

# Seasonal Changes in the Abundance and Composition of Plant Pigments in Particulate Organic Carbon in the Lower Mississippi and Pearl Rivers

SHUIWANG DUAN\* and THOMAS S. BIANCHI†

*Department of Earth and Environmental Sciences, Tulane University, 120 Dinwiddie Hall, New Orleans, Louisiana 70118*

**ABSTRACT:** Plant pigments in particulate organic carbon were examined in the lower Mississippi and Pearl Rivers (U.S.), along with physical variables and nutrients to study seasonal changes in the abundance and composition of phytoplankton. Water samples were collected monthly from September 2001 to August 2003 in the lower Mississippi River (MR; no samples were taken in February 2002) and from August 2001 to July 2003 in the Pearl River (PR). High concentrations of total suspended solids (TSS), nutrients, and chlorophyll *a* (chl *a*; dominated by diatoms) were observed in the lower MR. The smaller blackwater PR was characterized by lower nutrients and chl *a*, higher ultraviolet absorbance, and a phytoplankton biomass dominated by chlorophytes. Chl *a* concentrations in the lower MR was high in summer low-flow periods and also during interims of winter and spring, and did not couple with physical variables and nutrients, likely due to a combination of in situ production and inputs from reservoirs, navigation locks, and oxbow lakes in the upper MR and Missouri River. Chl *a* concentrations in the PR was only high in summer low-flow periods and were controlled by temperature and concentrations of chromophoric dissolved organic matter (CDOM). The high, diatom-dominated phytoplankton biomass in the lower MR was likely the result of decreasing TSS (increased damming in the watershed) and increasing nutrients (enhanced agricultural runoff) over the past few decades. Lower phytoplankton biomass (dominated by chlorophytes) in the PR was likely linked with intense shading by CDOM and lower availability of nutrient inputs. An increase in the relative importance of phytoplankton biomass in large turbid rivers, such as the MR, could have significant effects on the age and lability of riverine organic matter entering the ocean, the stoichiometric balance of nutrients delivered to coastal margins, and the sequestration of atmospheric CO<sub>2</sub> in these dynamic regions.

## Introduction

Rivers contribute an estimated  $2 \times 10^{14}$  g of particulate organic carbon (POC) to the world's oceans each year (Hedges and Keil 1995). Much of the POC in rivers is derived from both allochthonous (e.g., soil organic matter, algal inputs from streams, and aquatic emergent and submergent wetland vegetation) and autochthonous sources (e.g., phytoplankton, benthic algae; Onstard et al. 2000; Kendall et al. 2001; Wetzel 2001). Dam construction has reduced the suspended load of many rivers around the world, increasing light availability and the potential role of phytoplankton biomass in riverine biogeochemistry (Thorp and Delong 1994; Humborg et al. 1997, 2000; Ittekkot et al. 2000; Sullivan et al. 2001). It is well established that phytoplankton can significantly alter the composition and cycling of dissolved and particu-

late matter in rivers (Wetzel 2001; Turner et al. 2003). The uptake of dissolved silicon (DSi) by river diatoms can dramatically affect the fate of Si as it is transported from continents to the oceans (DeMaster et al. 1983; Conley 1997). To better constrain global riverine flux estimates of dissolved and particulate matter to the oceans, it is important to understand the cycling dynamics of autochthonous sources of POC in rivers.

The abundance and composition of phytoplankton in rivers are largely determined by the availability of light, temperature, inorganic nutrients, and rates of loss from grazing, sedimentation, respiration, and hydraulic flushing (continuous removal by downstream flow and mixing within the water column; Skidmore et al. 1998; Bledsoe and Philips 2000). Rivers are generally turbulent and well-mixed systems with less light availability than standing water systems (Wehr and Sheath 2003). Limiting light levels for phytoplankton in rivers result from high amounts of total suspended solids (TSS) and chromophoric dissolved organic matter (CDOM; McPherson and Miller 1987; Bledsoe and Philips 2000), as well as vertical mixing of cells to deeper regions of the water column (Cole et al. 1992). The

\* Corresponding author; current address: Texas A&M University at Galveston, Department of Marine Sciences, 5007 Avenue U, Galveston, Texas 77551; tele: 409/740-4772; fax: 409/740-4787; e-mail: duans@tamug.edu

† Current address: Department of Oceanography, Texas A&M University, College Station, Texas 77843-3146

loading of TSS to rivers is largely controlled by the size, slope, lithology, and intensity of mechanical and chemical weathering of the drainage basin (Gaillardet et al. 1999). In large river basins the bulk composition of particles entering the main stem of the river will vary seasonally as a function of contributions from subbasins (Stallard and Edmond 1983; Canfield 1997). Inputs of dissolved and particulate materials to rivers with small drainage basins should be better linked to local and regional changes in land use and weather patterns (e.g., rainfall events).

