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Variability in the Bulk Composition and Abundance of Dissolved Organic Matter In the Lower Mississippi and Pearl Rivers

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[1] In this study, we examined the temporal and spatial variability of dissolved organic matter (DOM) abundance and composition in the lower Mississippi and Pearl rivers and effects of human and natural influences. In particular, we looked at bulk C/N ratio, stable isotopes (δ^{15}N and δ^{13}C) and ^{13}C nuclear magnetic resonance (NMR) spectrometry of high molecular weight (HMW; 0.2 μm to 1 kDa) DOM. Monthly water samples were collected at one station in each river from August 2001 to 2003. Surveys of spatial variability of total dissolved organic carbon (DOC) and nitrogen (DON) were also conducted in June 2003, from 390 km downstream in the Mississippi River and from Jackson to Stennis Space Center in the Pearl River. Higher DOC (336−1170 μM), C/N ratio,% aromaticity, and more depleted δ^{15}N (0.76−2.1‰) were observed in the Pearl than in the lower Mississippi River (223−380 μM, 4.7−11.5‰, respectively). DOC, C/N ratio, δ^{13}C, δ^{15}N, and % aromaticity of Pearl River HMW DOM were correlated with water discharge, which indicated a coupling between local soil inputs and regional precipitation events. Conversely, seasonal variability in the lower Mississippi River was more controlled by spatial variability of a larger integrative signal from the watershed as well as in situ DOM processing. Spatially, very little change occurred in total DOC in the downstream survey of the lower Mississippi River, compared to a decrease of 24% in the Pearl River. Differences in DOM between these two rivers were reflective of the Mississippi River having more extensive river processing of terrestrial DOM, more phytoplankton inputs, and greater anthropogenic perturbation than the Pearl River.

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1. Introduction

[2] Temporal and spatial variation in the abundance and composition of riverine dissolved organic matter (DOM) is essential to better understand the hydrological and biogeochemical processes in rivers and their drainage basins [*Ittekkot et al.*, 1985; *Spitzy and Leenheer*, 1991; *Hedges et al.*, 2000; *E. Kaiser et al.*, 2004; *Dagg et al.*, 2005]. In most small streams, DOC and DON concentrations increase with water discharge [*Malcolm and Durum*, 1976; *Moore*, 1989; *Boyer et al.*, 1997], indicative of the origin of DOM from local soils and surface plant litter [e.g., *Engelhaupt and Bianchi*, 2001]. However, this relationship becomes more complicated for larger rivers that receive inputs from a broader diversity of tributaries that are hydrologically and chemically distinct [*Richey et al.*, 1990; *Leenheer et al.*, 1995; *Coynel et al.*, 2005]. While spatial variation in DOC concentrations for some near-pristine rivers have been shown to be minimal [*Richey et al.*, 1990; *Battin*, 1998; *Lara et al.*, 1998; *Brookshire et al.*, 2005], large decreases in downstream concentrations have been observed in human-perturbed large rivers (e.g., the Mississippi River [*Leenheer et al.*, 1995]). Thus separating natural versus anthropogenic controls in river biogeochemistry is becoming more critical with the expansion of human populations in watersheds around the world [*Meybeck*, 2003].

[3] Recent studies have shown that natural in situ processing and human activities may be important in controlling temporal and spatial changes in riverine DOM abundance and composition. For example, both in situ photochemical

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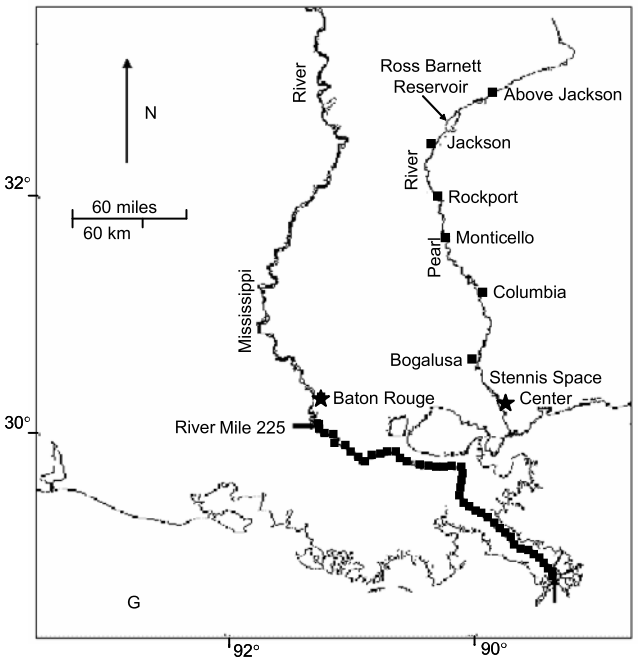

Figure 1. Map of the lower Mississippi and the Pearl rivers. Seasonal sampling at a site in the Mississippi River was above Baton Rouge (Louisiana), and near Stennis Space Center (Mississippi) for the Pearl River (stars in the map). Spatial samples were collected in the Mississippi River from river km 390 (just below Baton Rouge) to river mile 0 (Head of Passes). Downstream samples were collected in the Pearl River from above Jackson, Jackson, Rockport, Monticello, Columbia (Mississippi), Bogalusa (Louisiana), and two sites in Stennis Space Center (SSC and SSC′).

and microbial oxidation have been shown to be significant or even dominant mechanisms for removal of labile and alteration of refractory DOC [*Miller and Zepp*, 1995; *Amon and Benner*, 1996a, 1996b; *Opsahl and Benner*, 1998; *Obernosterer and Benner*, 2004; *Seitzinger et al.*, 2005]. In fact, outgassing of CO_2, the final product of bacterial and photochemical oxidation, from rivers and wetlands in the Amazon basin, was an order of magnitude greater than fluvial export of organic carbon to the ocean [*Richey et al.*, 2002]. Human activities also have caused changes in the sources and residence time of DOC in rivers around the world. For example, man-made levees have cut off inputs of terrigenous material from floodplains, while dam construction has increased the residence time of DOM and in situ processing in rivers [*Beckett and Pennington*, 1986; *Baker et al.*, 1991; *Wiener et al.*, 1996]. Intensive agricultural activities (e.g., tilling) have been shown to enhance organic carbon cycling in soils, thereby reducing the accumulation of organic carbon in subsoils [*Donigian et al.*, 1994; *Reicosky et al.*, 2002]. While the potential importance of these natural and anthropogenic factors of DOC cycling in rivers has recently received attention, few comparisons have been made on the overall differences in processing of organic matter across divergent river systems with significantly different watershed size [*Krusche et al.*, 2002].

[4] In this study, we compared a large anthropogenically altered river (Mississippi River) with a smaller less-perturbed river (Pearl River) to determine the effects of river size and human activities on the abundance and composition of riverine DOM. Our three working hypotheses for this study were that: (1) significant temporal changes in the abundance and bulk composition of DOM in the Pearl River are more controlled by hydrological transport of local inputs (forest soils and wetlands) from the drainage basin than in the Mississippi River which are largely controlled by upstream inputs from primary tributaries and in situ processing; (2) local inputs of DOM from forest soils and wetlands in the Pearl River result in greater spatial variability in DOC concentrations than the lower Mississippi River which should have a more "stable" signal produced from more distant upstream sources; (3) human perturbations have resulted in a more highly degraded terrestrial, as well as phytoplankton-derived DOM, in the lower Mississippi River than the Pearl River. These hypotheses were tested by examining the abundance and composition of bulk carbon and nitrogen of DOM in the lower reach of each river for two years. In addition to seasonal sampling, we also conducted a one-time spatial survey of DOM abundance in both rivers. Finally, bacterial abundance and production measurements were performed to better understand the role of bacterial degradation of DOM in these two rivers.

2. Materials and Methods

2.1. Drainage Basins

[5] The Mississippi is the largest river in North America which drains 40% of the continental United States, and a small part of Canada [*Meade*, 1996]. On average, it annually discharges 439 to 530 km^3 of freshwater, 3.5×10^9 kg DOC, and 0.38×10^9 kg DON to the Gulf of Mexico [*Leenheer*, 1982; *Goolsby and Battaglin*, 2000]. The drainage basin contains one of the most productive farming regions in the world, with cropland representing about 58% of the entire basin [*Goolsby et al.*, 2000]. Construction of high and low dams in the drainage basin has substantially reduced sediment discharges of the Mississippi River via sediment trapping [*Keown et al.*, 1986; *Meade et al.*, 1990]; the lower Mississippi River, from Cairo, Illinois, to the Gulf of Mexico, is constrained by a system of flood-control levees.

[6] The Pearl River is a small black-water river draining east-central Mississippi and southeastern Louisiana, and it enters into the Gulf of Mexico via Lake Borgne and the Mississippi Sound. It is approximately 790 km long and drains an area of 22,690 km^2. The drainage basin is dominated by natural forests (43%), followed by agricultural regions (27%). Marsh and/or swamp areas make up 10% of the land cover, and are all distributed along the river corridor (see http://www.dequation state.ms.us).

