Controls on dissolved organic carbon quantity and chemical character in temperate rivers of North America

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[1] Understanding the processes controlling the transfer and chemical composition of dissolved organic carbon (DOC) in freshwater systems is crucial to understanding the carbon cycle and the effects of DOC on water quality. Previous studies have identified watershed-scale controls on bulk DOC flux and concentration among small basins but fewer studies have explored controls among large basins or simultaneously considered the chemical composition of DOC. Because the chemical character of DOC drives riverine biogeochemical processes such as metabolism and photodegradation, accounting for chemical character in watershed-scale studies will improve the way bulk DOC variability in rivers is interpreted. We analyzed DOC quantity and chemical character near the mouths of 17 large North American rivers, primarily between 2008 and 2010, and identified watershed characteristics that controlled variability. We quantified DOC chemical character using both specific ultraviolet absorbance at 254 nm ($SUVA_{254}$) and XAD-resin fractionation. Mean DOC concentration ranged from 2.1 to 47 mg C L^{-1} and mean $SUVA_{254}$ ranged from 1.3 to 4.7 L mg C^{-1} m^{-1}. We found a significant positive correlation between basin wetland cover and both bulk DOC concentration ($R^2 = 0.78$; $p < 0.0001$) and $SUVA_{254}$ ($R^2 = 0.91$; $p < 0.0001$), while other land use characteristics were not correlated. The strong wetland relationship with bulk DOC concentration is similar to that found by others in small headwater catchments. However, two watersheds with extremely long surface water residence times, the Colorado and St. Lawrence, diverged from this wetland relationship. These results suggest that the role of riverine processes in altering the terrestrial DOC signal at the annual scale was minimal except in river systems with long surface water residence times. However, synoptic DOC sampling of both quantity and character throughout river networks will be needed to more rigorously test this finding. The inclusion of DOC chemical character will be vital to achieving a more complete understanding of bulk DOC dynamics in large river systems.

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1. Introduction

[2] Dissolved organic carbon (DOC) quantity and chemical character in rivers and streams play key biogeochemical roles influencing drinking water quality, heavy metal transport, stream ecosystem processes, coastal eutrophication, and the global carbon cycle [*Aiken et al.*, 2011; *Buffam et al.*, 2001; *Cole et al.*, 2007; *Frey and Smith*, 2005; *Gattuso et al.*, 1998; *Lehtoranta et al.*, 2009; *Sholkovitz*, 1976; *Singer*, 1999]. Large rivers are particularly important because they are a major source of material to the coastal ocean and they indicate dynamics across broad regions. However, most previous basin-scale riverine organic carbon studies have focused either on small or individual watersheds, with many finding that bulk DOC variability is related to basin-scale characteristics such as wetland cover and runoff [*Buffam et al.*, 2007; *Chorover and Amistadi*, 2001; *Clair and Ehrman*, 1996; *Creed et al.*, 2003; *Dalzell et al.*, 2007; *Gergel et al.*, 1999; *Mulholland and Kuenzler*, 1979; *Raymond and Hopkinson*, 2003]. We sought to address whether the processes that appear to control DOC quantity in small basins also scale to large and continental-scale systems. In addition, current global land-to-ocean carbon flux

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models continue to rely on DOC concentration data of questionable quality, often collected more than 30 years ago [*Alexander et al*., 1998; *Harrison et al*., 2005; *Lauerwald et al*., 2012; *Meybeck and Ragu*, 1996; *Seitzinger et al*., 2005]. Here we present updated estimates of DOC concentration and flux from 17 large rivers in North America that may be used in future modeling efforts.

[3] Interpreting variability in the quantity of DOC and predicting its impact in natural systems are difficult without also taking into account its chemical character. The chemical character of DOC is largely determined by its source material and past biogeochemical transformations [*Schlesinger*, 1997] and as a result, DOC is made up of thousands of different molecules with a broad spectrum of characteristics and reactivity [*Maurice et al*., 2002]. Knowledge of DOC chemical character can improve understanding of both the sources and fate of DOC in river systems. In addition, the chemical makeup of DOC in aquatic systems influences the transport and bioavailability of heavy metals [*Dittman et al*., 2010] and anthropogenic organic compounds [*Neale et al*., 2011]. The chemical character of DOC also determines how it interacts with natural and engineered nanoparticles [*Aiken et al*., 2011] and impacts the production of harmful byproducts of chlorine disinfection during drinking water sanitization [*Singer*, 1999]. Therefore, a more complete understanding of DOC chemical character in rivers and streams will aid in our interpretation of bulk DOC variability and its influences on water quality.

[4] Some previous large and continental-scale studies have explored controls on DOC quantity and chemical character, though each had limitations. *Aitkenhead and McDowell* [2000] found a strong link between soil C:N and DOC flux at the annual scale among biomes ($R^2 = 0.992$; $p < 0.0001$). Despite the strength of this relationship, when it is applied to predicting DOC flux from individual watersheds, particularly large ones, its utility is limited by the necessity of geospatially extensive soil C:N data. *Frost et al*. [2006] characterized DOC concentration and chemical character throughout a single large river network. They found that concentration was related to a range of landscape variables including percent wetland cover and the total drainage area of individual sub-catchments. They also found that the molecular weight of DOC and its aromaticity were related to the percent lake cover and percent wetland cover of individual sub-catchments. *Shih et al*. [2010] developed a continental-scale total organic carbon flux model based on a variety of watershed parameters using the SPARROW modeling framework [*Alexander et al*., 2000]. They found that in-stream processes were significant in controlling both the quantity and inferred sources of DOC. However, implicit in their model was the assumption that all organic carbon in a reach, irrespective of chemical character, was remineralized at the same rate. This type of model simplification may be adequate to predict bulk organic carbon quantity, but it does not reflect important complexities in the underlying biogeochemical processes and makes the interpretation of model predictions problematic. By not taking into account the spectrum of organic matter chemical character among different sources, the authors likely overestimated the contribution to basin exports by more easily remineralized autochthonous sources and underestimated the more refractory allochthonous sources [*Benner*, 2003; *del Giorgio and Davis*, 2003; *del Giorgio and Pace*, 2008]. Unfortunately, few comparative large-basin DOC studies have been conducted that also incorporate chemical character. Here we update large-river DOC flux estimates and improve understanding of the processes underlying DOC variability in freshwater systems by examining DOC quantity together with chemical character among 17 large rivers throughout temperate North America. We address two primary research questions:

[5] 1. Are the biogeochemical processes underlying the observed relationships between watershed-scale characteristics and DOC quantity among small rivers also important among large and continental-scale systems?

[6] 2. Can watershed-scale characteristics explain the variability of DOC chemical character among large river systems?

[7] Answers to these questions will also help to clarify the role of in-stream processes accumulated at network scales in altering the quantity and chemical character of DOC transferred from the continents to the oceans.

2. Methods

2.1. Study Sites

[8] Our study sites included 17 large watersheds from across a wide range of biomes in North America (Figure 1 and Table 1), 11 of which are monitored by the U.S. Geological Survey's National Stream Quality Accounting Network (NASQAN; http://water.usgs.gov/nasqan/). Basins were selected based on two criteria: large drainage areas ($>1000\ km^2$) and complete daily discharge records available for the sampling period. NASQAN locations in Alaska (Yukon River) were excluded to eliminate the confounding influence of permafrost from the analysis. The primary sampling period (2008–2010) occurred during years of average temperature and only slightly elevated precipitation [*NOAA-NCDC*, 2012]. Site information, including geospatial coordinates, contributing drainage area, and most discharge data, was acquired through the USGS National Water Information System (NWIS; http://waterdata.usgs.gov/nwis/). Discharge data for the Rio Grande were obtained from the International Boundary and Water Commission [*IBWC*, 2010]. In all cases, runoff was calculated as discharge divided by drainage area.

