Using Dissolved Organic Carbon Concentration and Character Data to Assess Land Use Change Effects on Coastal Waters

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ABSTRACT. We are studying the high-productivity terrestrial and estuarine ecosystems of the southeastern U.S. coastal zone and the carbon and water cycles in this region. We investigated the water quality of coastal waters in South Carolina with a focus on how rapid land use and land cover change in the Charleston, SC region may be influencing aquatic dissolved organic carbon (DOC). We show that analysis of DOC and its chemical nature helps us understand the role of DOC in coastal ecosystems that are under anthropogenic stress.
Synoptic sampling of water from tidal creeks, rivers, and shallow groundwater in the Charleston, SC region has been ongoing since 2015. Sampled areas include the Francis Marion National Forest (freshwater), the Filbin and Noisette Creek watersheds (fresh-brackish and saltwater urban stream systems, respectively, in North Charleston, SC), the Ashley River (a brackish to saltwater estuarine river), Charleston Harbor (saltwater), and the Ashley-Combahee-Edisto (ACE) Basin (brackish to saltwater estuarine rivers). Filtered and acidified water samples were analyzed for DOC concentration (mg/L) using a Total Organic Carbon (TOC) Analyzer. The fraction of aromatic carbon was determined by analyzing water samples on a UV-Visible Spectrophotometer and normalizing absorbance by DOC concentration to determine specific absorbance (SUVA) of the organic carbon. The SUVA value is a surrogate measure of the percent aromaticity of organic carbon, which may reflect decomposing of terrestrially-derived humic material (e.g., leaf litter).

Preliminary results indicate that (i) water salinity is inversely correlated with DOC concentrations and has no relationship with aromatic properties, (ii) DOC and SUVA values are correlated to land cover and not land usage, (iii) DOC in forested systems had significantly larger fraction of aromatic carbon, and (iv) DOC is easily mobilized in more-developed watersheds by rain events. This study provides a broad look at DOC concentrations and character in natural waters with varying salinity in coastal South Carolina. We will present analytical results of the sampling campaign as well as watershed maps to help visualize the DOC-surface water dynamics in coastal waters around the Charleston and ACE Basin estuaries. These data will be useful to scientists and coastal resource managers who are working to understand and mitigate the impacts of coastal land development on aquatic ecological health and water quality in this region.

INTRODUCTION

The chemical properties of DOC are a predictor of its fate and transport in the environment, origin, geochemical function in water systems, and the microbiological activity in the water system (Bianchi 2007). Fluoremetric techniques are used to determine the origin of a DOC molecule (Westerhoff and Anning 2000). Measurements using a Carbon-13 Nuclear Magnetic Resonance (^{13}C-NMR) are an accurate and effective way to determine chemical functionality of DOC molecules such as percent aromatic or aliphatic (Bauer and Bianchi 2011). Presence of aliphatic DOC molecules are attributed to autochthonous (in-place) sources, e.g., the decomposition of the water system's biomass such as plankton and algae (Aitkenhead-Peterson et al. 2003; 2009). Aromatic DOC is attributed to allochthonous (transported from ourside the system) sources like detritus and soil organic matter represented by humic substances such as highly aromatic humic and fulvic acids (Weishaar et al. 2003). The specific ultraviolet absorbance (SUVA) of dissolved organic carbon at 254 nanometers (nm) wavelength is a simple but informative measurement regarding the chemistry of a DOC molecule. $SUVA_{254}$ is a surrogate measurement of the amount of aromatic DOC (humic substances as presumed sources) or rather, the carbon derived from terrestrial sources. DOC can serve as a proton donor or acceptor and therefore acts as a *p*H buffer effecting the transport and fate of pollutants (inorganic species and potentially organic chemicals) in water systems (Weishaar et al. 2003). The literature generally agrees that increasing levels of DOC enhances the mobility of methyl mercury in a water system shown through positive correlation of DOC levels and methyl mercury (Cai et al. 1999). The larger the proportion of aromatic DOC the more the transport of mercury is enhanced (Weishaar et al. 2003). It is not certain whether DOC can enhance the mobility of hydrocarbons from human activities such as polycyclic aromatic hydrocarbons (PAHs), and results may serve useful to inform on policy decisions regarding urban land use planning. DOC can act as a land based runoff tracer in water systems with the chemical structure providing information on the important hydrological processes for a given watershed (Westerhoff and Anning 2000). Understanding how urbanization influences storm water runoff and the chemistry of DOC in aquatic systems is imperative to understand the impacts to ecological health and the broader carbon cycle (Sickman et al. 2007).