2.2. Sample Collection

[7] Monthly water samples were collected from September 2001 to August 2003 in the lower Mississippi River, and from August 2001 to July 2003 in the Pearl River. The lower Mississippi River sampling site was upstream of the U.S. Hwy. 190 Bridge, north of Baton Rouge, Louisiana. Samples from the Pearl River were collected at the Stennis

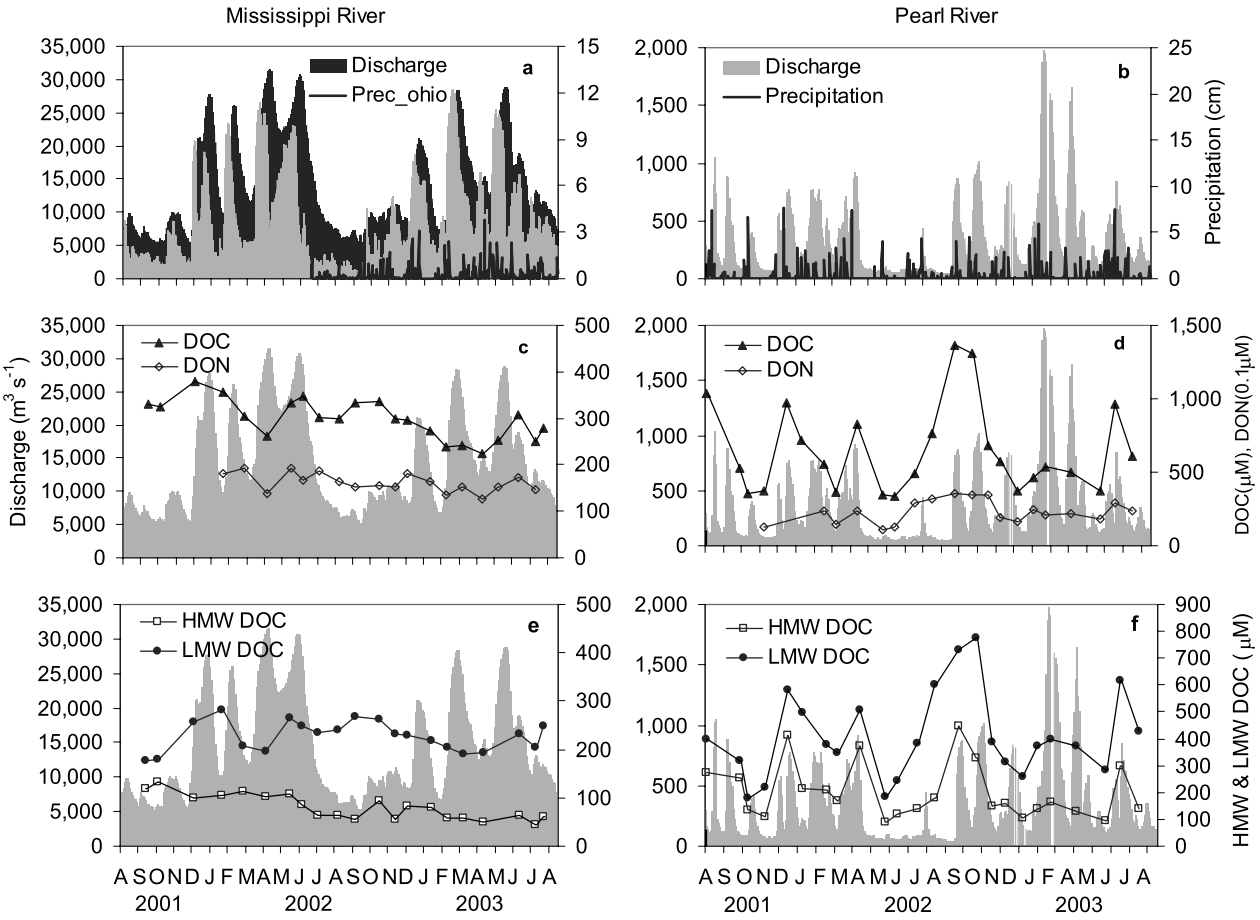

Figure 2. Water discharge, precipitation, DOC, DON, HMW DOC, and LMW DOC in the Mississippi River at Baton Rouge and in the Pearl River at Stennis Space Center from August 2001 to August 2003. (a) Black and gray area graphs are water discharges for the lower Mississippi River from Tarbert Landing and the Ohio River from Metropolis (Illinois); data of precipitation (prec-ohio) are means of seven hydrological stations in the main stem of the Ohio River. (b) Water discharge and precipitation were obtained from Bogalusa (Louisiana) and Columbia (Mississippi), respectively. DOC, HMW DOC, LMW DOC, and %HMW DOC in the Pearl River were significantly higher than in the lower Mississippi River ($p < 0.01$, one-way ANOVA, two tailed).

Space Center (NASA), Mississippi (Figure 1). In a limited attempt to investigate spatial variability of DOM abundance within the lower regions of these rivers, downstream samples were collected in June 2003. In the Mississippi River, we participated in an elaborate downstream Lagrangian experiment, which attempted to examine the chemical changes in a water mass, from just below Baton Rouge (LA) (river km 390) to Head of Passes (river km 0) [*Dagg et al.*, 2005] (Figure 1). Water samples were collected every two hours (or 6 to 10 km) for 4 days (noon of 20 June to noon of 24 June). For the Pearl River, samples were collected on June 5 at a few sites from a station several kilometers above Jackson (MS) downstream to our regular seasonal sampling site at the Stennis Space Center.

[8] For both seasonal and downriver sampling, duplicate whole water samples (2 liters) were collected midstream (just below the surface) in both rivers. During regular monthly sampling, approximately 40 L of filtered water samples were also collected by pumping (Masterflex peristaltic pump) water through a 0.2 μm Nuclepore filter cartridge (Whatman Co., England) for the collection of HMW DOM. Measurements of pH were determined at the time of sample collection using a temperature-compensated Beckman pH I-11 meter. HMW DOM was collected in the lab using an Amicon Proflux Tangential System Model M_{12} and a single spiral-wound ultrafiltration cartridge, with nominal pore size 1 kDa (Separation Engineering INC, CA). The integrity of the ultrafiltration cartridge was checked using the following macromolecules: raffinose, vitamin B-12, and cytochrome-c, according to the methods of *Guo and Santschi* [1996]. Percent recovery of total DOC during the ultrafiltration process ranged from 91.0 to 110.7%, indicating minimal loss and/or contamination during ultrafiltration. Immediately after ultrafiltration, HMW DOM was frozen and freeze-dried (lyophilized) with a LABCONCO (Freezone-6) System.

2.3. Chemical Analyses

[9] Samples for total DOC and total dissolved nitrogen (TDN) were filtered through precombusted (450°C) Whitman glass fiber filters (GF/F) after adding 100 μL of 2N HCl, to

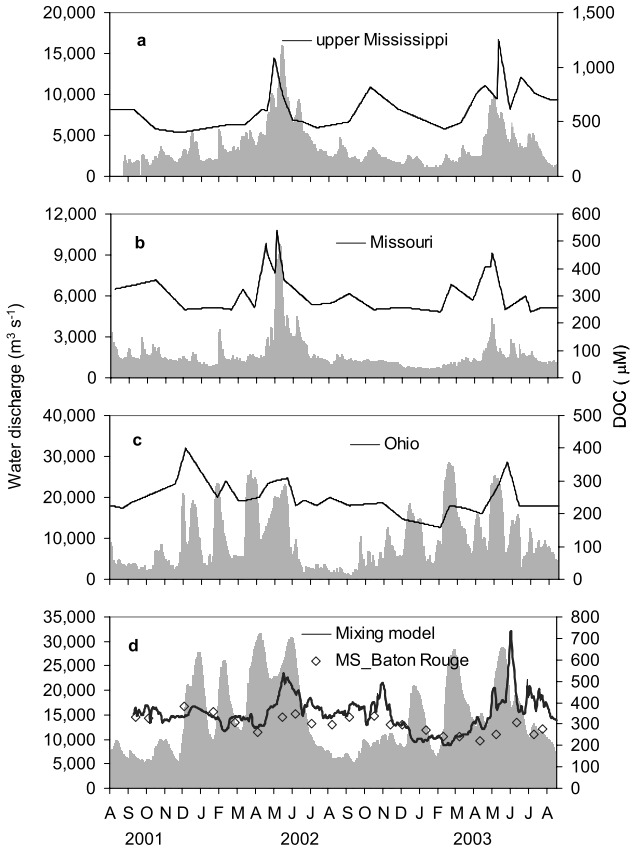

Figure 3. Seasonal variation in DOC concentration in the Mississippi River system: upper Mississippi River, Missouri and Ohio rivers, and lower Mississippi River at Baton Rouge. Predicted values of DOC in lower Mississippi River obtained by using a simple mixing model were used to compare with those in lower Mississippi River.

remove inorganic carbon. Both DOC and TDN were measured using high-temperature catalytic oxidation (HTCO) and chemiluminescence, respectively, on a Shimazu TOC-$V_{CSH/CSN}$ with precision of ±3% for both [*Guo et al.*, 1994; *Sharp et al.*, 2002]. Concentrations of dissolved organic nitrogen (DON) were obtained by subtracting total dissolved inorganic nitrogen (DIN) from TDN. Ultraviolet/visible (UV/VIS) spectra of GF/F filtered samples were measured using a 1601 UV/VIS spectrophotometer (Shimadzu Corp., Japan).