[9] For several rivers, daily discharge data were available only at a nearby USGS gauging station located on the same main stem. In these cases, discharge (Q) was scaled by the percent difference in upstream drainage areas (A) for the nearby and the NASQAN stations:

$$Q_{\mathrm{NASQAN}} = Q_{\mathrm{nearby}}\left(A_{\mathrm{NASQAN}}/A_{\mathrm{nearby}}\right) \tag{1}$$

[10] Very little scaling was done in any case; the Altamaha, Potomac, Androscoggin, and Mobile Rivers were each scaled by 5% or less. The Penobscot River was scaled by just under 15%, but the suitability of this particular assumption was explicitly addressed by *Hodgkins* [1999].

[11] We used ESRI ArcGIS 9.3 to extract land cover and mean annual temperature from the National Hydrography Dataset (NHDPlus) [*USGS*, 2006] and spatially joined our gauging stations with the NHDPlus topological stream network. Each gauging station's corresponding stream reach

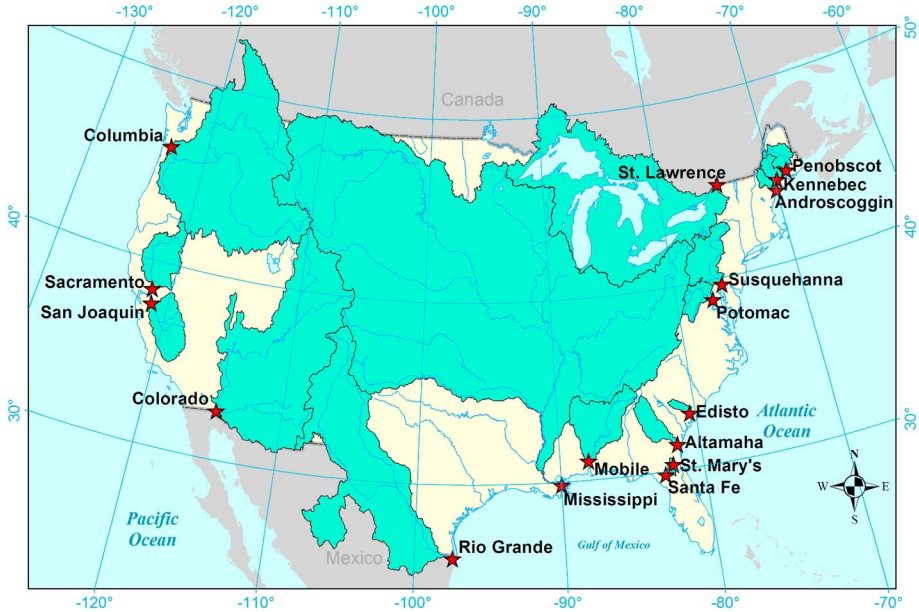

Figure 1. Map showing the drainage basins and sampling locations for 17 North American rivers.

record was joined with cumulative upstream percent land covers from the National Land Cover Database (NLCD) [*Homer et al.*, 2004], including agricultural, forest, grassland, shrubland, urban, and wetland land cover types. Stream reach records were also joined with cumulative-upstream mean basin air-temperature [*Daly and Taylor*, 1998]. Both land cover and air-temperature records were available as a part of the NHDPlus. Unfortunately, the NHDPlus topological network did not correctly model the flow path of the St. Lawrence River, and thus land cover data were unavailable. Instead we used a St. Lawrence watershed polygon provided by NASQAN [*Butman et al.*, 2012] to extract land cover data from the Commission for Environmental Cooperation's North American Environmental Atlas [*NRCan/CCRS et al.*, 2010]. We used BasinDelineator (v2.009), a tool provided as a part of the NHDPlus, to build watershed polygons for each of the other gauging stations. These polygons were then used to extract, for each basin, the percent cover of reservoirs, small lakes, and large lakes from the Global Reservoir and Dam database [*Lehner et al.*, 2011] and the Global Lake and Wetland Database [*Lehner and Doll*, 2004].

2.2. Quantity and Chemical Character

[12] Stations were sampled approximately monthly over 2 to 4 year periods between 2002 and 2010 by the U.S. Geological Survey, with most samples taken between 2008 and 2010 (Table 2). Samples were either filtered in the field using 0.45 μm Gelman capsule filters or shipped on ice to the U.S. Geological Survey in Boulder, Colorado, within 24 h of collection and immediately filtered using pre-combusted Whatman GF/F filters of 0.7 μm nominal pore size. DOC concentration was measured utilizing the platinum catalyzed persulfate wet oxidation method on an O.I. Analytical Model 700 TOC Analyzer™ using established methods [*Aiken et al.*, 1992]. Reported values are the averages of duplicate analyses. Standard deviation for the DOC measurement was determined to be ±0.2 mg C L^{-1}. We also measured DOC chemical character in terms of specific ultraviolet absorbance ($SUVA_{254}$), which is defined as a sample's spectral absorbance at 254 nm (UVA) normalized to its DOC concentration. All samples were analyzed for UVA using a Hewlett-Packard photo-diode array spectrophotometer, and $SUVA_{254}$ was calculated by dividing UVA by DOC concentration. We chose $SUVA_{254}$ as the primary measure of chemical character because it is a good indicator of DOC aromaticity [*Weishaar et al.*, 2003].

[13] The proportion of bulk DOC as hydrophobic organic acids (HPOA) was determined using XAD-resin fractionation analysis following *Aiken et al.* [1992]. In brief, samples were acidified to pH 2 using HCl and passed through a column of XAD-8 resin. The HPOA fraction was retained on the XAD-8 resin and then back eluted with 0.1 *M* NaOH. The concentration of HPOA was determined by direct measurement of the eluent and is presented here as a fraction of bulk DOC. XAD fractionation is useful because it allows us to directly identify the hydrophobic and generally more aromatic and allochthonous compounds in the bulk DOC pool such as fulvic and humic acids [*Aiken et al.*, 1979; *Aiken et al.*, 1992].

[14] For each station daily values and the flow-weighted overall-mean for the entire sampling period (henceforth simply referred to as "mean") for DOC concentration and $SUVA_{254}$ were estimated using LoadRunner, a graphical front-end to the USGS application LOADEST [*Booth et al.*, 2007; *Runkel et al.*, 2004]. LOADEST incorporates daily discharge, seasonality, and measured constituent data to parameterize a multiple-regression model that allows a continuous time series to be estimated from discrete measurements. Root mean square error in mg C L^{-1} (RMSE) for each basin was calculated as

$$\mathrm{RMSE} = \sqrt{\frac{\sum([\mathrm{DOC}]\mathrm{modeled} - [\mathrm{DOC}]\mathrm{measured})^2}{n}} \qquad (2)$$

where [DOC] is DOC concentration in mg C L^{-1} and n is the number of observations. Annual discharge-weighted

Table 1. Table Showing Station Information, Upstream Drainage Area, Mean Runoff, Mean Temperature, and LOADEST Results for Annual Mean Dissolved Organic Carbon (DOC), Specific Ultraviolet Absorption at 254 nm ($SUVA_{254}$), and Hydrophobic Organic Acids (HPOA)[a]