An additional consideration is that DOC concentration and composition may affect the transport of pollutants in an aqueous system, such as causing the formation of disinfection by-products (DPBs) within effluent of water treatment plants (Bauer and Bianchi 2011). Typically, aromatic DOC is troublesome in effluent of water treatment plants, and may contribute to formation of carcinogenic DPBs such as trihalomethane (Weishaar et al. 2003). Furthermore, some urban water systems have experienced an increase in nutrient concentrations due to leaching of nutrients from soils as a result of reduced terrestrial vegetation (Tufford et al. 2003).

In the Charleston, SC area, population has grown dramatically since the 1990s (Allen and Lu 2003) and the metropolitan area as of 2014 has more than 700,000 people. Population growth and related land development can be stressors on environmental systems and services such as storm water runoff mitigation and aquatic biological systems. In coastal South Carolina, urbanization in forested and estuarine systems may be linked to the changing character of dissolved organic carbon and a shift from allochthonous to autochthonous sources (Reed et al. 2015). This may have major implications on DOC chemical properties and could contribute to anoxic zones causing fish kills and poor drinking water quality (Buzzelli et al. 2004). Urbanization around streams can lead to a reduced aquatic photic zone due to increased suspended sediment loads and this can alter the DOC load in streams (Sickman et al. 2007). This study categorized DOC suspected to be sourced from urban activities: hydrocarbons from human activities such as petrochemicals, pesticides, and urban sewage (Sickman et al. 2007). These additional sources could be part of what is changing the nature of DOC in the tidal creek.

The main question this study is addressing: is urbanization changing the concentration of DOC and its chemistry in coastal waters? A secondary set of questions is: does runoff from precipitation mobilize DOC into water systems and what is the role of impervious surface coverage in coastal watersheds? The main objective was to quantify urbanization impact on DOC and this was done using GIS capabilities and collecting samples for carbon analysis from developed and less developed tidal creeks in coastal South Carolina. Parallel efforts also involved comparison of precipitation data (Brown et al. 2014) and measurement of environmental conditions in coastal South Carolina tidal creeks to investigate the hydrology and chemistry linkages in tidal creeks. We report in this paper a characterization of DOC concentration and composition in tidal creeks with a focus on the land use and land cover at the study site watersheds.

METHODS

DOC was analytically defined in this study as organic carbon that can pass through a glass filter ≤ 0.70 μm; organic carbon that cannot pass through the filter was defined as particulate organic carbon (POC) but was not measured for this study. Field sites that had > 35% of the total area classified as urban, suburban, and/or commercial classes were considered developed and those sites < 35% of the land area as such were considered less developed sites.

The lighter color shades on the map loosely indicate the developed "footprint" of the central coast of South Carolina, centered on the Charleston metropolitan area (Figure 1). Sites 2, 3, 4, and 6 were the four developed locations for this study; sites 1, 5, and 7 were considered less developed. Table 1 lists the site identifications.

