HYDROGEOMORPHIC AND LANDSCAPE INFLUENCES ON DISSOLVED ORGANIC MATTER IN STREAMS AND RIVERS ON THE SOUTH CAROLINA COASTAL PLAIN

Setsen Altan-Ochir[1] and Daniel L. Tufford, Ph.D.[2]

[1]Cornell College, Mount Vernon, IA, USA; [2]University of South Carolina, Columbia, SC, USA

Abstract

Dissolved organic matter (DOM) is recognized as a major component in the global carbon cycle and is an important driver of numerous biogeochemical processes in aquatic ecosystems, both in-stream and downstream in estuaries. This study sought to characterize chromophoric DOM (CDOM) in major rivers and their tributaries of the South Carolina Coastal Plain to assess the impact of land use and other factors on water quality. During eight trips from June 11 to July 9 of 2014 throughout the South Carolina Coastal Plain, we visited 54 sites, where we measured field parameters (temperature, dissolved oxygen, pH, and specific conductance) and collected water samples for laboratory analysis of dissolved organic carbon (DOC) and dissolved nutrients. Sample sites included headwater wetlands and springs, streams and rivers, and water table monitoring wells. Spectral analysis of the filtered water samples was done from 200-800 nm using a Shimadzu UV-1700 spectrophotometer. We calculated absorption coefficients, spectral slope coefficients, and related metrics to facilitate broad characterizations of the nature of the CDOM in the water based on source and other landscape factors. We performed principle components analysis (PCA) to further understand variability in the data from a landscape perspective.

Highest concentrations of CDOM occurred in black waters and in smaller streams and rivers. There were significant differences in SR, DOC concentration, and pH among the different water types and stream orders, while SUVA254 showed significant variations only for the different water types. PCA showed that DOC in black water is strongly associated with the occurrence of wetlands. Land cover sources are more variable in brown and clear water.

Overall, our results are consistent with other studies of DOC and CDOM on the Coastal Plain. Interestingly, DOC concentration looks to be higher in the lower Coastal Plain than in the upper Coastal Plain.

Introduction

Natural organic matter is produced from decay of plant and animal tissues and is found in soil, sediments, and natural waters. Together with the biota, they constitute an important part of the global carbon cycle (1). Organic matter in natural waters consists of dissolved organic matter (DOM) and particulate organic matter (POM), the former being operationally defined as the fraction that passes the 0.1-0.7 µm wide filter pores. DOM is a mixture of aromatic and aliphatic hydrocarbon structures. It has been shown to constitute a significant portion of detrital carbon pool in aquatic systems and is the focus of this research (2).

DOM in riverine waters can be derived (i) allochthonously from microbial decomposition of animal residues, plant material, and root exudates in the surrounding soils; (ii) autochthonously by leaching from algal and phytoplankton cells or as a byproduct of animal ingestion; and (iii) from man-made synthetic organic substances originating from domestic and industrial effluents as well as sewerage. The properties of DOM vary depending on the source and its diagenetic state (3). Its compositions are crucial in natural ecosystems because of the biogeochemical processes in which DOM is involved (4).

While most DOM in marine pelagic systems is generated autochthonously, DOM of allochthonous origins dominates freshwater streams, constituting approximately 30-80% of DOM in river and lake waters (4). Riparian ecosystems in low gradient Coastal Plain streams have pronounced effects on water quality (5). Streams and rivers on the South Atlantic Coastal Plains are high in DOM concentration, which is reflected in their often tea-colored to black waters. Their headwaters arise in swamps which often are accompanied by wide floodplains with rich vegetation. Floodplain and riparian soils have low permeability and infiltration rates, so most leached DOM is washed into streams and rivers during precipitation runoff events (6).

Given the importance and utility of DOM for understanding aquatic ecosystems, this study was conducted as part of a larger endeavor to characterize possible impacts of land use on water quality in coastal watersheds. Water samples throughout the South Carolina Coastal Plain were taken from headwater seepage springs and wetlands, wetland streams, creeks, rivers, and water table monitoring wells in 14 major watersheds from June 11 and July 9 of 2014 along with field parameters and stream flow measurements. The samples were then analyzed for UV-visible absorption properties, [DOC], and nutrients.