Site Number	River Name	Location	Lat	Long	Drainage (km^2)	Runoff (cm/yr)	Temperature (°C)	DOC Yield ($g\ C\ yr^{-1}\ m^{-2}$)	DOC Load ($kg\ C\ d^{-1}$)	Mean [DOC] ($mg\ C\ L^{-1}$)	Mean $SUVA_{254}$ ($L\ mg\ C^{-1}\ m^{-1}$)	Mean HPOA (Fraction [DOC])	HPOA Load ($kg\ C\ d^{-1}$)
01036390	Penobscot River	Eddington, ME	44.83	−68.70	19460	80.66	4.4	7.55	403000	9.3	3.8	*ND*	*ND*
01049265	Kennebec River	North Sidney, ME	44.47	−69.68	13990	78.12	4.3	4.97	191000	6.4	3.6	*ND*	*ND*
01059400	Androscoggin River	Brunswick, ME	43.92	−69.97	8894	88.00	4.9	5.31	129000	6.0	3.6	*ND*	*ND*
01578310	Susquehanna River[b]	Conowingo, MD	39.66	−76.17	70200	52.41	8.7	1.38	266000	2.7	2.3	0.39	90700
01646580	Potomac River[b]	Washington, D.C.	38.93	−77.12	29970	39.66	11.0	1.64	134000	4.3	2.6	0.36	45000
02175000	Edisto River	Givhans, SC	33.03	−80.39	7071	16.86	17.6	1.96	37900	11.2	4.0	0.66	24000
02226160	Altamaha River[b]	Everett City, GA	31.43	−81.61	36000	28.76	17.5	2.99	297000	10.1	4.2	0.44	128000
02231000	St. Mary's River	MacClenny, FL	30.36	−82.08	1800	39.01	19.7	18.52	92000	46.8	4.7	0.71	65600
02322500	Santa Fe River	Fort White, FL	29.85	−82.72	2634	34.88	20.1	5.54	40000	12.9	4.0	0.66	29300
02470500	Mobile River[b]	Mount Vernon, AL	31.09	−87.98	111030	25.17	16.5	1.36	414000	5.7	3.4	0.52	209000
04264331	St. Lawrence River[b]	Cornwall, ON	45.01	−74.79	773900	30.58	*ND*	1.24	1800000	2.8	1.3	0.29	529000
07374525	Mississippi River[b]	Belle Chasse, LA	29.86	−89.98	2930000	16.44	9.8	0.66	5260000	4.0	3.0	0.43	2050000
08475000	Rio Grande[b]	Brownsville, TX	25.88	−97.45	456700	0.11	18.0	0.01	9200	5.9	2.1	0.35	3180
09522000	Colorado River[b]	Morelos Dam, AZ	32.72	−114.72	639000	0.30	10.3	0.01	16700	3.1	1.7	0.37	5490
11303500	San Joaquin River[b]	Vernalis, CA	37.68	−121.27	35058	5.16	12.0	0.19	18400	3.6	2.5	0.44	5160
11447650	Sacramento River[b]	Freeport Bridge, CA	38.46	−121.50	69457	21.11	12.0	0.63	119000	2.9	2.7	0.39	33400
14246900	Columbia River[b]	Quincy, OR	46.18	−123.18	665400	30.59	6.5	0.65	1180000	2.1	2.7	0.42	461000

[a]Rivers are sorted clockwise around the North American coastline starting in the Northeastern United States. *ND* indicates no data available.
[b]Denotes NASQAN monitoring.

Table 2. Table Showing LOADEST Model Information[a]

River Name	n	Year Begin	Year End	R^2	DOC RMSE (mg C L^{-1})	NS	R^2	SUVA RMSE (L mg C^{-1} m^{-1})	NS	R^2	HPOA RMSE (%[DOC])	NS
Penobscot River	61	2004	2008	0.97	1.8	0.60	0.99	0.2	0.39	*ND*	*ND*	*ND*
Kennebec River	12	2006	2007	0.99	0.5	0.75	0.99	0.1	0.43	*ND*	*ND*	*ND*
Androscoggin River	12	2006	2007	0.99	0.4	0.81	0.99	0.1	0.58	*ND*	*ND*	*ND*
Susquehanna River	22	2008	2010	0.94	0.4	0.39	0.96	0.3	0.09	0.90	0.04	0.18
Potomac River	21	2008	2010	0.99	0.3	0.80	0.99	0.1	0.81	0.99	0.03	0.92
Edisto River	18	2005	2008	0.96	1.6	0.81	0.99	0.2	0.28	0.96	0.04	0.81
Altamaha River	19	2008	2009	0.99	1.1	0.67	0.99	0.3	0.66	0.90	0.11	−0.51
St. Mary's River	31	2002	2006	0.99	8.5	0.68	0.99	0.3	0.17	0.98	0.04	0.67
Santa Fe River	29	2002	2004	0.93	5.3	0.78	0.98	0.4	0.79	0.93	0.07	0.62
Mobile River	25	2008	2010	0.98	0.6	0.71	0.99	0.2	0.72	0.98	0.04	0.36
St. Lawrence River	16	2008	2009	0.93	0.1	0.80	0.74	0.1	0.53	0.68	0.02	0.36
Mississippi River	23	2008	2010	0.94	0.3	0.50	0.99	0.1	0.71	0.98	0.03	0.80
Rio Grande	21	2008	2009	0.99	0.3	0.44	0.98	0.2	0.32	0.98	0.02	0.30
Colorado River	27	2008	2010	0.92	0.4	0.17	0.96	0.1	0.54	0.99	0.03	0.37
San Joaquin River	23	2008	2010	0.90	0.8	0.48	0.98	0.2	0.27	0.81	0.06	0.21
Sacramento River	24	2008	2010	0.95	0.4	0.80	0.97	0.2	0.82	0.97	0.05	0.95
Columbia River	18	2009	2010	0.97	0.2	0.66	0.96	0.3	0.61	0.94	0.03	0.60

[a]R^2, Nash-Sutcliffe coefficient, and root mean square error are shown for dissolved organic carbon (DOC), specific ultraviolet absorption at 254 nm ($SUVA_{254}$) and hydrophobic organic acids (HPOA). *ND* indicates that no data were available.

concentration means were automatically calculated from the daily modeled values, and fluxes were simply the sum of daily concentrations multiplied by daily discharge over the time period of interest. Mean concentration, flux, and yield were calculated by taking the average of the annual means for each basin. In order to compare among watersheds, we divided flux by basin area to obtain DOC yield.

3. Results

3.1. Basin Attributes and Mean DOC Characteristics

[15] Basins ranged in drainage area from 1800 km^2 for the St. Mary's River in Florida to 2,930,000 km^2 for the Mississippi River in Louisiana (Table 1). Compared to the Mississippi, the St. Mary's River basin is quite small, but it is still much larger than most basins found in comparative riverine DOC studies. In total, the watersheds for all 17 rivers accounted for more than 70% of the land area of the contiguous United States and 26% of the land area of North America. The most northerly river was the Columbia in Oregon with a mean watershed latitude of 46.2°N, though the coldest watershed belonged to the Kennebec River in Maine, with a mean annual temperature of 4.3°C. The most southerly and the warmest was the Santa Fe River in Florida, with a mean watershed latitude of 29.9°N and a mean annual temperature of 20.1°C. Mean runoff during each basin's sampling period ranged from 0.11 cm/yr for the Rio Grande in Texas to 88.00 cm/yr for the Androscoggin River in Maine (Table 1).