The River Continuum Concept (Vannote et al. 1980) predicted that large river systems (greater than sixth order) would be too turbid and deep to support high levels of phytoplankton production. In more recent years, this view has been challenged by studies that showed significant inputs from the floodplain and littoral zone communities as well as in situ production in large rivers (Junk et al. 1989; Thorp and Delong 1994; Sullivan et al. 2001). Most large rivers are regulated to varying degrees by channelization (bank stabilization) and high or low (navigation) dams and have been altered substantially due to anthropogenic inputs (e.g., high nutrient loading). Nitrogen (N) and phosphorus (P) levels have increased considerably in many large rivers in recent decades owing to extensive application of chemical fertilizers and inflow of urban effluent; these nutrient inputs favor greater phytoplankton productivity and induce species changes in large rivers (Admiraal et al. 1994; Wehr and Descy 1998; Smith et al. 1999; Turner et al. 2003). To our knowledge, very little has been done to study the abundance and composition of phytoplankton in these large lowland rivers.

The objective of this study was to provide comparisons of the seasonal abundance and composition of plant pigments in POC and nutrients in small (Pearl River: PR) and large river (Mississippi River: MR) systems. Both of these rivers enter the northern Gulf of Mexico in close proximity to each other, providing an ideal situation for comparing how regional or seasonal variability affects the delivery of POC and nutrients to the Gulf from two very different rivers. Plant pigment biomarkers were used to document seasonal changes in the abundance and composition of POC, which largely exists as phytoplankton in these rivers. When considering the long-term changes in anthropogenic inputs and alterations to drainage basins, a reevaluation of the cycling of organic carbon (C) in large and small rivers is clearly needed. These biogeochemical and phytoplankton comparisons also provide important information that will better constrain seasonal variability in the role of riverine phytoplankton and nutrients (in both small and

large river systems) as they relate to global estimates of inorganic and organic inputs of materials from rivers to the ocean.

## Materials and Methods

### STUDY SITES AND SAMPLING

The MR is one of the world's largest rivers; it ranks 7th in water and sediment discharge and 2nd in drainage basin size (Milliman 1991). It drains 40% of the continental United States and part of Canada and is the dominant forcing function for coastal processes in the northern Gulf of Mexico. Approximately 60% of the total suspended matter and 66% of the total dissolved materials transported from the continent to the Gulf of Mexico are carried by the MR (Presley et al. 1980). On average, it has a freshwater discharge of  $380 \text{ km}^3 \text{ yr}^{-1}$ , suspended sediment discharge of  $150 \times 10^9 \text{ kg yr}^{-1}$ , and particulate organic C and N flux of  $2.53 \times 10^9 \text{ kg C yr}^{-1}$  and  $0.21 \times 10^9 \text{ kg N yr}^{-1}$ , respectively (Trefry 1994; Goolsby et al. 2000). Suspended sediment concentrations have been decreasing in the main stem of the MR from the 1950s to present when the largest natural sources of sediment in the drainage basin were cut off from the MR main stem by the construction of large reservoirs on the Missouri and Arkansas Rivers (Keown et al. 1986; Meade et al. 1990). The flux of nitrate has approximately tripled in the last 30 yr with most of the increase occurring between 1970 and 1983, due to chemical fertilizer loss from agricultural land of the upper drainage basin (Goolsby et al. 2000).