Methods

Study sites

A total of 54 sites were sampled in the upper and lower Coastal Plain during eight trips from June 11 to July 9 of 2014 (Fig. 1). Each sample was classified as either a (1) water table well, (2) seepage spring, or (3) 2nd, 3rd, or 4th+ order stream. Stream order was based on either existing literature or assessment of digitized USGS topographic maps.

Field sampling

Surface water grab samples were collected during baseflow in acid washed 1-liter brown plastic bottles and carried back to lab in coolers. Field parameters were measured *in situ* using a YSI sonde.

Sample preparation and analysis

Water samples were filtered within 12 hours of collection using 1 µm glass fiber filters. The filtrates were stored in a refrigerator at 10C. Samples for DOC analysis were preserved with HCl.

Spectral analysis of CDOM was done from 200-800 nm with a Shimadzu UV-Visible Spectrophotometer. Absorbance was recorded at 0.5 nm intervals.

DOC analysis was done using a Shimadzu total organic carbon TOC-V analyzer equipped with an autosampler.

Land cover

The catchment for each sample site was determined using ESRI ArcMap v10.1 and a combination of existing layers of Hydrologic Unit Code (HUC) watersheds and on-screen delineation (for smaller catchments). These catchments were used to clip data from the 2011 National Land Cover Database (http://www.mrlc.gov/). The proportions of each cover type were calculated for each catchment.

Spectral properties

Absorption coefficients (m^{-1}), slope coefficients (nm^{-1}; from 275-295 and 350-400 nm), slope ratios (SR), and specific UV absorption at 254 nm ($L\ m^{-1}\ mg^{-1}$; SUVA254) were derived from the measured absorbance values (3, 7).

Statistical analysis

Data was analyzed using SAS v9.4 PROC MEANS, PROC GLM, and PROC PRINCOMP. Significance was determined at p<=0.05.