[10] Triplicate 5 mL and 10 mL subsamples of whole water were collected for bacterial abundance and production measurements, respectively. The 5 mL subsamples were fixed in 2% (final concentration) phosphate-buffered gluteraldehyde and stored at 4°C. Bacteria were stained with DAPI (5.0 μg mL^{-1}) concentrated on 0.2 μm polycarbonate filters (Poretics) [*Porter and Feig*, 1980], and counted at 1000 X magnification under epifluorescence illumination using an Olympus BX-50 microscope. Bacterial biomass production was estimated on the basis of shipboard measurements of ^{3}H-leucine incorporation [*Kirchman*, 1993]. Subsamples of 10 mL were transferred to sterile plastic 50 mL centrifuge tubes which resulted in a 10 nM final concentration of ^{3}H-leucine (American Radiolabled Chemicals Inc.; 60 Ci/mM). The tubes were then incubated for 45 min in a water bath containing ambient-temperature river water. Incubations were terminated by adding 1 mL 50% TCA to each tube. In the laboratory, the contents of each tube were filtered through a 25 mm 0.45 μm cellulose filter, rinsed twice with 3 mL of 5% ice-cold TCA, and then twice with 2 mL of ice cold 80% ethanol. Filters were then transferred to scintillation vials, allowed to dry completely, dissolved with 0.5 mL ethyl acetate, and assayed for ^{3}H after adding 10 mL hionic fluor (Packard). Bacterial production was calculated according to the methods of *Kirchman* [1993].

[11] Lyophilized samples of HMW DOM were placed in small combusted glass vials and acidified with 12 N HCl vapor for 24 hours to remove inorganic carbon [*Hedges and Stern*, 1984]. Acidified HMW DOM samples were then dried at 50°C for 1 hour and packed into solvent-cleaned tin boats and sent to the Stable Isotope Facility at University of California, Davis (http://stableisotopefacility.ucdavis.edu/) for total organic C, total N, δ^{13}C, and δ^{15}N analyses.

[12] Lyophilized HMW DOM samples were analyzed by solid-state cross polarization, magic-angle spinning (CP MAS) ^{13}C nuclear magnetic resonance (NMR) to determine carbon functionality. NMR spectra were obtained using the ramp CP MAS pulse program [*Metz et al.*, 1994], and two pulse phase modulated (TPPM) decoupling [*Bennett et al.*, 1995] on a Bruker DSX 300 NMR spectrometer, operating at a frequency of 75.48 MHz for ^{13}C. Approximately 40 to 80 mg of samples were placed in a 4 mm (outside diameter) NMR rotor with a Kel-F cap. Samples were spun at a frequency of 13 kHz using a contact time of 2 ms and a 1 s recycle delay time; 80,000 to 200,000 acquisitions (scans) were collected. For each sample, a free induction decay of 1,024 complex data points was collected and zero-filled to a total of 4096 data points. The acquired data were Fourier-transformed, and a 100 Hz line-broadening approach was applied and phased appropriately. The carboxyl carbon of glycine (176.03) provided a secondary reference for all ^{13}C-NMR solid-state spectra.

2.4. DOC Mixing Model

[13] A conservative mixing model was used to predict DOC concentration in the lower Mississippi River at Baton Rouge ($[DOC]_{LMR}$). The data for DOC concentrations of the upper Mississippi River (below Grafton, Illinois), the Missouri (at Hermann, Missouri), and Ohio River (at Dam 53 near Grand Chain, Illinois) were obtained from USGS websites (http://water.usgs.gov/nasqan). Daily water discharges of each tributary were available from USGS webpage (http://waterdata.usgs.gov/nwis/rt). Daily DOC data were interpolated from available measurements assuming linear variations. One outlier of DOC data of the Upper Mississippi River was excluded when interpolating. River water residence time from the confluence of the Missouri River to that of the Ohio River was estimated to be 4 days, and was assumed to be 11 days from the Ohio River confluence to Baton Rouge. DOC concentrations in Baton Rouge on day i were calculated by

$$\{[DOC]_i\}_{LMR} = \{(Q_{i-15} \times [DOC]_{i-15})_{UMR} + (Q_{i-15} \times [DOC]_{i-15})_{MO} + Q_{i-11} \times [DOC]_{i-11})_{OH}\} / \{(Q_{i-15})_{UMR} + (Q_{i-15})_{MO} + (Q_{i-11})_{OH}\},$$

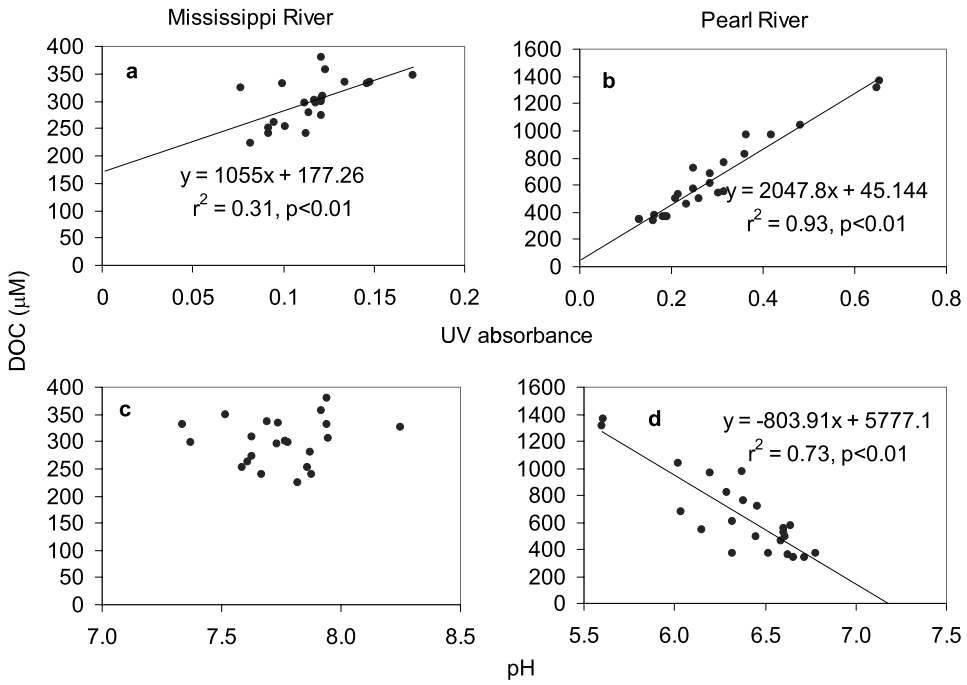

Figure 4. Relationship between UV absorbance at 254 nm (UV_{254}) or pH and DOC in the Mississippi and Pearl rivers. All the data sets were from seasonal sampling sites: Baton Rouge and Stennis Space Center. UV_{254} was significantly higher and pH was significantly lower in the lower Mississippi than in the Pearl River ($p < 0.01$, one-way ANOVA, two-tailed).

where, $(Q_{i\text{-}15}, [DOC]_{i\text{-}15}\}_{UMR}$ are water discharge and DOC concentration of Upper Mississippi River 15 days before day i (the residence time from confluence of upper Mississippi River to Baton Rouge); we also used a 15 day residence time for the Missouri River (MO) and 11 days for the Ohio River (OH). The assumption is that DOC behaved conservatively during transport and mixing, and that there was no loss or gain of DOC during transport in the lower Mississippi.

2.5. Statistical Analyses

[14] Correlation analysis was performed using Spearman Rank Correlation coefficient (EXCEL 2000, Microsoft Corporation, Washington). Statistically significant differences between the two rivers were determined using a One-way ANOVA ($\alpha = 0.01$) in the SPSS system. Means are reported with a 95% confidence interval.

3. Results

3.1. Seasonal Variations in Abundance of DOM

[15] Water discharge in the lower Mississippi River (at Tarbert Landing) was characterized by large seasonal shifts and was coupled with the discharge of Ohio River, the major contributor of water to the Mississippi River (Figure 2a). Water discharge in the Pearl River (at Bogalusa, Louisiana) was an order of magnitude lower and characterized by a high frequency of temporal variability (Figure 2b). The hydrograph of the Pearl River was highly coupled with local rainfall events, with precipitation peaks typically preceding those of water discharge.

[16] Concentrations of DOC and DON in the lower Mississippi River ranged from 223 to 380 μM and 12.7 to 19.3 μM, respectively, and showed small temporal variations (coefficients of variations (CVs) = 14% and 12%) (Figure 2c). No significant correlation was observed between DOC or DON and water discharge. DOC and DON concentrations in the Pearl River, at Stennis Space Center, ranged from 336 to 1370 μM and 11.4 to 35.6 μM, respectively, and DOC was significantly higher than that in the lower Mississippi River (Figure 2d). Larger seasonal variations were observed in DOC and DON in the Pearl River (CVs = 47% and 32%) than the lower Mississippi River, with highest values occurring during hurricane season in October 2002, and the lowest in summer during low-flow periods (e.g., May–June, 2002). DOC and DON were positively correlated with water discharge in the Pearl River ($r^2 = 0.49$ and 0.55, n = 22 and 17, respectively), only if the data from two extreme flooding events were excluded, as shown in March and April 2003 (Figure 2b).