The PR is a small (3rd order) river draining east-central and southwest Mississippi and southeastern Louisiana; 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  $22,690 \text{ km}^2$  (0.7% of the Mississippi drainage basin). Freshwater and suspended sediment discharges in the PR in 2002 were  $9.06 \text{ km}^3$  and  $0.32 \times 10^9 \text{ kg}$  (this study), respectively. The PR was selected for comparisons with the MR, because in contrast to the MR it is a small blackwater river that is intimately tied to local changes in the watershed and is less affected by human activities than the MR. As mentioned earlier, these rivers also enter the northern Gulf of Mexico in close proximity to each other, providing an ideal situation for comparing controls on regional inputs of phytoplankton in very different rivers. The PR drainage basin is dominated by natural forest (43%), which includes evergreen, deciduous, and mixed forests, followed by agricultural area (27%). Marshy and swampy areas make up 10% of the land cover and are distributed all along the river corridor (Pearl River Basin Team 2000). The Ross Barnett Reservoir, the only large

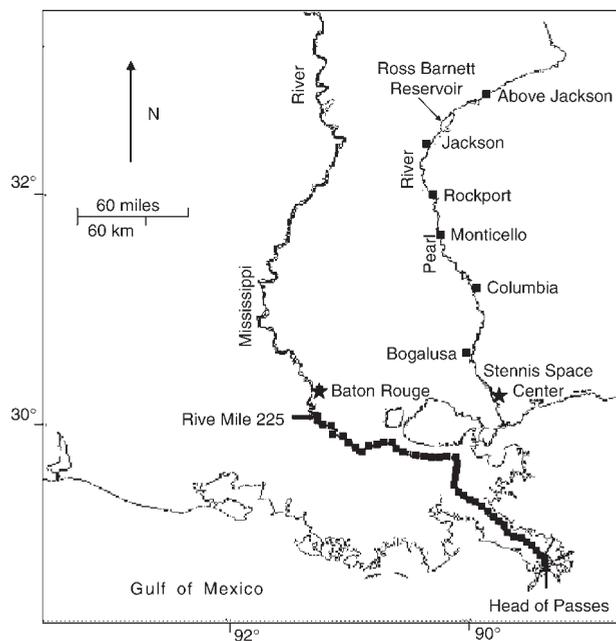


Fig. 1. Map of the lower Mississippi and Pearl Rivers showing the water sampling locations of this study.

impoundment of some 33,000 acres in the upper drainage basin, is located just north of Jackson, Mississippi, stretching about 75 km in length.

Water samples were collected monthly from September 2001 to August 2003 in the lower MR (no samples were taken in February 2002) and from August 2001 to July 2003 in the PR. The lower MR sampling site was upstream of the U.S. Highway 190 Bridge north of Baton Rouge, Louisiana. The samples from the PR were collected at Stennis Space Center (NASA), Mississippi (Fig. 1). It should be emphasized that while we only sampled one station in each river on a seasonal basis, our primary goal was to characterize general physicochemical parameters and phytoplankton prior to their delivery to the Gulf of Mexico. While acknowledging the importance of upstream processes in controlling the downstream signature of phytoplankton, we were more interested in the downstream product as it relates to source inputs to the ocean.

In a limited attempt to investigate some indication of the downstream variability of phytoplankton abundance within these rivers, downstream samples were collected in June 2003. For the PR, samples were collected from six sites from a site just a few kilometers above Jackson downstream to Bogalusa, Louisiana, on June 5, 2003 (Fig. 1). Samples were collected on the next day at our regular seasonal sampling site nearby the Stennis Space Center. In the MR, we participated in a more elaborate downstream Lagrangian experi-

ment, which attempted to sample within a water mass from just below Baton Rouge (river mile 225) to Head of Passes, Louisiana (river mile 0; Fig. 1). Water samples were collected every 2 h (or 6–10 km) for 4 d (noon of June 20 to noon of June 24). A simple physical model (Walden 1992), originally developed to predict the transport of chemical spills in the lower MR, was used to calculate water transit during our 4-d study. At each station, the boat was allowed to drift with the current during sampling. A 5-l Niskin bottle was lowered to approximately 1 m, closed using a brass messenger slid along the winch cable, and returned to the deck. The water sample was drained into a carboy and taken into the shipboard laboratory. More details of the results from this experiment can be found in Dagg et al. (2005). For both regular seasonal and downriver samplings, replicate ( $n = 2$ ) whole water samples were collected mid stream (just below the surface) in both rivers. Filtered water samples were also collected mid stream by pumping (Masterflex pump) water through a 0.2  $\mu\text{m}$  Nuclepore filter cartridge (Whatman Co., Maidstone, England) for analyses of nutrients and ultraviolet (UV) absorbance. Samples for nutrient measurements were not collected until 2002, except for November 2001 in the PR. All collected water samples were put on ice in a cooler and transported to Tulane University, New Orleans, Louisiana (within 1 to 2 h). Water temperature was measured at the time of sample collection. Water discharge data of the MR at Tarbert Landing, Louisiana and the PR at Bogalusa were obtained from U.S. Army Corps of Engineers and U.S. Geological Survey, respectively.