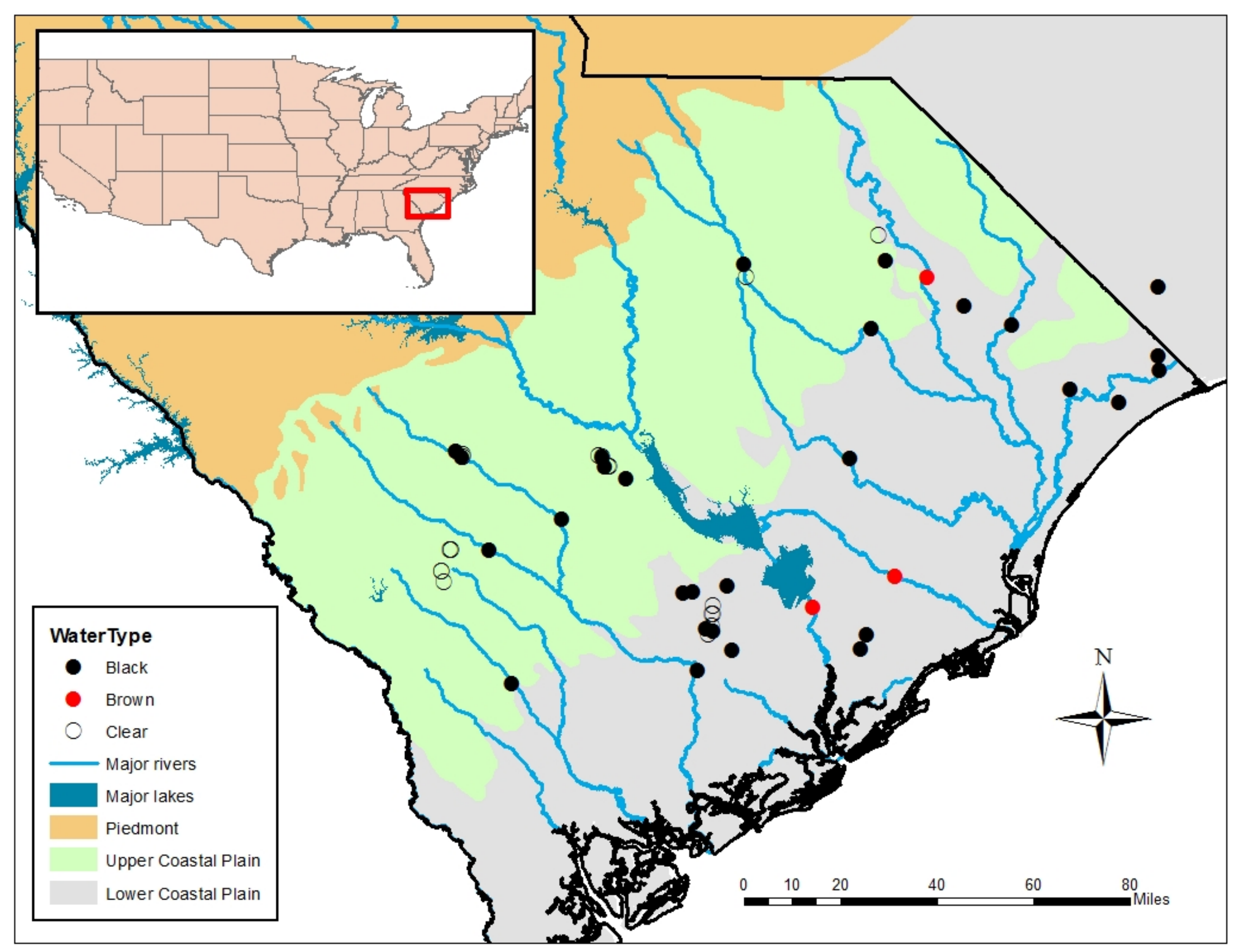


Figure 1. Study area and location of sites by water type that were sampled during this study.

Collecting a water sample for laboratory analysis.

Results

Study sites were a heterogeneous mix of water source and magnitude, catchment size, and land covers (Tables 1 and 2). Black water are tea-colored streams and rivers that are common on the Coastal Plain. Brown are alluvial rivers that carry significant sediment loads from the Piedmont. Clear is water that originates on the Coastal Plain but is not black and often quite clear. Although none of our samples were taken on the Piedmont (Fig. 1), three sites were large rivers with watersheds that mostly drain from there. These are the brown water sites.

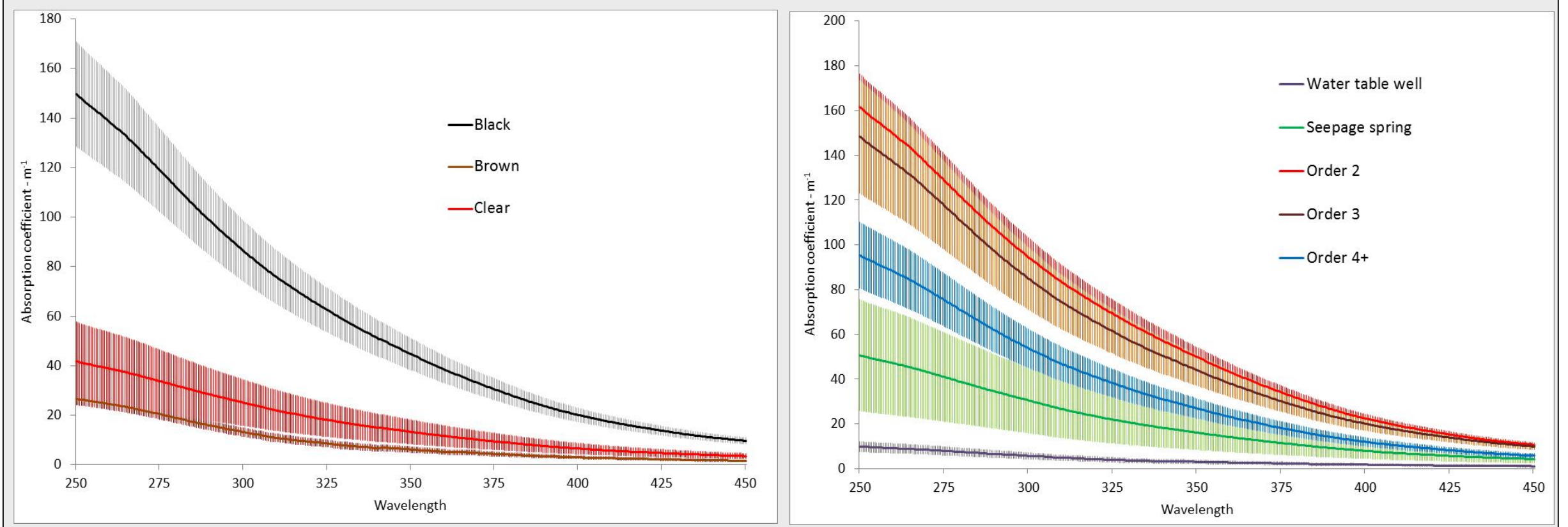
Table 1. Summary of site information.