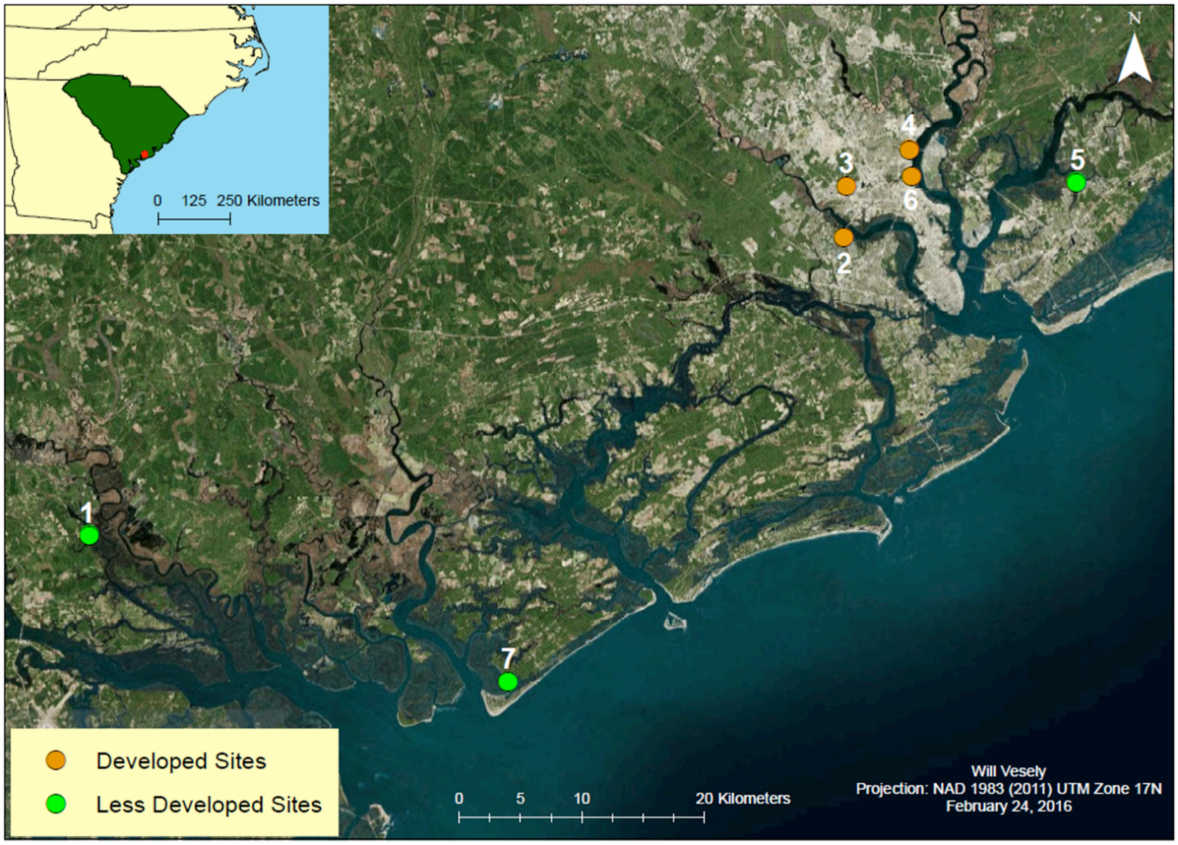

Figure 1: Study site location map showing creek and stream locations for the study. See Table 1 for location identifiers.

Table 1: Site IDs for the acronyms in the map above and the graphs below for the four developed and three less developed sites.

#	Site ID	Site Name
1	BBC	Big Bay Creek
2	BC	Bull Creek
3	FC	Filbin Creek
4	FC_HP	FC_ Hendricks Park
5	HBC	Horlbeck Creek
6	NC	Noisette Creek
7	WC	Wimbee Creek

DOC and SUVA Analysis

Acidified samples were run on the Shimadzu Total Organic Carbon (TOC) Analyzer using a total carbon (TC) method. TC is assumed to be DOC because the inorganic carbon was dissolved from the water sample with the addition of HCl. The samples were analyzed within 28 days of sample collection to ensure accurate results. Calibration curves from freshly prepared standards (1-50 mg/L) of potassium hydrogen phthalate ($C_8H_5KO_4$) were produced for each set of analyses on the TOC to avoid problems with calibration standards. Only calibration curves with a R^2 value of 0.99 or greater were accepted prior to sample analysis. Praxair compressed zero air was used as the air source for the TOC. The TOC reported DOC values as mg/L and the resulting values were converted to micromolar (μM) for data reporting.

The samples that were not acidified were used to quantify the SUVA value of the DOC in the water samples. It has been stated that the $SUVA_{254}$ method is a surrogate indicator on how aromatic a DOC molecule is and the average absorptivity of a DOC molecule (Weishaar et al. 2003). SUVA was determined by using equation 1 below (Weishaar et al. 2003). On the Thermo Scientific Evolution 220 UV-Vis, samples were analyzed with a fixed wavelength set at 254 nm, the determined wavelength of DOC (Karanfil et al. 2003). A blank with DI water was used and quartz cell with a 1.0 cm path length. Calibration standards (1-50 mg/L) of $C_8H_5KO_4$ were run before the samples and only curves with a R^2 of 0.99 or higher were accepted.

Analyzing Urbanization Impact

The study measured urbanization impact on DOC concentration and SUVA by quantifying percent developed, forested and wetlands of the seven watersheds using a geospatial approach on GIS. This was done to measure the relationship between percent developed, forested, and wetlands and DOC concentration/composition in coastal South Carolina tidal creeks. Watersheds were digitized using United States Geological Survey (USGS) elevation derivatives for national applications (EDNAs) map information for five sites and manual digitization was done for two watersheds. The NOAA C-CAP Land Cover Atlas data were used to determine percent developed, forested, and wetlands at each site and equation 2, 3, and 4 was used to determine those values.

RESULTS

DOC Concentration and SUVA Values

This part of the study was to see if there was significant difference between the developed and less developed sites' DOC concentration and SUVA values. Below is the graph of the DOC concentration in the water samples from the seven sites.