#### TSS, UV ABSORBANCE, AND BULK C AND N ANALYSES

Suspended particulate material was determined by filtering a known volume of water sample (80–300 ml) through preweighed Whatman GF/F filters (47 mm diam). Filters were oven-dried for 24 h at 52°C and reweighed for determination of TSS concentration ( $\text{mg l}^{-1}$ ).

Ultraviolet-visible (UV-VIS) spectra of filtered samples were measured using a 1601 UV-VIS spectrophotometer (Shimadzu Corp., Japan). Water samples were also analyzed for UV absorbance at the specific wavelength of 254 nm ( $\text{UV}_{254}$ ), as a general indicator of the character and aromaticity of CDOM (Chin et al. 1994). Absorbance of samples was automatically corrected for the absorbance of pure water.

Samples of POC, total particulate nitrogen (PN), and plant pigments were obtained by vacuum filtering water (80–250 ml) through precombusted (450°C, 4 h) Whatman GF/F filters (25 mm diam). Filters were folded, kept in the dark, and stored at

–80°C. Frozen filters were freeze-dried (lyophilized) with a LABCONCO (Freezone-6) System. The lyophilized filters were placed in small combusted glass vials and acidified with 12 N HCl vapor for over 24 hours to remove inorganic C (Hedges and Stern 1984). Acidified filters were then dried at 50°C for 1 h and packed into solvent-cleaned tin boats for analysis on an elemental analyzer (EA 1108, FISOONS Instruments, Beverly, Massachusetts).

#### NUTRIENT ANALYSES

Nutrient measurements were performed by using a Lachat QuickChem FIA+ Automated Ion Analyzer. Nitrate was first reduced to nitrite with copper coated cadmium and then nitrate + nitrite was determined by diazotization with sulfanilamide under acidic conditions (Anderson 1979). Ammonium was determined by the automated phenate method (Patton and Crouch 1977). Colorimetric soluble reactive phosphorus (SRP) determinations were based on the formation of 12-molybdophosphoric acid and subsequent reduction by ascorbic acid (Murphy and Riley 1962). DSi concentrations were determined by forming a silicomolybdate complex followed by reduction with a metal oxalic acid solution (Mullin and Riley 1955). The limits of detection were 70 nM for nitrate + nitrite and phosphate, 100 nM for ammonia, and 80 nM for DSi.

#### PIGMENT EXTRACTION AND ANALYSIS

Pigments were extracted according to the methods of Bianchi et al. (1995), as modified by Chen et al. (2001). Pigment extracts were injected into a Waters (HPLC) coupled with an online 996 photodiode array detector and fluorescence detector (Shimadzu-RF 535). The absorbance detector was set at 438 nm, and the fluorescence detector at an excitation of 440 nm and an emission of 660 nm, according to the methods of Wright et al. (1991), as modified by Bianchi et al. (1995) and Chen et al. (2001). Pigment standards (obtained from Danish Hydraulic Institute (DHI) Water and Environment Co., Denmark) were run individually to determine retention times and spectra. Pigment identification was performed by comparing retention times and UV spectra of the peaks in each sample chromatogram to those of the standards. Detection limits was ca. 1 nmol l<sup>-1</sup> g OC<sup>-1</sup>. Degradation products of chlorophyll *a* (chl *a*), chlorophyllide, and pheophorbide were used as general indicators of phytoplankton cell senescence (Ridout et al. 1985; Bianchi et al. 1988; Spooner et al. 1994) and grazing (Jeffrey 1980; Bianchi et al. 1991; Strom 1993; Cartaxana et al. 2003).