[16] Wetland cover ranged from 0.1% for the Rio Grande in Texas to 41.6% for the St. Mary's River (Table 3). Agricultural land cover ranged from 1.5% for the Penobscot River in Maine to 42.3% for the Mississippi River. The Rio Grande had the greatest grassland cover, at 34.2%, while several basins possessed 0.0% grassland cover, including nearly all eastern basins. The Rio Grande was the least forested, at 11.3% cover, and was tied with the Colorado River in Arizona for the least urban, at 0.5%. The most forested

Table 3. Table Showing Various Land Cover Attributes in Percent Basin Cover[a]

River Name	Agricultural (ag)	Forest	Grassland (grass)	Shrubland (shrub)	Urban	Wetland (wet)	Reservoir	Lake
Penobscot River	1.5	89.3	0.0	0.3	0.6	5.5	2.3	5.3
Kennebec River	6.0	85.0	0.0	0.4	1.2	3.9	3.8	5.9
Androscoggin River	5.6	87.7	0.0	0.2	1.7	3.5	2.3	4.1
Susquehanna River	28.7	67.4	0.0	0.0	2.6	0.5	0.1	0.7
Potomac River	34.7	61.2	0.0	0.0	2.8	0.5	0.0	0.3
Edisto River	32.3	45.4	0.0	0.0	1.6	15.3	0.0	0.0
Altamaha River	24.0	58.4	0.0	0.0	3.5	8.3	0.4	0.6
St. Mary's River	2.0	46.1	1.2	0.2	1.5	41.6	0.0	0.2
Santa Fe River	16.9	46.4	11.2	1.5	2.4	16.0	0.0	1.5
Mobile River	18.5	70.8	0.0	0.0	1.8	6.4	0.5	0.9
St. Lawrence River	18.2	37.7	1.9	0.4	3.1	3.9	3.5	34.3
Mississippi River	42.3	23.0	25.2	4.7	1.7	2.5	0.5	0.9
Rio Grande	1.8	11.3	34.2	50.1	0.5	0.1	0.2	0.1
Colorado River	2.1	23.7	12.3	57.1	0.5	0.2	0.3	0.2
San Joaquin River	16.9	36.3	15.3	16.2	2.2	0.8	0.6	0.6
Sacramento River	9.9	54.6	15.2	14.5	1.7	0.7	0.9	0.7
Columbia River	12.9	42.3	10.4	29.7	0.8	0.4	0.7	0.6

[a]Corresponding variables in LOADEST models (Table 4) are shown in parenthesis.

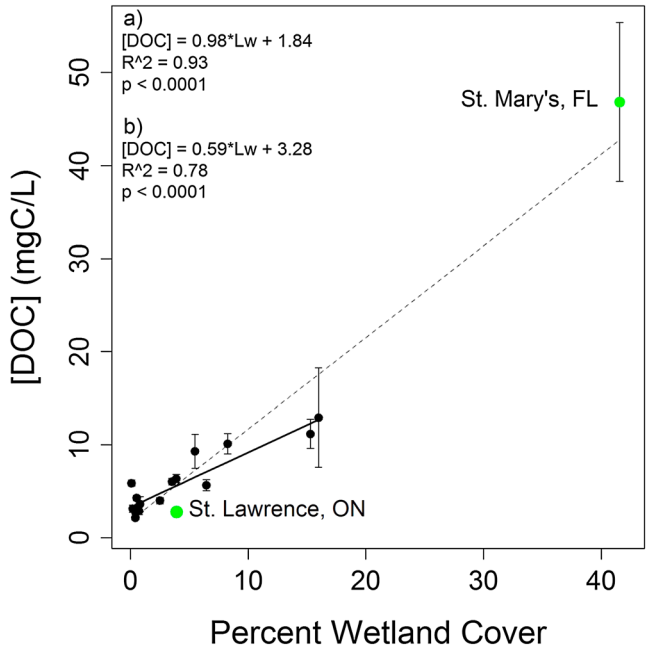

Figure 2. Mean dissolved organic carbon (DOC) concentration versus percent wetland cover (a) for all 17 sites, represented by a dashed line and (b) excluding the St. Mary's River, represented by a solid black line. The St. Mary's River and the St. Lawrence River are highlighted in green. Error bars represent root mean square error for the LOADEST model and are smaller than the size of the data point in some cases.

and the most urban were the Penobscot River at 89.3% and the Altamaha River at 3.5%, respectively. Shrubland ranged from 0.0% for the Mobile, Susquehanna, Potomac, Edisto, and Altamaha Rivers to 57.1% for the Colorado River. For reservoirs, the Potomac, Edisto, St. Mary's, and Santa Fe Rivers were least covered at 0.0% and the Kennebec River was the most covered at 3.8%. Finally, lake cover ranged from 0.0% for the Edisto River to 34.3% for the St. Lawrence River.

[17] Mean DOC concentrations from LOADEST ranged from 2.1 mg C L^{-1} for the Columbia River in Oregon to 46.8 mg C L^{-1} for the St. Mary's River, while DOC load ranged from 9200 kg C d^{-1} for the Rio Grande to 5,260,000 kg C d^{-1} for the Mississippi River. DOC yield ranged from 0.01 g C yr^{-1} m^{-2} for the Colorado River in Arizona and the Rio Grande, to 18.5 g C yr^{-1} m^{-2} for the St. Mary's River. Mean $SUVA_{254}$, ranged from 1.3 L mg C^{-1} m^{-1} for the St. Lawrence River to 4.7 L mg C^{-1} m^{-1} for the St. Mary's River. Mean HPOA fraction ranged from 0.29 for the St. Lawrence River to 0.71 for the Santa Fe River in Florida, while HPOA load ranged from 3180 kg C d^{-1} for the Rio Grande to 2,050,000 kg C d^{-1} for the Mississippi River. Total DOC and HPOA flux for all basins studied was 3.80 Tg C yr^{-1} and 1.34 Tg C yr^{-1}, respectively (Table 1).

[18] All LOADEST models used to estimate mean DOC concentration, $SUVA_{254}$, and HPOA concentration were significant to the level of $\alpha = 0.01$, with $p < 0.0001$ in all cases except the $SUVA_{254}$ and HPOA models for the St. Lawrence River where $p = 0.0008$ and 0.002, respectively. For DOC, R^2 ranged from 0.90 to 0.99 and for $SUVA_{254}$, from 0.74 to 0.99. Nash-Sutcliffe coefficients [*Nash and Sutcliffe*, 1970] ranged from 0.17 to 0.81 for DOC and from 0.09 to 0.82 for $SUVA_{254}$. For HPOA, R^2 ranged from 0.68 to 0.99 and Nash-Sutcliffe coefficients ranged from −0.51 (for the Altamaha River in Georgia) to 0.95. The positive Nash-Sutcliffe values presented here indicate that with the exception of the Altamaha HPOA model, all LOADEST models predicted measured values with more accuracy than a simple mean (Table 2).

3.2. DOC Quantity Patterns

[19] We found a strong positive correlation between percent wetland cover (L_W) and mean DOC concentration in mg C L^{-1} ($R^2 = 0.93$, $p < 0.0001$; Figure 2a and Table 3). However, the slope of this relationship was highly skewed by the wetland-dominated St. Mary's River. When we excluded the St. Mary's as an outlier, the model better fulfilled the assumptions of a linear regression and the DOC

Table 4. Table Showing Relationships Between Both Dissolved Organic Carbon (DOC) Concentration and Specific Ultraviolet Absorption at 254 nm ($SUVA_{254}$) and a Variety of Land Cover Attributes (Table 3)[a]

Predictor	Land Cover Versus DOC	R^2	p-Value	Land Cover Versus $SUVA_{254}$	R^2	p-Value
Wetland	[DOC] = 0.590 × wet + 3.278	0.78	<0.0001	SUVA = 0.440 × log(wet) + 2.884	0.91	<0.0001
Agricultural	[DOC] = 0.004 × ag + 5.733	0.00	0.954	SUVA = −0.052 × log(ag) + 3.187	0.00	0.812
Forest	[DOC] = 0.033 × forest + 4.072	0.05	0.387	SUVA = 0.821 × log(forest) + −0.085	0.23	0.054
Grass	[DOC] = −0.071 × grass + 6.364	0.05	0.405	SUVA = −0.109 × log(grass) + 2.96	0.18	0.092
Shrub	[DOC] = −0.064 × shrub + 6.504	0.13	0.177	SUVA = −0.127 × log(shrub) + 2.989	0.19	0.077
Urban	[DOC] = 0.29 × urban + 5.284	0.01	0.770	SUVA = 0.177 × log(urban) + 2.99	0.01	0.663
Reservoir	[DOC] = −0.295 × reservoir + 6.099	0.01	0.684	SUVA = −0.163 × log(reservoir) + 2.863	0.12	0.173
Lake	[DOC] = −0.074 × lake + 6.066	0.03	0.493	SUVA = −0.087 × log(lake) + 3.042	0.03	0.518
Predictor	**Land Cover Versus Residual-DOC**	**R^2**	**p−Value**	**Runoff versus Residual $SUVA_{254}$**	**R^2**	**p−Value**
Agricultural	RD = −0.096 × ag + 1.551	0.21	0.062	RS = −0.12 × log(ag) + 0.28	0.06	0.359
Forest	RD = −0.001 × forest + 0.071	0.00	0.964	RS = 0.172 × log(forest) + −0.658	0.03	0.532
Grass	RD = 0.061 × grass + −0.456	0.06	0.358	RS = −0.034 × log(grass) + −0.033	0.05	0.411
Shrub	RD = 0.05 × shrub + −0.517	0.12	0.175	RS = −0.008 × log(shrub) + −0.005	0.00	0.868
Urban	RD = −0.98 × urban + 1.739	0.11	0.195	RS = −0.284 × log(urban) + 0.122	0.09	0.241
Reservoir	RD = −0.039 × reservoir + 0.037	0.00	0.944	RS = −0.069 × log(reservoir) + −0.086	0.06	0.355
Lake	RD = −0.083 × lake + 0.277	0.06	0.324	RS = −0.136 × log(lake) + −0.037	0.19	0.083