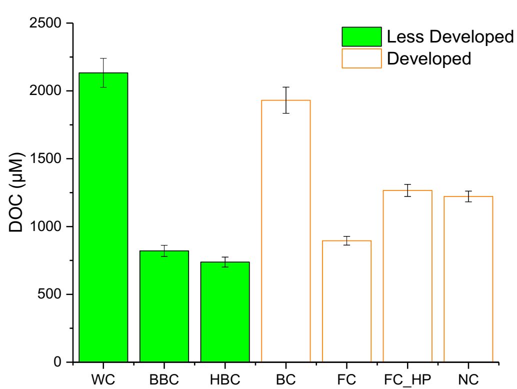

Figure 1: Mean DOC concentrations for the seven sites. Vertical bars represent the standard deviation for each site.

Wimbee Creek samples had the highest DOC levels of all seven sites; Bull Creek has the highest DOC levels for the four sites in the urban/suburban area (Figure 2). Comparatively to other environments, the DOC levels in this area are high due to the nature of coastal South Carolina blackwater streams (Goni et al. 2003). The comparison is showing that DOC levels are likely more controlled by land cover (amount of vegetation) and a system's biomass (plankton and algae) than land usage (amount of land developed). An important detail is that each site has different land use characteristics such as the degree and type of development. For example, Bull Creek and the North Charleston sites (Filbin Creek and Noisette Creek) have an important and in some sense similar history of land use change but have different soils and percent of impervious cover in the surrounding watersheds.

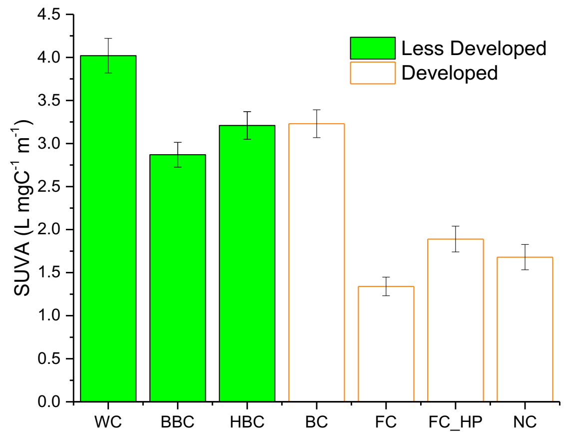

Figure 2: Mean SUVA results for the seven sites. Vertical bars represent the standard deviation.

SUVA values are showing to be the highest for Wimbee Creek (Figure 3). Besides Bull Creek, highly developed sites (North Charleston) have significantly lower SUVA values than the less developed sites and this was a major finding (Figure 3).

Urbanization Impact Data

Land use data (percent developed, forested, and wetland) were compared to DOC concentration and SUVA values (Figure 4). There was a moderate relationship between the percent developed land cover and SUVA values for all sites, with qualitatively higher values for the less developed sites. This relationship shows that development could be reducing the amount of terrestrial DOC being released into the water system.

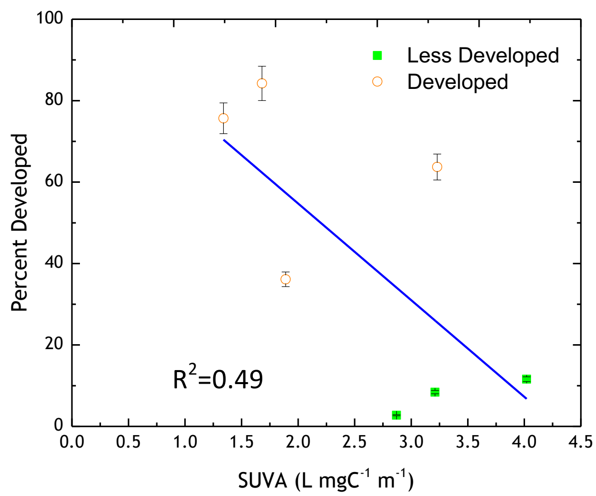

Figure 3: SUVA values compared to percent developed land classes for the study watersheds.

Figure 5 shows that there was a weak relationship between the amount of forest and the SUVA value in coastal South Carolina tidal creeks. This relationship makes sense because SUVA is an indicator of the humic load of DOC and forests deposit high amounts of humic compounds into water systems (Holland et al. 2004). The curve below shows the relationship between percent wetlands and SUVA values.