[17] HMW DOC and low molecular weight (LMW) DOC (fraction <1 kDa) showed minor seasonal changes with river discharge in the lower Mississippi River. Conversely, their temporal variabilities were larger in the Pearl River, and were positively correlated with water discharge, if the data from the two extreme flooding events were excluded ($r^2 = 0.67$ and 0.39, n = 22) (Figures 2e and 2f). HMW DOC represented a minor fraction of total DOC in both the lower Mississippi and Pearl rivers. However, % HMW DOC in the lower Mississippi (13–38%, $\bar{x}$ = 25%) was significantly lower than in the Pearl River (23–47%, $\bar{x}$ = 35%).

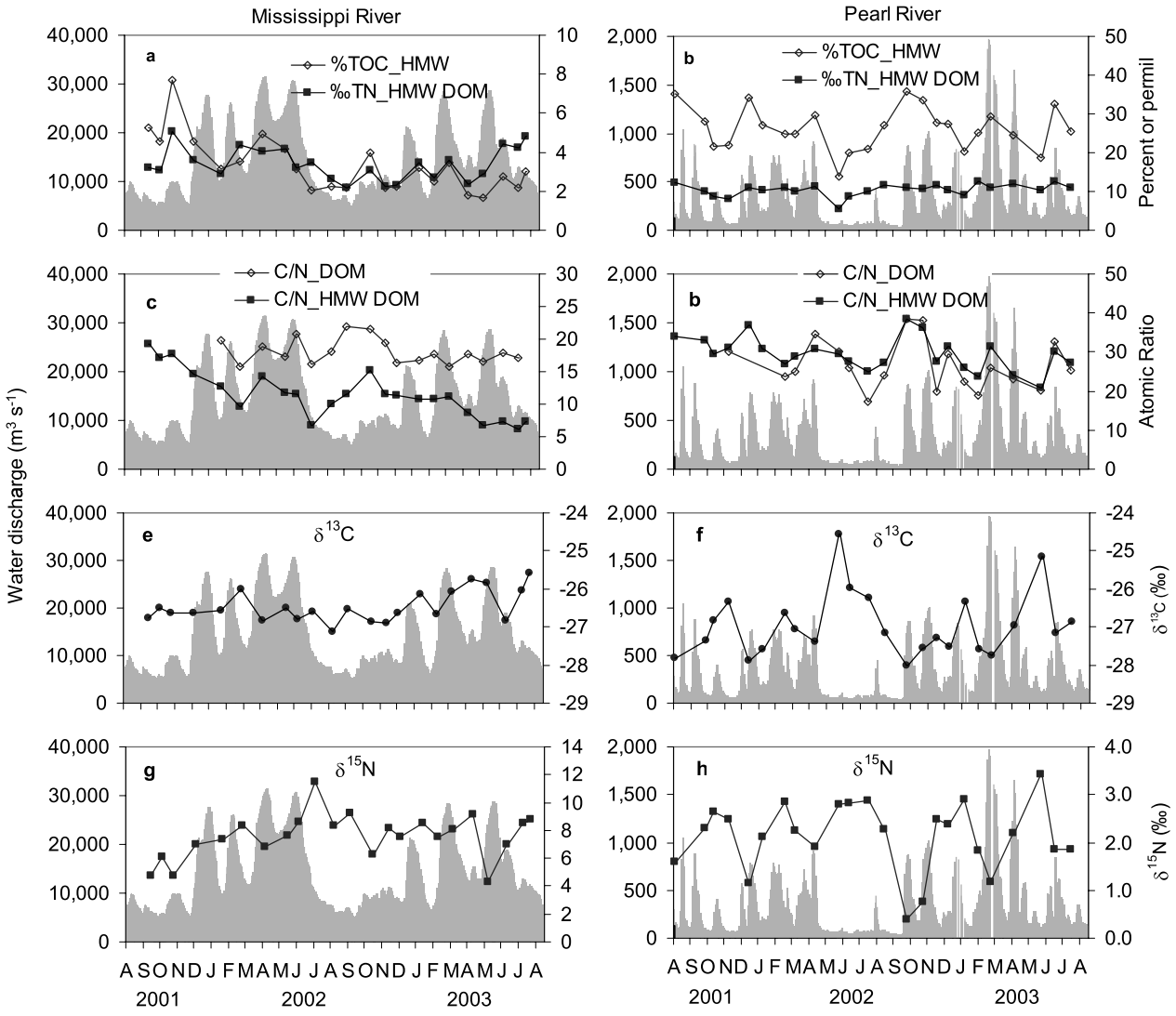

Figure 5. Organic carbon and nitrogen content, C/N ratios, and $\delta^{13}C$ and $\delta^{15}N$ of HMW DOM isolates in the lower Mississippi and Pearl rivers during August 2001 to August 2003. In Figures 5c and 5d, C/N ratios of DOM are also displayed for comparison. The Pearl River HMW DOM was significantly higher in C/N ratio, and more depleted in $\delta^{13}C$ and $\delta^{15}N$ than in the lower Mississippi River ($p < 0.01$, one-way ANOVA, two-tailed).

[18] Unlike the lower Mississippi River, DOC concentrations in the upper Mississippi and the Missouri rivers displayed large temporal variations that were positively correlated with water discharge ($r^2 = 0.53$ and 0.60, n = 23 and 32) (USGS data; see Figures 3a and 3b); we did not find this relationship in the lower Ohio River (Figure 3c). The predicted DOC values of the Mississippi River at Baton Rouge varied within ±18% of the actual measurements during the periods of September 2001 to April 2002 and August 2002 to March 2003, but were consistently 27 to 64% lower than the measurements during May–July, 2002 and April–August 2003 (Figure 3d).

[19] UV absorbance at 254 nm (UV_{254}) in the lower Mississippi was significantly lower than that in the Pearl River (Figures 4a and 4b). UV_{254} in the Pearl River was significantly correlated with DOC concentration ($r^2 = 0.93$, n = 24), and had an intercept (45 μM) considerably lower than the average DOC concentration. In contrast, UV_{254} and DOC in the lower Mississippi River were not correlated ($r^2 = 0.31$, n = 23), but had a higher intercept (177 μM) that was half of the average DOC concentration. The pH in the Pearl River ranged from 5.6 to 6.8 and was inversely correlated with DOC concentration ($r^2 = 0.73$, n = 24) (Figure 4c). Conversely, pH was relatively higher (7.3–8.3) in the lower Mississippi River and was not correlated with DOC (Figure 4d).

3.2. Seasonal Variations in Bulk Composition of HMW DOM

[20] Total organic C and total N percent (TOC% and TN%) of freeze-dried HMW DOM isolates in the lower Mississippi River ranged from 1.7 to 7.7% and 0.22 to 0.51%, respectively (Figure 5a). The C/N ratios of HMW DOM ranged from 6 to 19, lower than those observed in

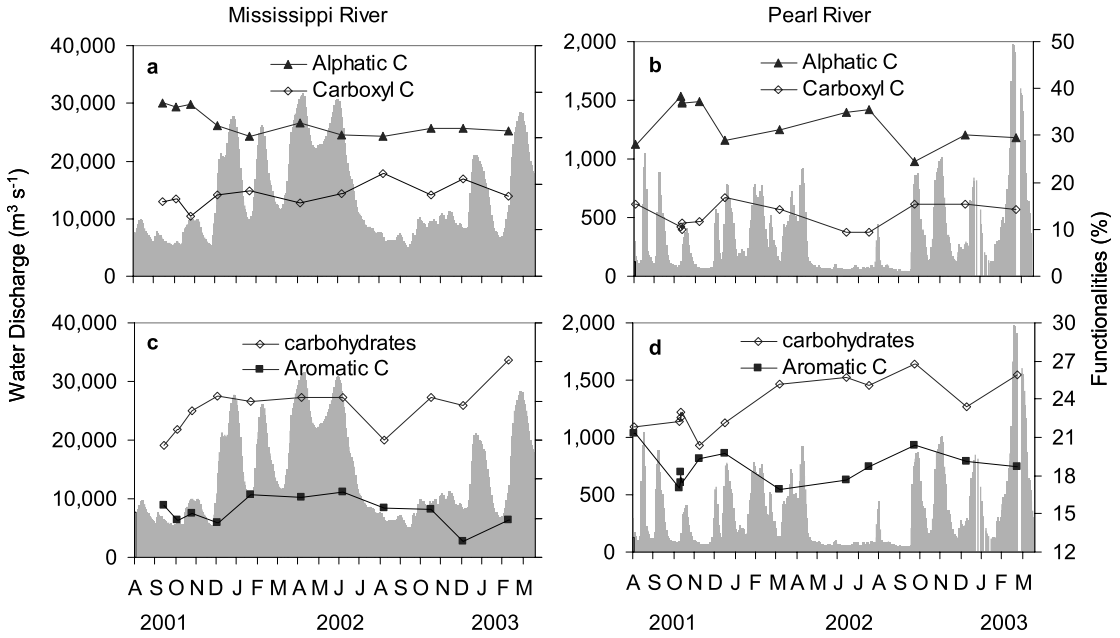

Figure 6. Percent area from ^{13}C-NMR spectra of HMW DOM collected from the lower Mississippi (at Baton Rouge) and Pearl rivers (at Stennis Space Center) from 2001 to 2003. Only selected samples of HMW DOM were analyzed by ^{13}C-NMR. Aliphatic carbons include paraffinic, methoxy, and carbon attached to amides. Anomeric carbon (90–110 ppm), and ketones and carbonyls (190–230 ppm) are not shown. The lower Mississippi River was significantly higher in carboxyl carbons and lower in aromatic carbons than the lower Mississippi ($p < 0.01$, one-way ANOVA, two-tailed).

total DOM (16–22) (Figure 5c). In the Pearl River, TOC% (14 to 36%), TN% (0.55 to 1.3%) and C/N ratios (21 to 38) averaged 7.9, 3.1, and 2.6 times higher than the same parameters in the lower Mississippi River, respectively (Figures 5b and 5d). Seasonally, TOC%, and C/N ratios of HMW DOM in the Pearl River were positively correlated with water discharge ($r^2 = 0.41$ and 0.31, $n = 22$), excluding the two extreme flooding events (e.g., March and April 2003).