Site type	n	Water type	n	Physiography	n
Water table well	7	Black	28	Lower CP	27
Seepage spring	14	Brown	3	Piedmont	3
Order 2	11	Clear	23	Upper CP	24
Order 3	11				
Order 4+	11				

Table 2. Summary of watershed areas and land cover proportions

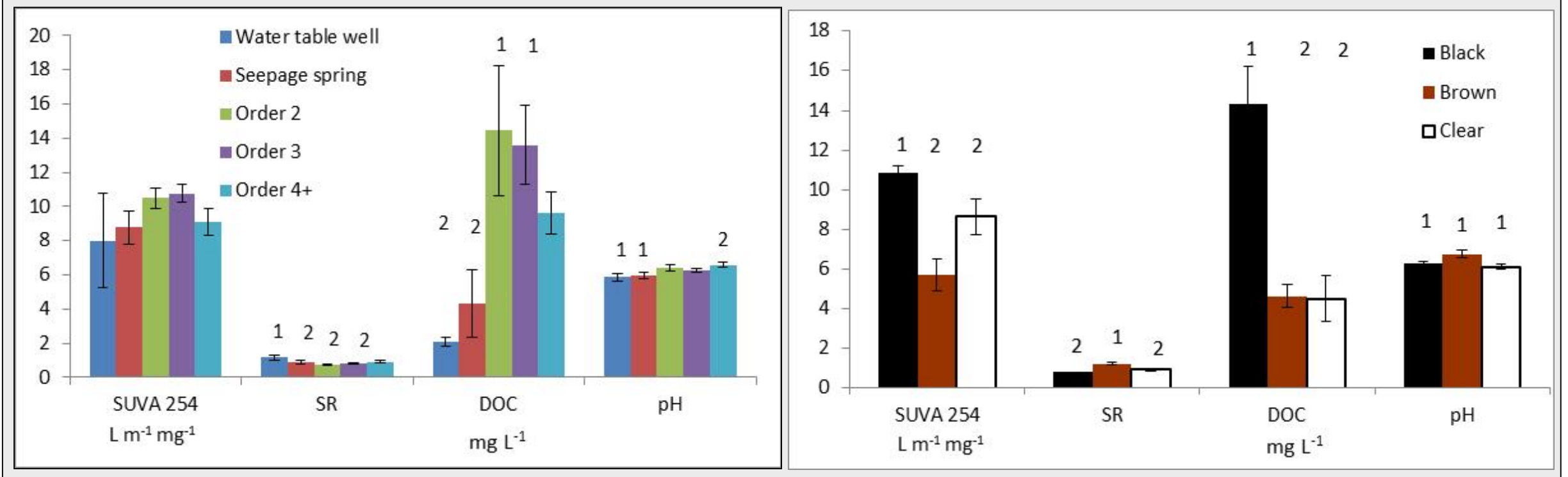
	Area (km^2)	Water	Developed	Other forest	Evergreen forest	Agriculture	Forested wetlands	Herbaceous wetlands	Other
Minimum	0.01	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
Maximum	7403.50	0.092	0.257	0.393	0.861	0.929	0.613	0.204	0.514
Mean	1142.18	0.007	0.065	0.049	0.257	0.222	0.216	0.015	0.169
Median	79.55	0.003	0.060	0.019	0.203	0.201	0.216	0.010	0.177

Plots of absorption coefficients indicate the highest concentrations of CDOM in black water, substantially less in clear water, and very little in brown water (Fig. 2). The highest concentrations were found in 2nd and 3rd order streams, less in larger rivers, and very little in the water table (Fig 3).



Figures 2 (left) and 3 (right). Mean absorption coefficients (± standard error) from 250-450 nm by water type and stream order .

There were no significant differences in SUVA254 by stream order but there were by water type. There were differences in SR, DOC concentration, and pH by both stream order and water type (Figs. 4 and 5).