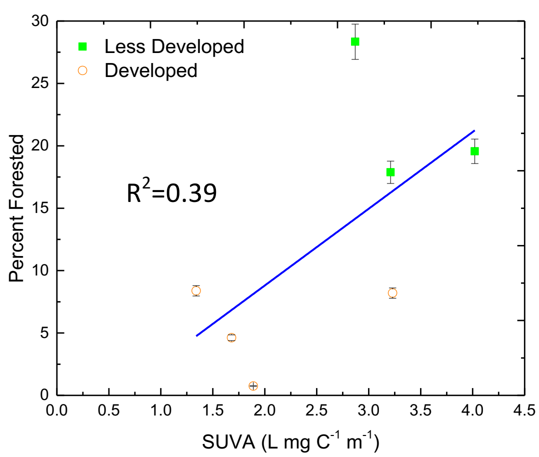

Figure 4: SUVA values compared to percent forested land classification for the studied watersheds.

There was a correlation between SUVA values and percent wetlands (Figure 6). The wetlands may be a source of terrestrial DOC, such as from vascular plant inputs (Evans et al. 2005).

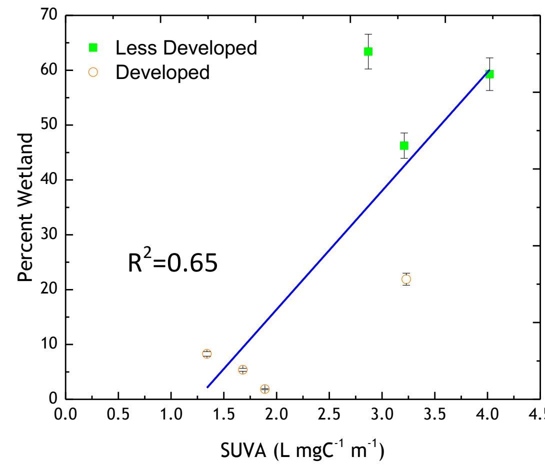

Figure 5: SUVA values compared to percent wetland land classification for the study watersheds..

DISCUSSION

Comparing the DOC results for the sites based on different land classifications illustrates some qualitative aspects. For example, Wimbee Creek (less developed) and Bull Creek (developed) had the highest DOC levels that were statistically the same as each other, yet Wimbee Creek had slightly larger SUVA values suggesting the surrounding forested areas may be a factor in the DOC content having a proportionately large fraction of humic substances presumably derived from terrestrial plant matter. DOC levels in aquatic systems may be influenced by vegetation density and type in a watershed rather than how developed it is (Bauer 2007). However, this study did not measure these two factors directly so it cannot be concluded as to the importance of plant biomass on DOC concentration or composition. However, the DOC composition data (SUVA values) from creeks at the developed sites was different than at the less developed sites.

The SUVA data suggest there was a reduced terrestrial input of DOC at the developed sites, likely due to past clearing of land and reduced soil organic matter in storm water runoff (e.g., see Tufford et al. 2003 and Mallin et al. 2009). The Bull Creek and Horlbeck Creek watersheds (suburban-developed and moderately-developed, respectively) may have been similar to Wimbee Creek before it became developed with larger SUVA values of DOC before it became altered (see Figure 3 above). Areas with more dense vegetation may produce larger SUVA values in water bodies; however, SUVA values are more related to a particular type of vegetation rather than simply vegetation density (Weishaar et al. 2003).

Percent forested land cover was moderately correlated with SUVA because less vegetation means less terrestrial sources leading to a lower SUVA (Figure 5). In the literature higher wetlands is attributed to a higher SUVA value and urbanization is causing fewer wetlands leading to reduced terrestrial sources (Weishaar et al. 2003). A relationship between percent developed, forested, and wetlands and DOC concentration was not found. This study was not able to establish a causal relationship to urbanization. Reed et al. (2014) provide important information on DOC and nitrogen concentrations in saline waters, especially regarding responses of microplankton in coastal South Carolina (also see Catalan et al., 2014 for related information on ecosystem dynamics). An additional detail not considered here was the importance of seasonal conditions on DOC concentrations and composition in the waters. Growing vs. dormant season has been shown to affect transport and cycling of carbon in the terrestrial and aquatic environments (Wahl et al. 1997; Osburn et al. 2015). Other urbanization impacts such as impervious surface amount or manipulated streams have been noted to affect carbon and nutrient runoff for many years (Vernberg et al. 1992). The results of this study provide a characterization of the chemistry of DOC in coastal South Carolina tidal creeks. Ongoing studies are collecting hydrological data of the creeks toward understanding water flow and chemical conditions in these systems.

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