Wetlands</th>
</tr>
</thead>
<tbody>
<tr>
<td>Neuse River at Clayton</td>
<td>2986.20</td>
<td>4.22</td>
<td>3.20</td>
<td>18.37</td>
<td>13.80</td>
<td>55.58</td>
<td>1.92</td>
<td>2.59</td>
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<tr>
<td>Walnut Creek</td>
<td>118.90</td>
<td>12.26</td>
<td>12.99</td>
<td>31.27</td>
<td>2.79</td>
<td>36.12</td>
<td>0.86</td>
<td>3.15</td>
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<td>Crabtree Creek</td>
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<td>11.00</td>
<td>10.98</td>
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<td>1.49</td>
<td>40.59</td>
<td>1.11</td>
<td>1.76</td>
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<td>Pigeon House Creek</td>
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<td>27.37</td>
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<td>0.00</td>
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<td>Umstead Park Stream</td>
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<td>0.00</td>
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<td>0.00</td>
<td>94.13</td>
<td>0.00</td>
<td>0.15</td>
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</tbody>
</table>

*Commercial, industrial and transportation land use, 80-100% impervious surfaces
**High intensity residential, 50-79% impervious surfaces
***Low intensity residential, less than 50% impervious surfaces

Data from National Land Cover Dataset 2006 (2011 edition), classification based on the modified Anderson Land Cover Classification System (Anderson et al. 1976)
Table 2. Neuse River at Clayton discharge (m$^3$ s$^{-1}$) and stage (m) at the time of sample collection, absorption at 254 nm (m$^{-1}$), specific UV absorption at 254 nm (L mg C$^{-1}$ m$^{-1}$), DOC (mg L$^{-1}$), and $\delta^{13}$C-DOC values (‰), and $S_{275-295}$ (nm$^{-1}$)

<table>
<thead>
<tr>
<th>Date</th>
<th>Discharge</th>
<th>Stage</th>
<th>$a_{254}$</th>
<th>SUVA</th>
<th>DOC</th>
<th>$\delta^{13}$CVPDB (%)</th>
<th>$S_{275-295}$</th>
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<tr>
<td>29-May-14</td>
<td>75.89</td>
<td>1.62</td>
<td>51.94</td>
<td>7.99</td>
<td>6.50</td>
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<td>24.52</td>
<td>0.77</td>
<td>44.75</td>
<td>8.79</td>
<td>5.09</td>
<td>-26.03</td>
<td>0.0138</td>
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<tr>
<td>20-Jun-14</td>
<td>9.94</td>
<td>0.48</td>
<td>41.52</td>
<td>7.98</td>
<td>5.20</td>
<td>-26.09</td>
<td>0.0157</td>
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<tr>
<td>3-Jul-14</td>
<td>8.01</td>
<td>0.44</td>
<td>39.25</td>
<td>7.25</td>
<td>5.42</td>
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<tr>
<td>11-Jul-14</td>
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<td>1.14</td>
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<td>8.13</td>
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<td>5.15</td>
<td>-26.77</td>
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<td>9-Sep-14</td>
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<td>7.53</td>
<td>-25.49</td>
<td>0.0141</td>
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</table>
Table 3. Correlation coefficient ($R^2$) values for DOC (mg L$^{-1}$), SUVA (L mg C$^{-1}$ m$^{-1}$), spectral slope ($S$), $\Sigma_8$ (µg L$^{-1}$), and carbon normalized lignin yield ($\Lambda_8$) (mg (100 mg OC$^{-1}$)) against discharge (m$^3$ s$^{-1}$) at $p < 0.05$ unless otherwise noted. The three main sample sites of this study were the Neuse River at Clayton, Walnut Creek, and Crabtree Creek.