[a]The second group of formulas represents the relationships between the residuals of the DOC or $SUVA_{254}$ versus percent wetland-cover regression (equations (3) and (5)) and the same land cover attributes. For all DOC relationships, the St. Mary's River is excluded as an outlier. For the SUVA254 versus percent wetland cover relationship, the Colorado River and the St. Lawrence River are excluded as outliers.

Table 5. Table Showing Within-Basin Runoff (RO) Relationships for Dissolved Organic Carbon (DOC) Concentration and Specific Ultraviolet Absorption at 254 nm ($SUVA_{254}$)[a]

River Name	Runoff-DOC Formula	R^2	p-Value	Runoff-$SUVA_{254}$ Formula	R^2	p-Value
Penobscot River	[DOC] = 0.01 × RO + 8.46	0.11	0.004	*N/S*	*N/S*	0.119
Kennebec River	[DOC] = −0.01 × RO + 7.40	0.28	0.043	*N/S*	*N/S*	0.275
Androscoggin River	*N/S*	*N/S*	0.191	*N/S*	*N/S*	0.915
Susquehanna River	*N/S*	*N/S*	0.963	*N/S*	*N/S*	0.227
Potomac River	*N/S*	*N/S*	0.706	*N/S*	*N/S*	0.058
Edisto River	[DOC] = 0.27 × RO + 4.63	0.40	0.003	*N/S*	*N/S*	0.055
Altamaha River	[DOC] = 0.03 × RO + 8.53	0.18	0.022	SUVA = 0.01 × RO + 3.89	0.27	0.006
St. Mary's River	*N/S*	*N/S*	0.336	*N/S*	*N/S*	0.101
Santa Fe River	[DOC] = 0.17 × RO + 2.78	0.62	< 0.001	SUVA = 0.01 × RO + 3.76	0.10	0.045
Mobile River	*N/S*	*N/S*	0.443	SUVA = 0.01 × RO + 3.06	0.35	0.001
St. Lawrence River	[DOC] = 0.06 × RO + 0.97	0.38	0.005	*N/S*	*N/S*	0.89
Mississippi River	*N/S*	*N/S*	0.086	SUVA = 0.02 × RO + 2.57	0.27	0.007
Rio Grande	*N/S*	*N/S*	0.06	SUVA = 2.05 × RO + 1.85	0.16	0.043
Colorado River	[DOC] = 1.67 × RO + 2.56	0.14	0.029	SUVA = 0.95 × RO + 1.35	0.20	0.011
San Joaquin River	*N/S*	*N/S*	0.583	*N/S*	*N/S*	0.107
Sacramento River	[DOC] = 0.06 × RO + 1.37	0.50	< 0.001	SUVA = 0.04 × RO + 1.67	0.71	< 0.001
Columbia River	[DOC] = 0.02 × RO + 1.47	0.47	0.001	SUVA = 0.02 × RO + 1.96	0.27	0.017

[a]Basins without a significant relationship are labeled *N/S*.

concentration variability was still well explained by percent wetland cover ($R^2 = 0.78$, $p < 0.0001$; Figure 2b and Table 4):

$$[\mathrm{DOC}] = 0.59 \times L_W + 3.28 \quad (3)$$

[20] In this relationship, the St. Lawrence River falls well below the regression line but is still included in the analysis. We found no relationships significant to the level of $\alpha = 0.01$ between any other land cover attribute (including land cover classes, lake cover, and reservoir cover) and DOC concentration. There were also no correlations between any land cover attribute and the residuals of the DOC concentration versus percent wetland regression (Table 4).

[21] We found no significant relationship at the level of $\alpha = 0.01$ between mean annual runoff (RO) and mean DOC concentration among basins. However, we did find a significant positive correlation between mean DOC yield (g C yr^{-1} m^{-2}) and runoff (cm/yr) which strengthened when the St. Mary's River was again excluded as an outlier ($R^2 = 0.68$, $p < 0.0001$):

$$\mathrm{DOC_{yield}} = 0.07 \times \mathrm{RO} - 0.158 \quad (4)$$

[22] It should be noted that runoff is used within the LOADEST model for estimating mean annual DOC concentration. Within individual systems, around half of basins exhibited a significant positive correlation between daily runoff and discrete DOC concentration. In these basins, runoff explained between 11% and 62% of concentration variability (Table 5). However, we found no correlation between the statistical significance of these relationships and a basin's percent wetland cover or mean annual runoff.

3.3. DOC Chemical Character Patterns

[23] Percent wetland cover also appeared to be an important variable in controlling DOC chemical character. We found a strong positive correlation between the logarithm of percent wetland cover and mean $SUVA_{254}$ among the rivers in our data set ($R^2 = 0.60$, $p = 0.0001$). In this relationship the St. Mary's River was not found to be an outlier. However, the St. Lawrence and Colorado Rivers exhibited far lower $SUVA_{254}$ in L mg C^{-1} m^{-1} than expected based on their wetland cover, and when they were excluded from the regression as outliers, the relationship between percent wetland cover and $SUVA_{254}$ improved ($R^2 = 0.91$, $p < 0.0001$; Figure 3 and Table 4):

$$\mathrm{SUVA_{254}} = 0.441 \times \log(L_W) + 2.884 \quad (5)$$

[24] No significant relationships were found between any other land cover attribute and $SUVA_{254}$, nor between any land cover attribute and the residuals of the $SUVA_{254}$ versus percent wetland regression (Table 4).

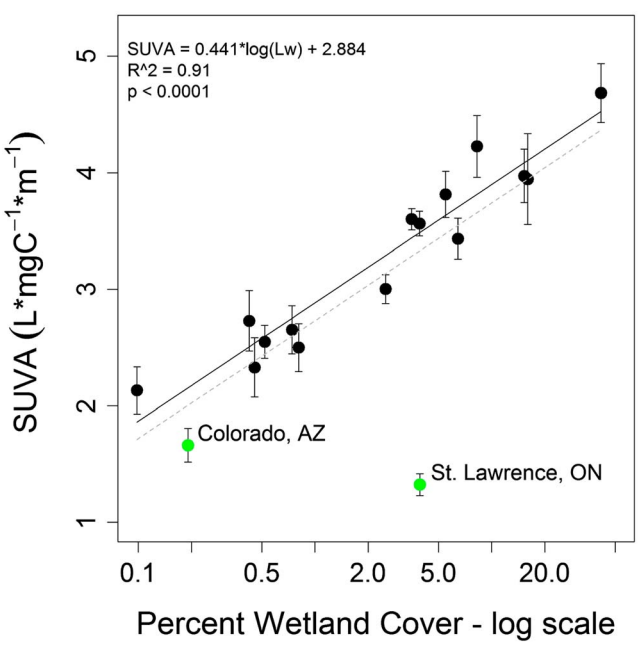

Figure 3. Mean specific ultraviolet absorption at 254 nm ($SUVA_{254}$) versus percent wetland cover for all basins. X axis is logscale and excluded outliers are in green. Final model is in black. Model before the outliers were excluded is shown in dotted grey. Error bars represent root mean square error for the LOADEST model.