[21] Bulk δ^{13}C and δ^{15}N values of HMW DOM from the lower Mississippi River ranged from −27.1 to −25.8‰ ($\bar{x}$ = −26.5) and 4.72 to 11.5‰ ($\bar{x}$ = 7.73), respectively (Figures 5e and 5g), with the highest δ^{15}N values (>8.4‰) occurring during the summer low-flow period of 2002. HMW DOM δ^{15}N and δ^{13}C ratios in the lower Mississippi River were not correlated with water discharge, but δ^{15}N ratios were inversely correlated with the C/N ratios (r^2 = 0.67, $n = 22$). δ^{13}C and δ^{15}N values of HMW DOM were more depleted in the Pearl River (−28.0 to −24.6‰, $\bar{x}$ = −27.0; 0.39 to 3.43‰, $\bar{x}$ = 2.16) than the same values in the lower Mississippi River (Figures 5f and 5h). The δ^{13}C and δ^{15}N ratios of HMW DOM from the Pearl River were inversely correlated with C/N ratios (r^2 = 0.51 and 0.58, $n = 24$) and water discharge (r^2 = 0.35 and 0.67, $n = 22$), again excluding data from the two extreme floods.

[22] HMW DOM from the Mississippi and the Pearl River displayed similar extents of carbon functionality (32% aliphatic carbons, 23–24% carbohydrates, 8% anomeric carbons, and 3–4% ketone and carbonyl carbons. However, HMW DOM from the lower Mississippi River was significantly higher in carboxyl C (13–22%, $\bar{x}$ = 18%) than the Pearl River (9.4–17%, $\bar{x}$ = 13%). The Pearl was significantly higher in aromatic C (or % aromaticity) (17–21%, $\bar{x}$ = 19%) than the lower Mississippi River (13–17%, $\bar{x}$ = 16%) (Figure 6). Seasonally, the percentage of carbohydrates in the lower Mississippi River appeared to increase during high discharge periods (e.g., through December 2001 to June 2002 and in February 2003) (Figure 6c). In the Pearl River, both carboxyl C and % aromaticity were higher during flooding stages (e.g., August and December 2001 and October 2002) and relatively lower during low-flow periods, while aliphatic C showed the opposite seasonal trend (Figures 6b and 6d).

3.3. Downstream Variation in DOM Abundance

[23] Concentrations of DOC and DON were largely unchanged during the lower Mississippi River transit from Baton Rouge (390 km) to Head of Passes during the experimental downstream sampling from 20 to 24 June 2003. C/N ratios and specific UV absorbance at 254 nm (SUVA) also showed no trend along the downstream transect, although DON and C/N ratios had larger CVs (13.7% and 13%) than DOC and SUVA (CV = 2% and 2.5%) (Figures 7a and 7c). Conversely, substantial decreases in both DOC (by 24.5%) and DON concentrations (by 44.9%) were observed during the downstream sampling in the Pearl River, resulting in an increase in C/N ratios from 25 to 35 (Figures 7b and 7d). SUVA in the Pearl River decreased by 16%, with the largest decrease from Monticello to Columbia, Mississippi (Figure 7d).

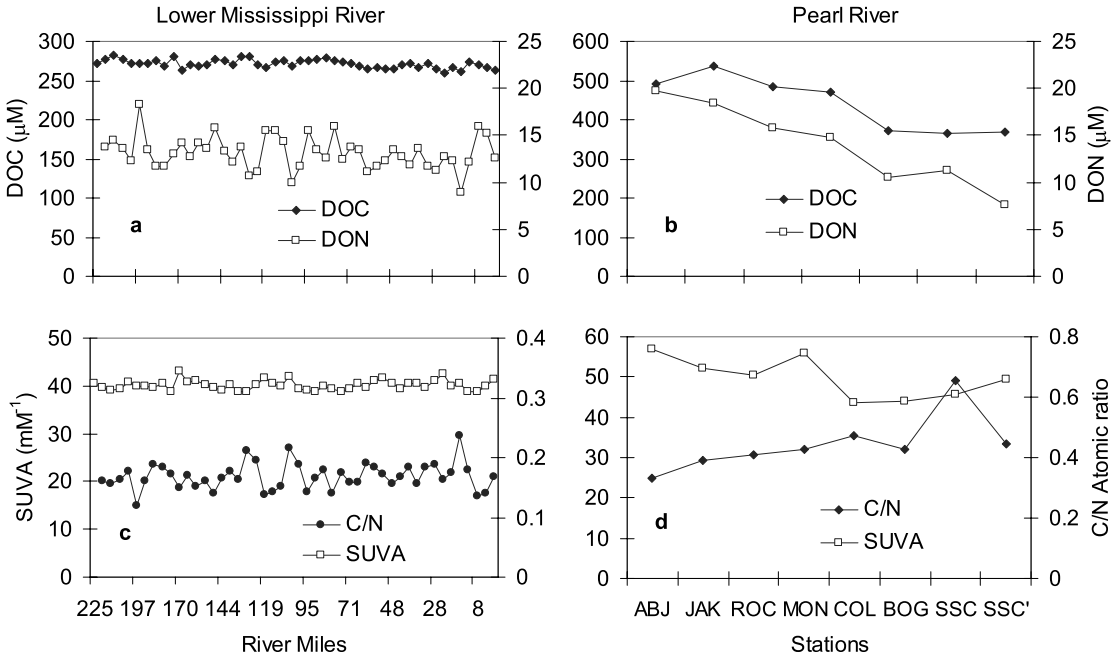

Figure 7. Downstream variations in DOC, DON, C/N of DOM and specific UV absorbance at 254 nm (SUVA) in (a, c) the lower Mississippi River and (b, d) the Pearl River. ABJ, JAC, ROC, MON, COL, BOG, SSC, and SSC′ stand for the station above Jackson, Jackson, Rockport, Columbia, Bogalusa, Stennis Space and Center (monthly sampling site), and another site in Stennis Space Center, respectively.

3.4. Bacterial Production and Abundance

[24] Bacterial production in the lower Mississippi River ranged from 0.7×10^{-4} μM C h^{-1} in November 2001 to 0.086 μM C h^{-1} in April 2002, with an average of 0.035 μM C h^{-1}. Bacterial production was positively correlated with water discharge and SUVA ($r^2 = 0.73$ and 0.64, n = 10), but not with other parameters (Figure 8). Bacterial abundance varied from 1.52×10^8 to 1.21×10^9 cell L^{-1}, with an average of 7.08×10^8. Only 3 bacterial samples were collected in the Pearl River during October 2001 (October 12 and October 13). The mean values of Pearl River bacterial production and abundance were 0.106 μM C h^{-1} and 7.25×10^8 cell L^{-1}, respectively. Bacterial production was 3 times higher in the Pearl River than that in the lower Mississippi River.