#### CHEMTAX ANALYSIS

A chemical taxonomy (CHEMTAX) program was used to calculate the relative abundance of the phytoplankton taxa, using the ratios of class-specific carotenoids and chlorophyll *b* relative to chl *a* (Mackey et al. 1996). The program was used to estimate the contribution of different classes of phytoplankton to the total chl *a* pool, assuming that each diagnostic pigment is constant within a given phytoplankton assemblage. Recent study found that application of the original CHEMTAX reference matrix (Mackey et al. 1996) to southeastern U.S. estuarine systems produced inaccurate results (Lewitus et al. 2005). The pigment ratios used for CHEMTAX algorithms in this study were based on ratios for freshwater phytoplankton, collected at depths of 4–9 m in northern Wisconsin lakes (Descy et al. 2000). The relative irradiance at this depth ranged from 3.3% to 10%; these values were chosen to allow for adequate adjustment of low light conditions in both the lower MR and PR. Diatoms, chlorophytes, cyanobacteria, dinoflagellates, cryptophytes, and euglenoid algae were chosen because they are typically found in many freshwater systems in North America (Wehr and Sheath 2003) and more specifically in sections of the Ohio River (Wehr and Thorp 1997).

#### STATISTICAL ANALYSES

Correlation analysis was performed using Spearman Rank Correlation coefficient (Excel 97, Microsoft Corporation, Washington, D.C.) in addition to a correlation matrix that was generated to examine linear predictability of phytoplankton abundance and composition using physical and chemical parameters. Principal component analysis (PCA) was carried out to examine the key abiotic factors affecting phytoplankton abundance and composition. A matrix was constructed using 10 variables in the SPSS (Statistics Package for Social Science) for Windows program. Variables were standardized by subtracting the mean, dividing by their standard deviation, and calculating the principal components (PC) using the normalized correlation matrix before performing PCA. A Varimax rotation was applied to the first three PC to simplify the physical interpretation of the PCA projections; this rotation maximized or minimized the loading of each variable on each PC while preserving trends. Statistically significant differences between physical variables, nutrients, and pigments between the two rivers were determined using one-way analysis of variance (ANOVA;  $\alpha = 0.05$ ) in the SPSS system. Means are reported with a 95% confidence interval.

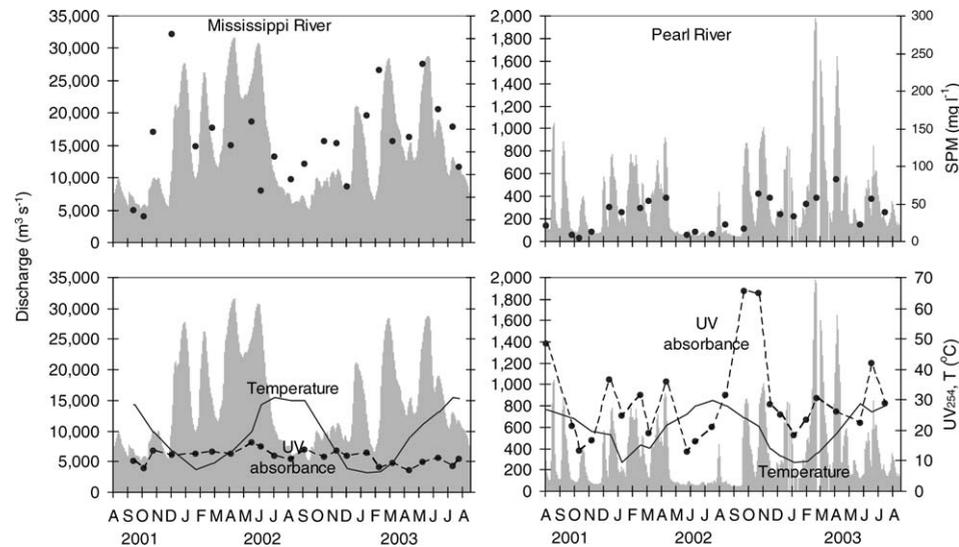


Fig. 2. Water discharge, concentrations of TSS, UV absorbance at 254 nm ( $UV_{254}$ ), and water temperature in the lower Mississippi and Pearl Rivers from August 2001 to August 2003. Area graphs in the background are water discharge. Data of water discharge of the lower MR at Tarbert Landing and PR at Bogalusa are from U.S. Geological Survey and U.S. Army Corps of Engineers, respectively.