Figures 4 (left) and 5 (right). Mean (± standard error) of indicated metric by stream order and water type. Numbers above the columns indicate whether means are significantly different (different numbers) or not (same numbers).

Principal components analysis (PCA) of DOC concentration and catchment land covers by water type showed widely varying results (Table 3). For black water, 81% of the variability in the original data is explained in three eigenvectors. In the first vector DOC concentration is directly correlated with both wetland categories and inversely correlated with developed and agriculture. In brown water 100% of the variability is explained by two eigenvectors. The correlation of DOC concentration is mixed with the wetland types, inversely correlated with forest and developed, and directly correlated with agriculture. For clear water, 76% of the variability in the data is explained by the first four eigenvectors. DOC concentration is not a major factor until the 4th vector, which accounts for only 12% of the variability in the data. It is directly correlated with developed and inversely correlated with forested wetland. The first three vectors are dominated by mixed associations of the other land cover categories.

Table 3. Results of the principal components analysis of the land cover and DOC concentration data stratified by water type. The first row in each column is the percent of the variability in the original data that is included in each

	Black			Brown		Clear			
	Vector1	Vector2	Vector3	Vector1	Vector2	Vector1	Vector2	Vector3	Vector4
Percent	47	20	14	78	22	25	21	18	12
DOC	-0.44	0.12	0.07	-0.36	-0.20	0.13	0.17	-0.18	0.64
Water	0.18	-0.03	0.63	0.36	-0.21	0.30	0.30	0.19	-0.19
Developed	0.41	0.29	-0.17	0.37	-0.06	0.21	0.24	0.40	0.47
Evergreen forest	-0.19	-0.59	-0.35	0.36	0.23	-0.53	-0.13	0.38	0.19
Other forest	0.27	-0.14	0.49	0.31	-0.41	0.35	-0.53	0.04	-0.22
Agriculture	0.35	0.46	-0.25	-0.37	-0.10	0.11	0.11	-0.73	0.05
Forested wetland	-0.44	0.20	0.11	-0.15	0.66	-0.13	0.46	0.12	-0.49
Herbaceous wetland	-0.35	0.25	0.33	0.27	0.50	0.36	0.46	0.11	-0.07
Other	0.25	-0.47	0.14	-0.38	0.02	0.54	-0.30	0.24	0.02

Discussion

1) The higher concentrations of CDOM in black water, over brown and clear water, are consistent with other studies of the origins and composition of the waters. Black water originates in floodplain and riparian soils where leached organic compounds can dissolve in high concentrations. Brown water has mixed origins, much from surface runoff in the Piedmont where the geomorphology works against organic matter dissolution. Clear water frequently originates from springs or small catchments that are significantly altered by anthropogenic activity.
2) There was very little CDOM in the water table, which is consistent with the understanding that organic material is mineralized during percolation through the upper soil layers. High concentrations in 2nd and 3rd order streams indicates the importance of the smaller streams in DOM mobilization.
3) The slope ratio (SR) is understood to be inversely related to the molecular weight (MW) of the DOM in the water (3). Our results suggest higher MW DOM in small streams and black water. High MW DOM is important for ecosystem metabolism (8). Although clear water has relatively less DOM than black water the SR suggests the DOM tends to be high MW.
4) Analysis of variance found that not only is the concentration of DOC highest in black water, it is higher in black water in the lower Coastal Plain than the upper Coastal Plain. This is consistent with the tendency for lower slopes, wider floodplains, and slower flow.
5) The PCA analysis shows a strong relationship between DOC and wetlands in black water catchments. There is a more mixed influence of natural and anthropogenic processes in brown and clear water catchments. This is consistent with our other results.

Conclusions

1) We found higher DOC concentrations in black water on the lower Coastal Plain (LCP) than the upper Coastal Plain. The LCP is under the most pressure for development, which raises concern about the potential loss of this component of ecosystem metabolism.
2) The land cover analysis showed that wetlands are a key component of DOC loading to streams. Loss of wetlands likely will have a negative impact on the quantity of DOC in Coastal Plain streams.
3) Sampling over a broad range of water sources and types provides a useful synoptic view of CDOM mobilization and transport during the summer. At the same time, generalizability of the results is limited due to only one sample at each site.

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For further information

Setsen Altan-Ochir – *saltonochir15@cornellcollege.edu*
Dan Tufford – *tufford@sc.edu*

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