<table>
<thead>
<tr>
<th>Site</th>
<th>DOC</th>
<th>SUVA</th>
<th>S</th>
<th>$\Sigma_8$</th>
<th>$\Lambda_8$</th>
<th>$S_{275-295}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Neuse River</td>
<td>0.75</td>
<td>n.s.</td>
<td>0.3</td>
<td>0.64</td>
<td>n.s.</td>
<td>n.s.</td>
</tr>
<tr>
<td>Walnut Creek</td>
<td>0.34*</td>
<td>n.s.</td>
<td>n.s.</td>
<td>0.46</td>
<td>0.43</td>
<td>n.s.</td>
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<tr>
<td>Crabtree Creek</td>
<td>n.s.</td>
<td>n.s.</td>
<td>0.68</td>
<td>n.s.</td>
<td>n.s.</td>
<td>0.63</td>
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</table>

* Significant at $p < 0.10$
Table 4. Lignin phenol vegetation index minimum, maximum, and means for NR, WC, and CC and published value ranges for plant tissue type.

<table>
<thead>
<tr>
<th>Site/plant tissue type</th>
<th>minimum</th>
<th>maximum</th>
<th>mean</th>
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<tr>
<td>Neuse River</td>
<td>125</td>
<td>1235</td>
<td>565</td>
</tr>
<tr>
<td>Walnut Creek</td>
<td>267</td>
<td>1160</td>
<td>716</td>
</tr>
<tr>
<td>Crabtree Creek</td>
<td>213</td>
<td>920</td>
<td>518</td>
</tr>
<tr>
<td>Gymnosperm- woody</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>Gymnosperm- nonwoody</td>
<td>12</td>
<td>27</td>
<td>19</td>
</tr>
<tr>
<td>Angiosperm- woody</td>
<td>67</td>
<td>415</td>
<td>181</td>
</tr>
<tr>
<td>Angiosperm- nonwoody</td>
<td>378</td>
<td>2782</td>
<td>1090</td>
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</table>
Table 5. Modeled PARAFAC components excitation and emission maxima and peak description from published matched fluorescence spectra in the OpenFluor database with a similarity score > 0.95.

<table>
<thead>
<tr>
<th>Component</th>
<th>Excitation peak (nm)</th>
<th>Emission peak (nm)</th>
<th># of OpenFluor correlations</th>
<th>Potential source description</th>
</tr>
</thead>
<tbody>
<tr>
<td>C1</td>
<td>&lt;240</td>
<td>494</td>
<td>17</td>
<td>Terrestrial humic acid-like fluorophore, ubiquitous</td>
</tr>
<tr>
<td>C2</td>
<td>&lt;240</td>
<td>402</td>
<td>4</td>
<td>Terrestrial soil fulvic-like fluorophore</td>
</tr>
<tr>
<td>C3</td>
<td>&lt;240(350)</td>
<td>432</td>
<td>0</td>
<td>Terrestrial fulvic-like, possible lignin or tannin related peak</td>
</tr>
</tbody>
</table>
Table 6. \( R^2 \) values of optical indices that were significantly correlated to lignin parameters \((p < 0.05)\) at all sample sites.