## Results

### PHYSICAL PROPERTIES

Water discharge of the lower MR at Tarbert Landing ranged from 5,126 to 31,605  $m^3 s^{-1}$  ( $\bar{x}$  = 14,385, coefficient of variation [CV] = 51%) from August 1, 2001, to August 31, 2003. The MR was characterized by large seasonal shifts in discharge (Fig. 2). Water discharge of the PR at Bogalusa was an order of magnitude lower and ranged from 44 to 1,980  $m^3 s^{-1}$  ( $\bar{x}$  = 340, CV = 98%). The hydrograph of the PR was characterized by a high frequency of temporal variability. The highest flow peaks in the PR occurred from March through April 2003 in addition to a prolonged low flow condition observed in summer 2002 (May–September).

Concentrations of TSS in the lower MR ranged from 22.3 to 262.0  $mg l^{-1}$  ( $\bar{x}$  = 87.6). The highest value was observed in December 2001 when the river shifted from low to high flow; lowest values occurred during low flow periods (Fig. 2). TSS concentrations in the PR (3.90–57.4  $mg l^{-1}$ ,  $\bar{x}$  = 29.4) was three times lower than in the MR ( $p < 0.01$ , one-way ANOVA). The highest and lowest TSS values occurred during flood and low flow periods, respectively.

$UV_{254}$  in the lower MR ranged from 0.070 to 0.162 ( $\bar{x}$  = 0.114) and showed little seasonal variation (CV = 21%; Fig. 2). UV absorbance in the PR was three times higher (0.129–0.656,  $\bar{x}$  = 0.293) than in the lower MR ( $p < 0.01$ , one-way ANOVA) and showed larger seasonal variation (CV = 48%); the highest values occurred in October 2002 shortly after two hurricanes.

Water temperature in the MR and PR ranged from 6.3°C to 31.1°C, and 9.3°C to 29.8°C, respectively (Fig. 2). Temperature increased from the lowest values in January to the highest (e.g., 30°C) in July–August, followed by a decrease in fall in both rivers.

### POC AND PN

Concentrations of POC and PN collected from the lower MR ranged from 48.3 to 249.9  $\mu M$  ( $\bar{x}$  = 135.4) and from 6.08 to 30.0  $\mu M$  ( $\bar{x}$  = 14.7), respectively (Fig. 3). In the PR, POC (41.2–225.7  $\mu M$ ,  $\bar{x}$  = 119.5) and PN (3.0–22.3  $\mu M$ ,  $\bar{x}$  = 12.2) were not significantly different ( $p > 0.05$ , one-way ANOVA) from those in the MR. Seasonal variation of POC was positively correlated with TSS in both the MR ( $r^2 = 0.71$ ) and PR ( $r^2 = 0.46$ ).

C to N atomic ratios (C : N) of TSS in the MR ranged from 7.9 to 12.3 ( $\bar{x}$  = 9.3, CV = 12%) and the highest values were observed during high flow seasons (Fig. 3). C : N ratios in the PR had a wider range (6.5–24.6, CV = 35%) and were 1.4 times higher ( $\bar{x}$  = 12.8) than in the MR on average. The highest C : N values occurred during the hurricane season (October 2002) and the lowest in the summer low flow period of 2002.

### DISSOLVED NUTRIENTS

Nutrients in the lower MR were characterized by high concentrations of nitrate and DSi, and low SRP and ammonium (50.8–121, 58.2–120.5, 0.16–6.4, and 0.84–10.5  $\mu M$ ,  $\bar{x}$  = 93.8, 96.1, 2.18, and 1.71, respectively; Table 1). Nitrate and DSi concentra-