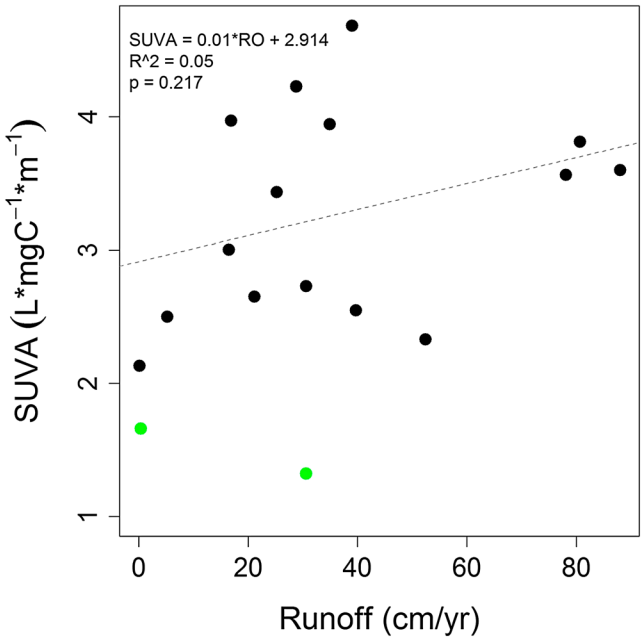

Figure 4. Mean specific ultraviolet absorption at 254 nm ($SUVA_{254}$) versus mean runoff for all basins. Excluded outliers (St. Lawrence and Colorado) are shown in green.

[25] We also did not find a statistically significant relationship between mean runoff and $SUVA_{254}$ among basins, with or without outliers (Figure 4), but within individual systems, around half of basins exhibited a significant positive correlation between discrete $SUVA_{254}$ and daily runoff, with runoff explaining between 10% and 71% of variability (Table 5). Basins with a significant relationship tended to be in the south and the west, whereas northern and eastern rivers did not tend to show significance. As with DOC concentration, we found no correlation between the statistical significance of these relationships and a basin's percent wetland cover.

[26] HPOA as a percentage of bulk DOC was positively correlated with $SUVA_{254}$ measurements in individual grab samples across 14 basins where both measurements were made ($R^2 = 0.89$, $p < 0.0001$). Within individual basins, the relationship between HPOA and $SUVA_{254}$ was significant for all but three basins (Mobile, Mississippi, and Colorado) with R^2 ranging from 0.24 for the St. Mary's River to 0.87 for the neighboring Santa Fe River. As a result, HPOA patterns were very similar to $SUVA_{254}$.

4. Discussion

4.1. DOC Quantity

[27] We identified a significant positive relationship between basin wetland cover and mean DOC concentration among large watersheds that was consistent with what has been reported for small basins [*Buffam et al.*, 2007; *Creed et al.*, 2003; *Eckhardt and Moore*, 1990; *Gergel et al.*, 1999; *Gorham et al.*, 1998; *Raymond and Hopkinson*, 2003]. Similar observations previously made among small basins have typically been explained by the hypothesis that runoff from a wetland to a stream channel would be less likely to have intersected the mineral soil horizon than runoff from non-wetland systems. These flow paths are important because DOC builds up in wetlands due to anaerobic conditions, while DOC in subsurface flow intersecting the mineral horizon is more likely to be removed from solution by biotic processing and adsorption [*Aitkenhead-Peterson et al.*, 2003; *Buffam et al.*, 2007; *Eckhardt and Moore*, 1990; *Tipping et al.*, 1999]. We found that these small-basin patterns also occurred in large river systems, demonstrating that the control exerted by wetlands on riverine DOC continued to be evident in large and continental scale systems. The lack of a significant relationship between any other land attribute and annual mean DOC concentration further highlighted the unique relationship between wetlands and riverine DOC.

[28] Mean runoff appeared to control variation in DOC yield among large basins at the annual scale (equation (4)) without directly influencing DOC concentration [*Mulholland and Kuenzler*, 1979; *Mulholland and Watts*, 1982]. The lack of a significant relationship between mean DOC concentration and mean runoff indicated that the controls exerted on mean yield by runoff were unrelated to the factors controlling mean concentration. Rather, when predicting DOC flux at annual scales from large rivers, annual runoff should be considered a vector, rather than an explanatory variable for concentration.

[29] Although percent wetland cover is a powerful explanatory variable, substantial unexplained DOC concentration variability remained among the seven least wetland-dominated watersheds. These watersheds are geographically diverse and include the San Joaquin, Rio Grande, Potomac, Colorado, Columbia, Sacramento, and Susquehanna Rivers, which all have less than 1% wetland cover and possess a mean DOC concentration of 3.5 ± 1.3 mg C L^{-1}. Among these basins, we found that DOC concentration was positively correlated with mean annual watershed temperature ($R^2 = 0.79$, $p = 0.004$; Figure 5) and it was not significantly

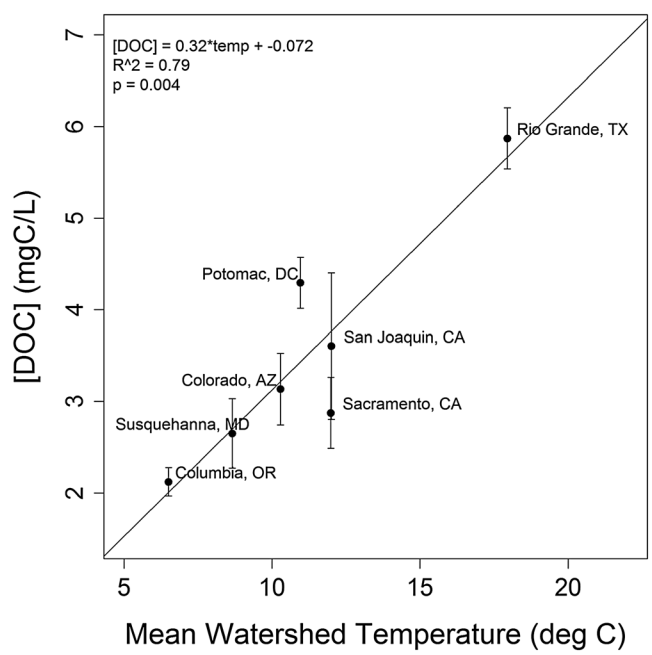

Figure 5. Mean dissolved organic carbon (DOC) concentration versus mean watershed temperature for systems with less than 1% wetland cover. Error bars represent root mean square error for the LOADEST model.

correlated with any type of land cover. In addition, when temperature was included with wetland cover in a multiple regression across all 17 sites, the prediction did not improve. These results suggested the possibility that climate effects dominate concentration variability among low-wetland systems at the annual scale. Mean annual temperatures may be correlated with DOC concentration because longer growing seasons allow for greater primary production and thus greater production of soil organic material. However, it is clear that wetland controls eclipse climate effects in basins where wetlands are more extensive.

[30] In this study, we sampled across the hydrograph and estimated annual mean concentration and flux using LOADEST, which led to estimates that differed from those made previously. The mean DOC concentration for the Mississippi River reported by *Leenheer* [1982] (8.79 mg C L^{-1}) was more than double the mean concentration found in this study (4.0 mg C L^{-1}). The Mississippi is the largest river in North America so even a small percentage error in its concentration can lead to a large absolute error in the estimation of total continental land-sea flux. For example, the DOC flux estimate made by *Leenheer* [1982] for the Mississippi exceeded our estimate by 1.6 Tg/yr, nearly as much as the combined annual DOC flux from all other rivers in this study (1.9 Tg/yr). This estimate was later used by *Ludwig et al*. [1996] in the parameterization of a global continent-to-ocean organic carbon flux model.