<table>
<thead>
<tr>
<th></th>
<th>( S (\mu m^{-1}) )</th>
<th>( a_{254} (m^{-1}) )</th>
<th>( a_{350} (m^{-1}) )</th>
<th>SUVA(_{254}) (mg C L(^{-1}) m(^{-1}))</th>
<th>( S_{275-295} (nm^{-1}) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \Sigma_8 ) (µg L(^{-1}))</td>
<td>0.13</td>
<td>0.46</td>
<td>0.28</td>
<td>n.s.</td>
<td>n.s.</td>
</tr>
<tr>
<td>( \Lambda_8 ) (mg (100 mg OC (^{-1})))</td>
<td>n.s.</td>
<td>n.s.</td>
<td>n.s.</td>
<td>0.17</td>
<td>n.s.</td>
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<tr>
<td>LPVI</td>
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<td>n.s.</td>
<td>n.s.</td>
<td>0.22</td>
<td>n.s.</td>
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<tr>
<td>C:V</td>
<td>n.s.</td>
<td>n.s.</td>
<td>n.s.</td>
<td>0.17</td>
<td>n.s.</td>
</tr>
<tr>
<td>S:V</td>
<td>n.s.</td>
<td>n.s.</td>
<td>n.s.</td>
<td>0.22</td>
<td>n.s.</td>
</tr>
</tbody>
</table>
Figure 1. Map of the Neuse River Basin and major rivers and tributaries in North Carolina.
Figure 2. Map of the sampling sub-catchments for each sample location. The three main sites, the Neuse River at Clayton, Walnut Creek, and Crabtree Creek are bolded.
Figure 3. Sample Sites and land use in the Neuse River Basin.
Figure 4. DOC concentrations for all stations during the sampling period.
Figure 5. Stream hydrograph and DOC concentration data and relationships between DOC concentration and discharge at the Neuse River at Clayton (a & b), Walnut Creek (c & d), Crabtree Creek (e & f).
Figure 6. Range and median of $\delta^{13}$C values across the three main sample sites. Boxes represent the 25th to 75th percentiles and outliers are indicated with red crosses.
Figure 7. Split half validated modeled components of EEM fluorescence and excitation/emission loadings from the 3 component PARAFAC model fit to the dataset for sites NR, WC, and CC and one sample from PHC.
Figure 8. Stream hydrograph at NR, WC, and CC during the sample period and the relationship between lignin phenol concentration ($\Sigma 8$) and discharge data at the Neuse River at Clayton (a & b), Walnut Creek (c & d), and Crabtree Creek (e & f).
Figure 9. Carbon-normalized lignin yields for all samples sites during the sampling period compared to 24-hour precipitation totals. Storm events are outlined in dotted boxes.
Figure 10. C:V and S:V ratios at each site. Boxes delineate the literature cited ranges of values for (A) woody angiosperms, (a) non-woody angiosperms, (G) woody gymnosperms, and (g) non-woody gymnosperms (modified from Hedges and Mann, 1979 and Goñi et al. 1998).
REFERENCES


APPENDICES
Appendix A. Discharge, DOC, SUVA$_{254}$, and lignin data for all sample sites (N/A refers to data not available).

<table>
<thead>
<tr>
<th>Location</th>
<th>Date</th>
<th>Discharge (m$^3$ s$^{-1}$)</th>
<th>Stage (m)</th>
<th>DOC (mg L$^{-1}$)</th>
<th>$\delta^{13}$C$_{vpdb}$ (%)</th>
<th>SUVA$_{254}$ (L mg OC$^{-1}$)</th>
<th>$\Sigma 8$ (µg L$^{-1}$)</th>
<th>$\Lambda 8$ (mg (100 mg OC)$^{-1}$)</th>
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<tbody>
<tr>
<td>NR</td>
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<td>1.62</td>
<td>6.50</td>
<td>-26.84</td>
<td>7.99</td>
<td>31.13</td>
<td>0.48</td>
</tr>
<tr>
<td>NR</td>
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<td>24.52</td>
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<td>-26.03</td>
<td>8.79</td>
<td>19.35</td>
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<td>20-Jun-14</td>
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<td>0.48</td>
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<td>Date</td>
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<td>Stage (m)</td>
<td>DOC (mg L$^{-1}$)</td>
<td>$\delta^{13}$C$_{vpdb}$ (‰)</td>
<td>SUVA$_{254}$ (L mg OC$^{-1}$ m$^{-1}$)</td>
<td>$\Sigma$8 (µg L$^{-1}$)</td>
<td>$\Lambda$8 (mg (100 mg OC$^{-1}$))</td>
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<td>----------</td>
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<td>-------------------</td>
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Appendix B. Baeyer-Villager oxidation reaction of aldehydes to carboxylic acid phenols

Figure B1. Baeyer-Villager reaction of vanillin to vanillic acid.