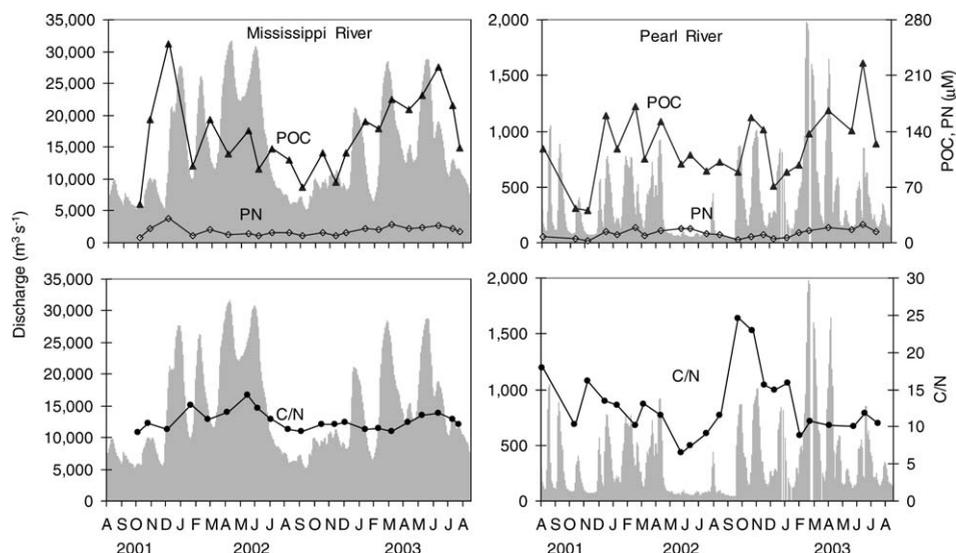


Fig. 3. Total POC, PN, and atomic C : N ratios of TSS in the Mississippi and Pearl Rivers.

tions were relatively stable ( $CV = 28\%$  and  $18\%$ ), but nitrate was generally higher in high flow periods; noticeable decreases of DSi were observed in August 2002 and February and April 2003 (Fig. 4). SRP and ammonium showed larger seasonal variations ( $CV = 45\%$  and  $105\%$ ), and ammonium was much higher in winter (December–March) when temperatures were low while SRP showed an opposite trend. In comparison to the MR, the concentrations of nitrate ( $0.43\text{--}19.0\ \mu\text{M}$ ,  $\bar{x} = 10.4$ ), SRP ( $0.27\text{--}2.27\ \mu\text{M}$ ,  $\bar{x} = 0.70$ ), and DSi ( $1.15\text{--}174.7\ \mu\text{M}$ ,  $\bar{x} = 41.4$ ) in the PR were 9, 2.2, and 2.3 times lower, and that of ammonium ( $0.84\text{--}10.5\ \mu\text{M}$ ,  $\bar{x} = 4.8$ ) was 2.8 times higher ( $p < 0.01$ , one-way ANOVA). Ammonium represented a more important source of dissolved inorganic nitrogen (DIN;  $5.2\text{--}51.1\%$ ) in the PR than in the MR.

The ratio of DSi to total DIN (Si : N) in the MR ranged from 0.7 to 2.1 ( $\bar{x} = 1.0$ ,  $CV = 30\%$ ); this mean generally remained near the Redfield ratio (Si : N = 1 : 1) throughout the year (Fig. 5). Ratios

of N : P and Si : P ranged from 23 to 294 ( $\bar{x} = 90$ ,  $CV = 79\%$ ) and 36 to 260 ( $\bar{x} = 83$ ,  $CV = 78\%$ ), respectively. The ratio of Si:N in the PR was higher and more widely distributed ( $0.1\text{--}40$ ,  $\bar{x} = 4.2$ ,  $CV = 212\%$ ) than in the MR, whereas the ratio of N : P was in a narrower range ( $3\text{--}77$ ,  $\bar{x} = 28$ ,  $CV = 68\%$ ) and closer to Redfield ratios (N : P = 16 : 1). Seasonal changes of Si : N and Si : P in the PR ratios generally followed DSi concentrations (Figs. 4 and 5).

#### HPLC PIGMENTS IN POC

Chl *a* concentrations in the lower MR varied from  $0.70$  to  $21.1\ \mu\text{g l}^{-1}$  ( $\bar{x} = 6.34$ ,  $CV = 82\%$ ) and represented  $0.03\text{--}1.25\%$  of POC (Fig. 6). Chl *a* concentrations in the PR were half ( $p < 0.05$ ;  $0.68\text{--}9.59\ \mu\text{g l}^{-1}$ ,  $\bar{x} = 3.03$ ,  $CV = 98\%$ ) those in the MR and accounted for  $0.03\text{--}0.56\%$  of total POC. Total pheopigments (defined here as the sum of pheophytin, pheophorbide, and chlorophyllide) accounted for  $9\text{--}119\%$  of the total chl *a* in the

TABLE 1. Means ( $\pm$ SD) and ranges of water quality data, approximately monthly from August 2001 to August 2003. Nutrient data are from the beginning of 2002 to August 2003.  $UV_{254}$  stands for UV absorbance at 254 nm.