4. Discussion

4.1. Temporal Variation in the Abundance and Composition of DOM

4.1.1. Pearl River

[25] Our first hypothesis was that significant temporal changes in the abundance and bulk composition of DOM in the Pearl River are controlled more by hydrological transport of local inputs from the drainage basin, whereas changes in the same parameters in the Mississippi River are controlled largely by upstream inputs from primary tributaries and in situ processing. In support of this working hypothesis, we observed significant temporal changes in the abundance and bulk composition of DOM in the Pearl River that were coupled with local rainfall events. The abundance of DOC, DON, HMW DOM and LMW DOC and the bulk composition of HMW DOM (%TOC, C/N ratio, δ^{13}C and δ^{15}N) were all characterized by large seasonal variations (C.V. = 15−47%). In fact, these DOM parameters were correlated with river discharge, and local precipitation, if the two outlier points were excluded ($r^2 = 0.30-0.67$, n = 16 to 22) (Figures 2 and 5). Significant temporal variations in Pearl River DOM abundance and composition were likely controlled by transport of organic matter from local surface or deep soils, depending on hydrologic conditions. During rainfall events, total DOC and carboxyl and aromatic carbons in HMW DOM were generally enriched in the river when overland flow and interflow percolated through surface forest soils and wetlands. Other studies have shown higher DOC, more hydrophobic and acid fractions of DOM in surface soils than deep layers [*Cronan and Aiken*, 1985; *Williams and Melack*, 1997; *K. Kaiser et al.*, 2004; *Yano et al.*, 2004, 2005]. However, the highest values of DOM abundance and % aromacity did not occur during the most extreme rainfall events (March and April 2003), likely because of exhaustion of stored DOM sources in soils and wetlands [*Tipping et al.*, 1997]. During base flow, when river water was principally supplied by groundwater inputs from deep layers of soils, total DOC was generally low and with a higher proportion of hydrophilic C in the HMW DOM, consistent with prior work by *K. Kaiser et al.* [2004] and *Yano et al.* [2004]. Rapid changes in Pearl River DOM, concurrent with local hydrologic conditions, clearly demonstrated a strong connection between this river and local watershed processes. The character and composition of DOM in the Pearl River revealed that the dominant fraction of DOM was largely from recently mobilized DOM in local soils and plant litter. The small DOC intercept in the DOC

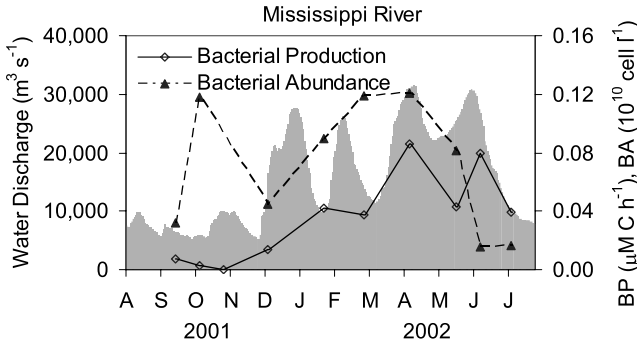

Figure 8. (a) Bacterial productivity and (b) abundance in the lower Mississippi from September 2001 to July 2002. BP, bacterial production; BA, bacterial abundance.

(45 μM) versus UV regression (Figure 4b), and the inverse relationship between pH and DOC (Figure 4d), suggested that Pearl River DOM largely consisted of CDOM. This may explain the larger degree of aromaticity of Pearl River HMW DOM compared to that of the Mississippi River HMW DOM. Moreover, HMW DOM δ^{13}C and δ^{15}N values of the Pearl River were in the range of C_3 plants [*Vitorello*, 1989; *Yoneyama*, 1996], which dominate in this watershed. High %TOC, %TN, and C/N ratios of HMW DOM also suggested that DOM in the Pearl River experienced minimal in situ river processing compared to the Mississippi River, presumably due to the shorter residence time of HMW DOM and rapid inputs from local adjacent soils and surface litter.

4.1.2. Mississippi River

[26] Minimal seasonal changes in DOM abundance and bulk composition showed no correlation with water discharge in the lower Mississippi River (Figures 3 and 5). This supports our working hypothesis that DOM was less controlled by hydrological transport of local inputs in this large river. DOM concentration in the lower Mississippi River was controlled more by upstream inputs from the primary tributaries and in situ processing. There is a general agreement between the observed DOC concentration and the model prediction during most months (September 2001 to April 2002, and August 2002 to March 2003) (Figure 3). This implies that seasonal variations in DOC abundance in the lower Mississippi River are largely the result of mixing water from the three primary tributaries. However, significantly lower values of DOC, compared to the predicted values during May–July 2002 and April–August 2003, indicates that in situ processing of DOM in the lower Mississippi River might have also played an important role during these periods. When considering that bacterial production in rivers is generally higher during high-flow periods (Figure 8), the difference during these two periods may have been due to greater uptake as a result of higher bioavailability of DOM. The higher bacterial production during high-flow periods, also observed in other studies [e.g., *Benner et al.*, 1995], was likely due to increased import of soil bacteria.

[27] The character of DOM and the composition of HMW DOM in the lower Mississippi River indicated that this material had been subjected to long-term in situ river processing. For example, the large positive intercept of the DOC-UV_{254} relationship and high pH values (7.3–8.3) (Figures 3a and 3c) indicated that the dominant fraction of DOM in the lower Mississippi was not CDOM or acidic in character. Rather, the DOM, which was likely derived from soils, appears to be "bleached" or oxidized on the basis of spectroscopic analyses. Additionally, the lower percentages of HMW DOC, TOC, TN and aromaticity in HMW DOM isolates, compared to the same parameters in the Pearl River, provides additional evidence for photochemical and microbial removal of organic matter [*Amon and Benner*, 1996a, 1996b; *Kohler et al.*, 2002; *Shiller et al.*, 2006]. Other work has also shown that when HMW DOM is exposed to bacterial decomposition and photochemical oxidation, aromatic carbons decrease and carboxyl carbons increase [*Engelhaupt and Bianchi*, 2001; *Osburn et al.*, 2001].

4.2. Spatial Variation in the Abundance of DOM

4.2.1. Pearl River

[28] Another key hypothesis in this study was that local inputs of DOM from forest soils and wetlands in the Pearl River result in greater spatial variability in DOC concentration compared to the DOC variability in the lower Mississippi River. While large downstream decreases in DOM abundance in the Pearl River do support this hypothesis, mechanisms responsible for such spatial variability remain largely unexplained. When considering the DOM character in field samples and in a photochemical incubation experiment [*Shiller et al.*, 2006], DOM in the Pearl River was more photoreactive. Thus photochemical loss likely contributed to the observed downstream decrease in the DOM abundance and SUVA (Figure 7). To further test the plausibility of this, we multiplied the rate of photochemical oxidation (0.233 μM C h^{-1}), obtained from our incubation study [*Shiller et al.*, 2006], with river residence time (6 days), acquired by comparing hydrographs at the station above Jackson to Stennis Space Center. Our results show an estimated loss of 33.6 μM of organic carbon via photochemical oxidation, which accounts for only 28% of the spatial differential. This estimated photooxidation rate is not likely an overestimate, considering the shallow water depths and low suspended particulate matter concentrations in the Pearl River [*Duan and Bianchi*, 2006]. Therefore other processes (e.g., bacterial degradation and dilution by low-DOC inputs) may account for most of the downstream decreases in DOC in the Pearl River. Other lab experiments with water from small streams showed that bacterial degradation can account for losses of DOC and DON up to 40 to 50% [*Kaushal and Lewis*, 2005; *Seitzinger et al.*, 2005]. Finally, downstream decreases in the DOM abundance may also be related to summer base-flow periods, where higher temperatures and more light availability may allow for greater bacterial and photochemical oxidation of DOM. Further work is clearly needed to examine the importance of these mechanisms in controlling temporal variations in DOM in river systems.

4.2.2. Mississippi River

[29] The lower Mississippi River was observed to have a spatially more "stable" DOC concentration than the Pearl River, further supporting our initial working hypothesis. This spatial stability was consistent with minimal temporal variation and lower bacterial production, compared to these

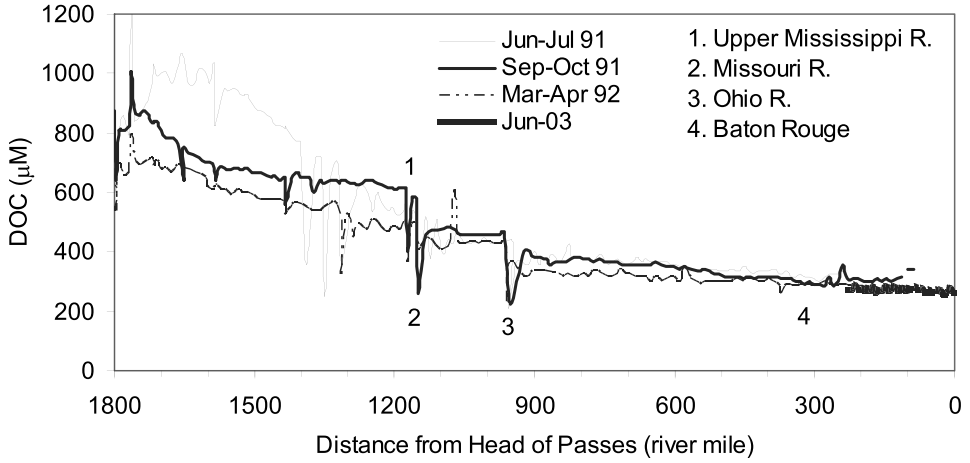

Figure 9. Downstream variation of DOC concentration in the Mississippi River, from river mile 1800 in upper Mississippi River to Head of Passes. Data for June–July 1991, September–October 1991, and March–April 1992 were obtained from U.S. Geological Survey.

parameters in the Pearl River. It suggests a refractory state for Mississippi River DOM. The relatively "stable" DOC signal in the lower Mississippi River was likely the result of long-term in situ processing that occurred during transport from the upper to lower river. This is further supported by USGS DOC data which display a more rapid reduction in DOC concentration in the upper Mississippi River (by 28–48%) than in the lower river (by 6.5–8.1%) (Figure 9). The decline in the rate of spatial decrease in DOC occurred because DOM became progressively more refractory downstream with increasing residence time and in situ processing. Sharp decreases in DOC (by 14 to 22%), downstream of the confluence of the Missouri and Ohio rivers, were likely due to a "dilution effect" because of the low DOC found in these tributaries (Figure 3). The more rapid loss of DOC in the upper Mississippi River, compared to the loss in the lower river, also might be attributed to different physical conditions; reduced water depth and lower suspended sediment load in the upper river might enhance photochemical oxidation.