[31] Some more recent studies are also partly based on values not updated in more than 30 years, which can include mean DOC concentrations based on only two to four measurements per year [*Alexander et al*., 1998; *Harrison et al*., 2005; *Lauerwald et al*., 2012; *Meybeck and Ragu*, 1996; *Seitzinger et al*., 2005]. For example, *Seitzinger et al*. [2005] and *Harrison et al*. [2005] use DOC concentration measurements at a Mississippi River gauging station recorded from 1978 to 1984, arriving at a mean concentration of 6.7 mg C L^{-1} ($n = 14$). However, we examined the USGS National Water Information System for historic DOC concentration measurements from the same station and found only a single value that exceeded 5 mg C L^{-1} in the period since 1997. The particular case of the Mississippi is illustrative because the historical USGS data show a dramatic shift between the 14 samples taken between 1978 and 1984 that led to the mean of 6.7 mg C L^{-1} and the far more numerous samples taken after 1997. In the early period, we found a mean concentration of 5.9 mg C L^{-1}, with a standard deviation of 2.6 mg C L^{-1} and during the later period from 1997 to 2012, the mean was 3.7 mg C L^{-1} with a standard deviation of only 0.5 mg C L^{-1}. The higher concentration and standard deviation in the early period were driven by a few very high concentration measurements. As previously shown, even a small overestimate of mean DOC concentration for a large river has the potential to result in huge absolute errors in the estimation of flux. By sampling for multiple years across the hydrograph, employing strict QA/QC, and estimating fluxes using the LOADEST model, we present an updated picture of the quantity of DOC recently delivered by these large rivers to estuaries and the coastal ocean.

4.2. DOC Chemical Character

[32] Basin-scale wetland cover was significantly correlated with mean DOC chemical character among large basins. The role of wetlands in controlling $SUVA_{254}$ has been previously demonstrated among small northern basins [*Agren et al*., 2008] but this is the first time such a clear relationship has been observed in a large and continental scale study. The role of wetlands in controlling $SUVA_{254}$ among large basins may be related to the previously discussed hypothesis that subsurface flow through mineral versus organic soil horizons can influence DOC concentration variability. Saturated, anaerobic conditions common in wetland soils can inhibit organic matter remineralization and lead to the persistence of semi-labile aromatic compounds in subsurface flow that would drive up $SUVA_{254}$ in the rivers and streams to which it is discharged [*Guillemette and del Giorgio*, 2011]. In the absence of wetlands, extensive biotic processing and the preferential sorption of strongly UV-absorbing, aromatic DOC molecules onto mineral soils, and in some specialized cases, onto sediments and particles within the stream channel, would drive down $SUVA_{254}$ [*Chorover and Amistadi*, 2001; *McKnight et al*., 2002; *McKnight et al*., 1992; *Meier et al*., 1999; *Perez et al*., 2011; *Tipping et al*., 1999]. Thus, if subsurface flow paths are less likely to intersect mineral horizons in watersheds with extensive wetland cover, less of the aromatic, strongly UV-absorbing DOC would be removed and DOC with a higher $SUVA_{254}$ would be more likely to enter river systems. The relationship between percent wetland cover and $SUVA_{254}$ in this study is strong, indicating that the wetland processes described here are important in large rivers at the annual scale. The lack of any statistically significant relationships between other land cover attributes and $SUVA_{254}$ further strengthens this interpretation. It is worth noting that the wetlands influencing the rivers described here range across a number of biomes and contain a wide range of vegetation types. In our analyses, we did not observe an influence of source (i.e., vegetation) differences on the $SUVA_{254}$ versus basin-scale wetland relationship and we found little evidence for source-based differences in DOC chemical character in the literature.

[33] The significant positive correlation between $SUVA_{254}$ and the HPOA fraction of bulk DOC was unsurprising because the HPOA fraction consists of aquatic fulvic and humic acids possessing greater aromaticity than other DOC fractions [*Aiken et al*., 1992]. These results suggest that $SUVA_{254}$ may be a useful surrogate for HPOA in organic carbon modeling applications [*Butman et al*., 2012; *Spencer et al*., 2012]. However, this relationship broke down within some individual basins (Mobile, Mississippi, and Colorado; Table 6), indicating that non-aromatic hydrophobic acids may constitute HPOA in some cases and that care should be taken when utilizing $SUVA_{254}$ as a proxy for HPOA.

4.3. Large River Versus Small Stream DOC Quantity and Chemical Character

[34] Several processes could lead to differences in DOC quantity and chemical character between small streams and large rivers including in-stream transformation of terrestrial headwater sources and additional DOC loads to large rivers not accounted for in small headwater catchment studies. While aquatic transformations may occur in smaller streams, we would expect their ability to influence DOC quantity and chemical character to be minimal at that point due to short residence times. Thus, headwater streams provide a signal of terrestrial influence. By the time water has reached large

Table 6. Table Showing Within-Basin Relationships Between Hydrophobic Organic Acid (HPOA) and Specific Ultraviolet Absorbance at 254 nm ($SUVA_{254}$)[a]

River Name	HPOA-$SUVA_{254}$ formula	R^2	*p*-value
Penobscot River	*ND*	*ND*	*ND*
Kennebec River	*ND*	*ND*	*ND*
Androscoggin River	*ND*	*ND*	*ND*
Susquehanna River	SUVA = 4.795 × HPOA + 0.346	0.64	< 0.001
Potomac River	SUVA = 6.584 × HPOA + −0.306	0.58	0.003
Edisto River	SUVA = 4.988 × HPOA + 1.061	0.54	0.001
Altamaha River	SUVA = 8.267 × HPOA + −0.577	0.39	< 0.001
St. Mary's River	SUVA = 2.738 × HPOA + 2.826	0.24	0.003
Santa Fe River	SUVA = 7.245 × HPOA + −0.19	0.87	< 0.001
Mobile River	*N/S*	*N/S*	0.201
St. Lawrence River	SUVA = 5.243 × HPOA + −0.18	0.64	< 0.001
Mississippi River	*N/S*	*N/S*	0.346
Rio Grande	SUVA = 6.013 × HPOA + −0.102	0.48	0.001
Colorado River	*N/S*	*N/S*	0.199
San Joaquin River	SUVA = 4.807 × HPOA + 0.43	0.40	0.009
Sacramento River	SUVA = 8.07 × HPOA + −0.825	0.76	< 0.001
Columbia River	SUVA = 8.754 × HPOA + −1.143	0.56	0.003

[a]Basins without a significant relationship are labeled *N/S*. *ND* indicates that no data were available.

rivers, aquatic processes such as microbial remineralization, sorption to sediments, and photodegradation could accumulate sufficiently to alter DOC [*Aufdenkampe et al.*, 2011; *McKnight et al.*, 2002; *McKnight et al.*, 1992; *Perez et al.*, 2011; *Richey et al.*, 1990; *Shih et al.*, 2010; *Weyhenmeyer et al.*, 2012]. Sources unique to large rivers could also alter large river DOC relative to smaller headwaters, including accumulated aquatic DOC production from primary producers [*Shih et al.*, 2010], different quantity or chemical character from large river floodplains compared to headwater wetlands, poorly understood groundwater inputs, and anthropogenic point sources [*Butman et al.*, 2012] which tend to be located on larger rivers due to the distribution of urban centers.

[35] Given all the potential factors that could alter DOC, it was surprising that the terrestrial wetland signal for both DOC quantity and character was so clear across most of the large watersheds. Percent wetland cover alone explained most of the DOC concentration and $SUVA_{254}$ variability among basins at the annual scale. When we compared the concentration versus wetland relationship observed here (equation (3)) to those observed in previous headwater studies [*Buffam et al.*, 2007; *Creed et al.*, 2003; *Eckhardt and Moore*, 1990; *Gergel et al.*, 1999; *Gorham et al.*, 1998; *Raymond and Hopkinson*, 2003], we found little obvious difference in absolute concentration, slope, or intercept (Figure 6).