4.3. Anthropogenic Effects on DOM in the Lower Mississippi River

[30] Our hypothesis that intense human influences lead to a more highly degraded terrestrial DOM source and greater phytoplankton-derived DOM in the lower Mississippi River is supported by this study. For example, consistent decreases in DOC below the confluence of the upper tributaries, followed by an asymptotic leveling of concentration in the lower Mississippi River (Figure 9), were likely reflective of "isolation" effects that artificial levees have on river water. Artificial levees in the lower Mississippi River have resulted in a reduction of about 90% of the local watershed inputs in the region of levee construction [*Beckett and Pennington*, 1986; *Baker et al.*, 1991; *Wiener et al.*, 1996]. Thus changes in DOM character are mostly from in situ production and processing. The composition of DOM in the lower river may actually reflect highly processed materials (both terrestrial and aquatic) that were introduced above and below the confluence. The long residence time and processing of these inputs from upstream sources may be responsible for the relative stability observed in DOC concentrations in the Mississippi River relative to the Pearl River. Natural levee systems in other large lowland river systems (e.g., the Amazon) allow local riparian inputs and display different spatial variability of DOC from the lower Mississippi River, despite similarities in residence time and in situ processing of DOM [*Lara et al.*, 1998; *Hedges et al.*, 2000]. The Mississippi River drains more cropland area (58%) than the Pearl River (27%) and contains thousands of dams compared to only one in the Pearl River Basin [*Meade et al.*, 1990; *Goolsby et al.*, 2000] (http://www.dequation state.ms.us). Dam construction increases in situ processing time of riverine DOM, while tilling activity enhances carbon cycling and reduces inputs of humic substances [*Donigian et al.*, 1994; *Reicosky et al.*, 2002]. Fluxes of organic carbon from agricultural catchments were found to be lower than those from natural systems [*Kaplan and Newbold*, 1993]. These differences in land-use practices, as well as in situ processing of DOM may also explain the lower concentrations of DOC in the lower Mississippi River.

[31] In addition to increased in situ residence time, the construction of dams in the Mississippi River has also decreased the concentration of total suspended solids and flow velocity [*Keown et al.*, 1986; *Meade et al.*, 1990]. These changes, together with increased nutrient concentrations, have greatly enhanced the growth of phytoplankton behind the dams and in the free-flowing portions of the Mississippi River [*Wehr and Thorp*, 1997; *Knowlton and Jones*, 2000; *Duan and Bianchi*, 2006]. Significantly lower C/N ratios of HMW DOM in the Mississippi River (Figure 5) [*Rostad et al.*, 1997] compared with those ratios in the Pearl River and other large less-disturbed rivers (e.g., Amazon [*Hedges et al.*, 2000]) further supports the importance of phytoplankton inputs to the lower Mississippi River DOM pool [*Bianchi et al.*, 2004]. Moreover, more enriched δ^{15}N values in the lower Mississippi River HMW DOM likely resulted from phytoplankton-derived organic matter sources, as suggested by recent findings that phytoplankton biomass in the Mississippi River was enriched in δ^{15}N [*Delong and Thorp*, 2006]. The lower % aromaticity and lower fraction of CDOM in the lower Mississippi River

compared to these values in the Pearl River are consistent with the input of phytoplankton DOM, which is less aromatic and photoreactive than terrestrially derived DOM [*Sannigrahi et al.*, 2005; *Obernosterer and Benner*, 2004].

5. Conclusions and Implications

[32] Seasonal variations in DOM abundance and composition in the Pearl River are controlled more by local rainfall events coupled with a shifting from groundwater inputs during base flow to surface soil inputs during rainfall events. However, minimal seasonal changes in DOM in the lower Mississippi River likely occurred because of a highly processed integrated signal from tributaries upstream, as well as the longer residence time for in situ processing of DOM from upper basin sources. A large proportion of DOM losses occurred during the "shorter" transport time in the Pearl River because local inputs of DOM were relatively "fresh" and more sensitive to bacterial and photochemical oxidation. The lower Mississippi River showed no significant downstream losses of DOC because the DOC in this region was composed of more highly processed soil-derived and phytoplankton-derived DOM which had lower % aromaticity, making it less photoreactive. Human activities such as replacement of forests/wetland with cropland and construction of levees and dams in the drainage basin also contributed to the temporal and spatial distribution of DOM in lower Mississippi River.

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References

Amon, R. M. W., and R. Benner (1996a), Bacterial utilization of different size classes of dissolved organic matter, *Limnol. Oceanogr.*, *41*, 41–51.

Amon, R. M. W., and R. Benner (1996b), Photochemical and microbial consumption of dissolved organic carbon and dissolved oxygen in the Amazon River system, *Geochim. Cosmochim. Acta*, *60*, 1783–1792.

Baker, J. A., K. J. Killgore, and R. L. Kasul (1991), Aquatic habitats and fish communities in the lower Mississippi River, *Rev. Aquat. Sci.*, *3*, 313–356.

Battin, T. J. (1998), Dissolved organic matter and its optical properties in a blackwater tributary of the upper Orinoco River, Venezuela, *Org. Geochem.*, *28*, 561–569.

Beckett, D. C., and C. H. Pennington (1986), Water quality, macroinvertebrates, larval fishes, and fishes of the lower Mississippi River—A synthesis, *U.S. Army Corps Eng. Tech. Rep. E-86-12*, 136 pp., Waterways Exper. Stn., Vicksburg, Miss.

Benner, R., S. Opsahl, G. ChinLeo, J. E. Richey, and B. R. Forsberg (1995), Bacterial carbon metabolism in the Amazon River system, *Limnol. Oceanogr.*, *40*, 1262–1270.

Bennett, A. E., C. M. Riensta, M. Auger, K. V. Lakshmi, and R. G. Griffin (1995), Heteronuclear decoupling in rotating solids, *J. Chem. Phys.*, *103*, 6951–6958.

Bianchi, T. S., T. Filley, K. Dria, and P. Hatcher (2004), Temporal variability in sources of dissolved organic carbon in the lower Mississippi River, *Geochim. Cosmochim. Acta*, *68*, 959–967.

Boyer, E. W., et al. (1997), Response characteristics of DOC flushing in an alpine catchment, *Hydrol. Processes*, *11*, 1635–1647.

Brookshire, E. N. J., H. M. Valett, S. A. Thomas, and J. R. Webster (2005), Coupled cycling of dissolved organic nitrogen and carbon in a forest stream, *Ecology*, *86*, 2487–2496.

Coynel, A., P. Seyler, H. Etcheber, M. Meybeck, and D. Orange (2005), Spatial and seasonal dynamics of total suspended sediment and organic carbon species in the Congo River, *Global Biogeochem. Cycles*, *19*, GB4019, doi:10.1029/2004GB002335.

Cronan, C. S., and G. R. Aiken (1985), Chemistry and transport of soluble humic substances in forested watersheds of the Adirondack Park, New York, *Geochim. Cosmochim. Acta*, *49*, 1697–1705.

Dagg, M. J., et al. (2005), Biogeochemical characteristics of the lower Mississippi River, USA, during June 2003, *Estuaries*, *28*, 664–674.

Delong, M. D., and J. H. Thorp (2006), Significance of instream autotrophs in trophic dynamics of the Upper Mississippi River, *Oecologia*, *147*, 76–85.

Donigian, A. S., et al. (1994), Assessment of alternative management practices and policies affecting soil carbon in agroecosystems of central United States, *Rep. EPA/600/R-94/067*, U.S. Environ. Prot. Agency, Athens, Ga.

Duan, S. W., and T. S. Bianchi (2006), Seasonal changes in the abundance and composition of plant pigments in particulate organic carbon in the lower Mississippi and Pearl rivers (USA), *Estuaries Coasts*, *29*, 427–442.

Engelhaupt, E., and T. S. Bianchi (2001), Sources and composition of high-molecular-weight dissolved organic carbon in a southern Louisiana tidal stream (Bayou Trepagnier), *Limnol. Oceanogr.*, *46*, 917–926.

Goolsby, D. A., et al. (2000), Nitrogen flux and sources in the Mississippi River Basin, *Sci. Total Environ.*, *248*, 75–86.

Guo, L. D., and P. H. Santschi (1996), A critical evaluation of the cross-flow ultrafiltration technique for sampling colloidal organic carbon in seawater, *Mar. Chem.*, *55*, 113–127.

Guo, L. D., C. H. Coleman Jr., and P. H. Santschi (1994), The distribution of colloidal and dissolved organic carbon in the Gulf of Mexico, *Mar. Chem.*, *45*, 105–119.

Hedges, J. I., and J. H. Stern (1984), Carbon and nitrogen determinations of carbonate-containing solids, *Limnol. Oceanogr.*, *29*, 657–663.

Hedges, J. I., et al. (2000), Organic matter in Bolivian tributaries of the Amazon River: A comparison to the lower mainstream, *Limnol. Oceanogr.*, *45*, 1449–1466.

Ittekkot, V., S. Safiullah, B. Mycke, and R. Seifert (1985), Seasonal variability and geochemical significance of organic matter in the River Ganges, Bangladesh, *Nature*, *317*, 800–803.

Kaiser, E., D. B. Arscott, K. Tockner, and B. Sulzberger (2004), Sources and distribution of organic carbon and nitrogen in the Tagliamento River, Italy, *Aquat. Sci.*, *66*, 103–116.

Kaiser, K., G. Guggenberger, and L. Haumaier (2004), Changes in dissolved lignin-derived phenols, neutral sugars, uronic acids, and amino sugars with depth in forested haplic arenosols and rendzic leptosols, *Biogeochemistry*, *70*, 135–151.

Kaplan, L. A., and J. D. Newbold (1993), Biogeochemistry of dissolved organic carbon entering steams, in *Aquatic Microbiology: An Ecological Approach*, edited by T. E. Ford, pp. 139–165, Blackwell Sci., Malden, Mass.

Kaushal, S. S., and W. M. Lewis (2005), Fate and transport of organic nitrogen in minimally disturbed montane streams of Colorado, USA, *Biogeochemistry*, *74*, 303–321.

Keown, M. P., E. A. Dardeau, and E. M. Causey (1986), Historic trends in the sediment flow regime of the Mississippi River, *Water Resour. Res.*, *22*, 1555–1564.

Kirchman, D. L. (1993), Leucine incorporation as a measure of biomass production by heterotrophic bacteria, in *Handbook of Methods in Aquatic Microbial Ecology*, edited by M. F. Kemp et al., pp. 509–512, CRC Press, Boca Raton, Fla.

Knowlton, M. F., and J. R. Jones (2000), Seston, light, nutrients and chlorophyll in the lower Missouri River, 1984–1998, *J. Freshwater Ecol.*, *15*, 283–297.

Kohler, S., I. Buffam, A. Jonsson, and K. Bishop (2002), Photochemical and microbial processing of stream and soil water dissolved organic matter in a boreal forested catchment in northern Sweden, *Aquat. Sci.*, *64*, 269–281.

Krusche, A. V., et al. (2002), Composition of particulate and dissolved organic matter in a disturbed watershed of southeast Brazil (Piracicaba River Basin), *Water Res.*, *36*, 2743–2752.

Lara, R. J., et al. (1998), Dissolved organic matter and nutrients in the Lena River, Siberian Arctic: Characteristics and distribution, *Mar. Chem.*, *59*, 301–309.

Leenheer, J. (1982), United States Geological Survey Data Information Service, in *Transport of Carbon and Minerals in Major World Rivers, Part I*, edited by E. T. Degens, Sonderbd. 52, pp. 355–356, SCOPE/U.N. Environ. Prog., Mitt. Geol.-Paläont. Inst., Univ. of Hamburg, Germany.

Leenheer, J. A., et al. (1995), Data on natural organic substances in dissolved, colloidal, suspended-silt, and -clay and bed-sediment phases

in the Mississippi River and some of its tributaries, 1991–1992, *U.S. Geol. Surv. Water Resour. Invest. Rep. 94-4191*, Denver, Colo.

Malcolm, R., and W. H. Durum (1976), Organic carbon and nitrogen concentrations and organic load of six selected rivers of the United States, *U.S. Geol. Surv. Water Supply Pap.*, *1817F*, 1–29.

Meade, R. H. (1996), River-sediment inputs to major deltas, in *Sea-Level Rise and Coastal Subsidence*, edited by J. Miliman and B. Haq, pp. 63–85, Springer, New York.

Meade, R. H., T. R. Yuzyk, and T. J. Day (1990), Movement and storage of sediment in rivers of the United States and Canada, in *Surface Water Hydrology*, edited by M. G. Wolman and H. C. Riggs, pp. 255–280, Geol. Soc. of Am., Boulder, Colo.

Metz, G., X. Wu, and S. O. Smith (1994), Ramped-amplitude cross polarization in magic-angle-spinning NMR, *J. Magn. Reson.*, *110*, 219–227.

Meybeck, M. (2003), Global analysis of river systems: From Earth system controls to Anthropocene syndromes, *Philos. Trans. R. Soc., Ser. B*, *358*, 1935–1955.

Miller, W. L., and R. G. Zepp (1995), Photochemical production of dissolved inorganic carbon from terrestrial organic matter: Significance to the oceanic organic carbon cycle, *Geophys. Res. Lett.*, *22*, 417–420.

Moore, T. R. (1989), Dynamics of dissolved organic carbon in forested and disturbed catchments, Westland, New Zealand: 1. Maimai, *Water Resour. Res.*, *25*, 1321–1330.

Obernosterer, I., and R. Benner (2004), Competition between biological and photochemical processes in the mineralization of dissolved organic carbon, *Limnol. Oceanogr.*, *49*, 117–124.

Opsahl, S., and R. Benner (1998), Photochemical reactivity of dissolved lignin in river and ocean waters, *Limnol. Oceanogr.*, *43*, 1297–1304.

Osburn, C. L., et al. (2001), Chemical and optical changes in freshwater dissolved organic matter exposed to solar radiation, *Biogeochemistry*, *54*, 251–278.

Porter, K. G., and Y. S. Feig (1980), The use of DAPI for identifying and counting aquatic microflora, *Limnol. Oceanogr.*, *25*, 943–948.

Reicosky, D. C., et al. (2002), Continuous corn with moldboard tillage: Residue and fertility effects on soil carbon, *J. Soil Water Conserv.*, *5*, 277–284.

Richey, J. E., J. I. Hedges, A. H. Devol, P. D. Quay, R. Victoria, L. Martinelli, and B. R. Forsberg (1990), Biogeochemistry of carbon in the Amazon River, *Limnol. Oceanogr.*, *35*, 352–371.

Richey, J. E., et al. (2002), Outgassing from Amazonian rivers and wetlands as a large tropical source of atmospheric CO_2, *Nature*, *416*, 617–620.

Rostad, C. E., J. A. Leenheer, and S. R. Daniel (1997), Organic carbon and nitrogen content associated with colloids and suspended particulates from the Mississippi River and some of its tributaries, *Environ. Sci. Technol.*, *31*, 3218–3225.

Sannigrahi, P., E. D. Ingall, and R. Benner (2005), Cycling of dissolved and particulate organic matter at station Aloha: Insights from C-13 NMR spectroscopy coupled with elemental, isotopic and molecular analyses, *Deep Sea Res., Part I*, *52*, 1429–1444.

Seitzinger, S. P., H. Hartnett, R. Lauck, M. Mazurek, T. Minegishi, G. Spyres, and R. Styles (2005), Molecular-level chemical characterization and bioavailability of dissolved organic matter in stream water using electrospray-ionization mass spectrometry, *Limnol. Oceanogr.*, *50*, 1–12.

Sharp, J. H., et al. (2002), A preliminary methods comparison for measurement of dissolved organic nitrogen in seawater, *Mar. Chem.*, *78*, 171–184.

Shiller, A. M., S. W. Duan, P. Erp, and T. S. Bianchi (2006), Photo-oxidation of dissolved organic matter in river water and its effect on trace element speciation, *Limnol. Oceanogr.*, *51*, 1716–1728.

Spitzy, A., and J. A. Leenheer (1991), Dissolved organic carbon in rivers, in *Biogeochemistry of Major World Rivers*, edited by E. T. Degens et al., *SCOPE Rep. 42*, pp. 105–125, John Wiley, Hoboken, N. J.

Tipping, E., et al. (1997), Organic carbon in the Humber rivers, *Sci. Total Environ.*, *194–195*, 345–355.

Vitorello, V. A. (1989), Organic-matter and natural C-13 distribution in forested and cultivated oxisols, *Soil Sci. Soc. Am. J.*, *53*, 773–778.

Wehr, J. D., and J. M. Thorp (1997), Effects of navigation dams, tributaries, and littoral zones on phytoplankton communities in the Ohio River, *Can. J. Fish. Aquat. Sci.*, *54*, 378–395.

Wiener, J. G., et al. (1996), Mississippi River, in *Status and Trends of Nation's Biological Resources*, vol. 1, pp. 351–384, Natl. Weather Res. Cent., U.S. Geol. Surv., Washington, D. C. (Available at http://www.nwrc.usgs.gov/sandt/Misisipi.pdf)

Williams, M. R., and J. M. Melack (1997), Solute export from forested and partially deforested catchments in the central Amazon, *Biogeochemistry*, *38*, 67–102.

Yano, Y., K. Lajtha, P. Sollins, and B. A. Caldwell (2004), Chemical and seasonal controls on the dynamics of dissolved organic matter in a coniferous old-growth stand in the Pacific Northwest, USA, *Biogeochemistry*, *71*, 197–223.

Yano, Y., K. Lajtha, P. Sollins, and B. A. Caldwell (2005), Chemistry and dynamics of dissolved organic matter in a temperate coniferous forest on andic soils: Effects of litter quality, *Ecosystems*, *8*, 286–300.

Yoneyama, T. (1996), Characterization of natural 15N abundance of soils, in *Mass Spectrometry of Soils*, edited by T. W. Boutton and S. Yamasake, pp. 205–223, Boca Raton, Fla.

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