[36] However, the presence of lakes and reservoirs with long residence times appears to alter this pattern, as suggested by the differing DOC quantity and/or chemical character in the Colorado River and St. Lawrence River outliers. Across all basins, we did not find a relationship between either percent reservoir cover or percent lake cover and DOC or $SUVA_{254}$. However, Lakes Mead and Powell on the Colorado River have a combined residence time of approximately 5 years [*USBR-LC*; *USBR-UC*], and Lake Ontario alone on the St. Lawrence has a residence time of approximately 6 years [*Beltran et al.*, 1995]. The extremely long residence times in these two outlier rivers might have driven down $SUVA_{254}$ by some combination of autochthonous production of less aromatic DOC, biotic processing, and photodegradation [*Miller*, 2012; *Spencer et al.*, 2012]. Previous studies suggest that in the Colorado River, artificially flooded canyons like Lake Powell act as a trap for organic material entering from upstream. Over time, settled organic matter can remineralize or adsorb onto precipitating calcite [*Reynolds*, 1978]. Water discharged from Glen Canyon Dam is left nutrient rich and nearly free of suspended particles. These conditions also facilitate autochthonous production of weakly UV-absorbing DOC in the downstream reach [*Henderson et al.*, 2008; *Stanford and Ward*, 1990].

[37] Extensive photodegradation and biological processing of terrestrially derived DOC during the long Great Lakes residence time and limited autochthonous production could explain the apparent conundrum in the St. Lawrence River

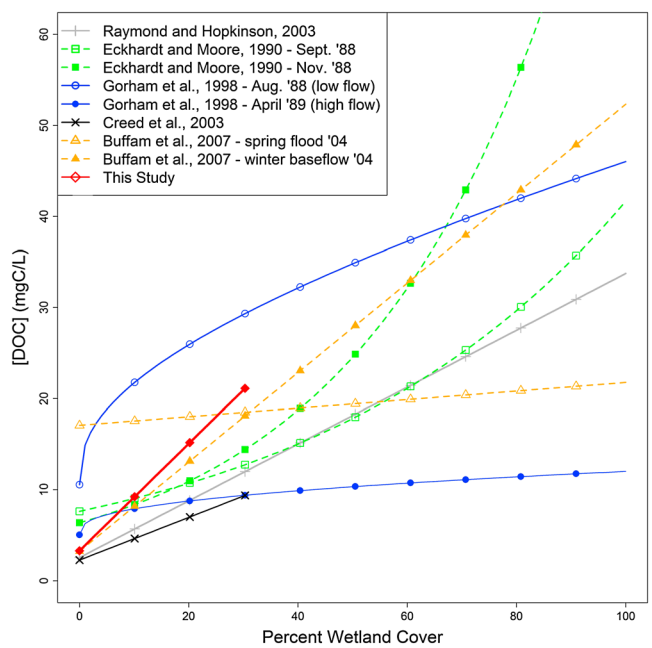

Figure 6. Dissolved organic carbon (DOC) concentration versus percent wetland cover relationships from Figure 2b, which excludes the St. Mary's River (red diamonds) and five previous small-basin studies.

of low DOC concentrations and very low $SUVA_{254}$ [*Helie and Hillaire-Marcel*, 2006]. Photodegradation acts primarily by breaking up strongly UV-absorbing molecules like terrestrial humic and fulvic acids [*Moran and Zepp*, 1997; *Waiser and Robarts*, 2004], which drive down $SUVA_{254}$ over time. Photodegradation of DOC has also been observed to result in an increase in its lability, leading to greater biotic remineralization [*Anesio et al.*, 2005]. Thus, in addition to driving down $SUVA_{254}$ in the St. Lawrence River, photodegradation could lead to increased biotic processing and provide an explanation for its comparatively low DOC concentration (Figure 2b).

[38] $SUVA_{254}$ end-members identified in this study were generally similar to those found in the literature [*Spencer et al.*, 2008; *Weishaar et al.*, 2003], further suggesting that larger river DOC is similar to that in smaller headwater streams. Maximum mean $SUVA_{254}$ in the wetland dominated St. Mary's (4.7 ± 0.3 L mg C^{-1} m^{-1}) was similar to that previously reported from specific wetland sites (3.2 to 5.3 L mg C^{-1} m^{-1}) [*Weishaar et al.*, 2003]. However, mean $SUVA_{254}$ for the six river basins with less than 1% wetland cover (Colorado River excluded) was 2.5 ± 0.2 L mg C^{-1} m^{-1}, significantly higher than algal or microbially derived $SUVA_{254}$ end-members found by *Stets et al.* [2010] for closed-basin, seepage lakes which ranged from 0.9 to 1.2 L mg C^{-1} m^{-1}. If biogeochemical processing played the primary role in driving $SUVA_{254}$ by breaking down aromatic allochthonous DOC, we would expect very low wetland systems to exhibit $SUVA_{254}$ values similar to previously identified end-members or values from very long residence time systems (St. Lawrence and Colorado Rivers: 1.3 and 1.7 L mg C^{-1} m^{-1}, respectively). Rather, these results support the hypothesis proposed by *del Giorgio and Pace* [2008] and *Richey et al.* [1990] that labile autochthonous material may be rapidly recycled while more refractory, generally allochthonous DOC is delivered to the coastal ocean.

[39] We found that in large systems lacking long residence time in surface waters, DOC concentration and chemical character were well predicted by percent wetland cover. This suggests that for these systems at annual scales, in-stream processes like autochthonous production, biotic remineralization, and photodegradation play a subordinate role in driving DOC quantity and chemical character compared to processes that load allochthonous DOC into the river system. It is likely that any new production is being quickly recycled by the biotic community rather than delivered in large quantities to the coastal ocean [*del Giorgio and Pace*, 2008; *Richey et al.*, 1990]. However, this finding is based on a relatively weak test that compares a mean annual DOC versus wetland relationship among heterogeneous large basins with snapshots from more homogeneous small basins in a variety of mostly northern regions. In addition, few comparative DOC chemical character studies in small basins have been conducted (but see *Jaffe et al.* [2008]). Finally, the tendency of smaller basins in this analysis to possess greater wetland coverage complicates the interpretation of our results because it is difficult to divorce the impact of basin size from wetlands. In order to fully evaluate the role of network-scale processing in driving annual DOC quantity and chemical character exported from large basins, more comprehensive, synoptic studies of DOC and DOC chemical character throughout river networks should be conducted.

5. Conclusion

[40] We demonstrated that wetlands play an integral role in controlling both DOC concentration and chemical character in 17 large and diverse North American rivers. The relationship between DOC and wetlands is similar to those previously reported for small watersheds. This result suggests that factors that may alter the terrestrial signal in large basins, such as in-stream processes, floodplain dynamics, or major anthropogenic inputs to large rivers, do not alter terrestrial control of carbon quantity and chemical character exports over annual time scales. The exceptions are surface water networks with long residence times, which suggest in-stream sources or transformations overwhelm the terrestrial signal. Our study is strengthened by the consistency of both DOC quantity and chemical character. These results supply valuable insight into the controls on mean DOC quantity and chemical character at broad spatial and temporal scales and provide new annual estimates of DOC flux and chemical character for several of the largest rivers in temperate North America. In order to better understand the source and fate of DOC in the environment, future efforts should include synoptic sampling of DOC quantity and chemical character, from headwaters through large river main stems, which would help unravel the hydrological processes that drive DOC variability within basins, the subsurface biogeochemical reactions that drive baseflow chemistry, and the biological and photolytic riverine processing that drives DOC quantity and chemical character over time.

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