	Mississippi			Pearl		
	Mean	Max	Min	Mean	Max	Min
TSS ( $\text{mg l}^{-1}$ )	87.6 (51.7)	262.0	22.3	29.4 (16.5)	57.4	3.9
$UV_{254}$	0.114 (0.024)	0.162	0.070	0.293 (0.141)	0.656	0.129
POC ( $\mu\text{M}$ )	135.4 (48.9)	249.9	48.3	119.4 (42.7)	225.7	41.2
PN ( $\mu\text{M}$ )	14.7 (5.69)	30.0	6.08	12.0 (5.34)	22.3	2.98
C : N	9.28 (1.12)	12.31	7.95	12.87 (4.46)	24.60	6.53
Phosphate ( $\mu\text{M}$ )	1.55 (0.69)	2.80	0.28	0.70 (0.52)	2.27	0.27
Ammonium ( $\mu\text{M}$ )	1.71 (1.81)	6.40	0.16	4.81 (3.06)	10.50	0.84
Nitrate + nitrite ( $\mu\text{M}$ )	93.8 (25.8)	157.3	50.8	10.4 (5.0)	19.0	0.43
DSi ( $\mu\text{M}$ )	96.1 (17.4)	120.5	58.2	41.4 (48.7)	174.7	1.15
Chl <i>a</i> ( $\mu\text{g l}^{-1}$ )	6.34 (5.20)	21.10	0.70	3.03 (2.97)	9.59	0.68

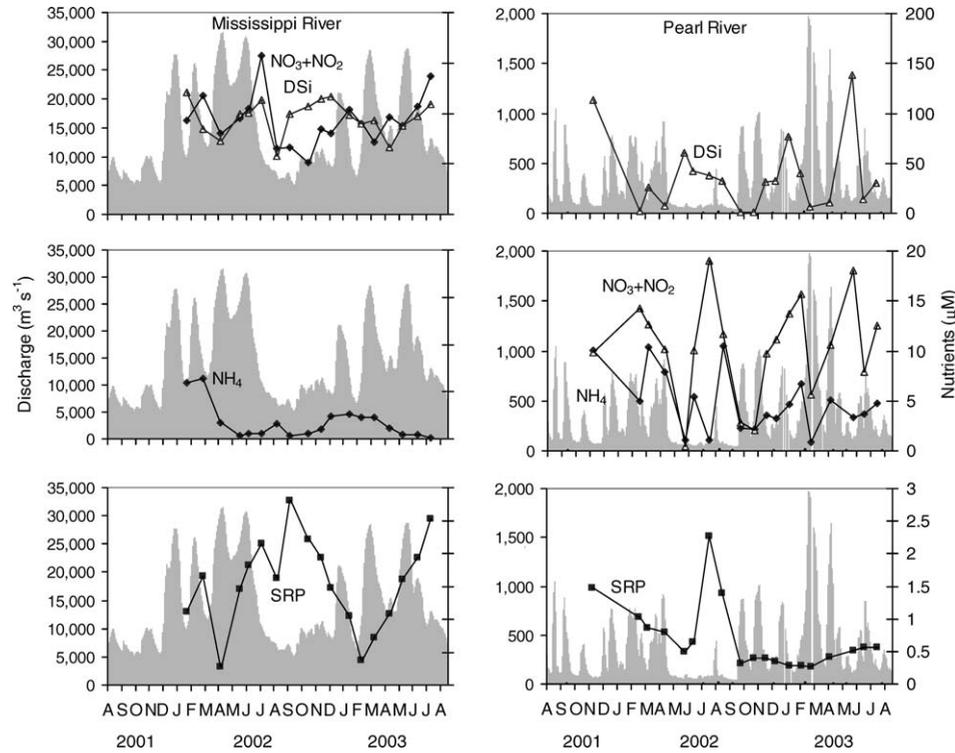


Fig. 4. Concentrations of nitrate + nitrite ( $\text{NO}_3^- + \text{NO}_2^-$ ), dissolved silicate (DSi), ammonium ( $\text{NH}_4^+$ ), and soluble reactive phosphorus (SRP) in the lower Mississippi and Pearl Rivers. Nutrient data are not available until the year 2002 except for a November cruise in 2001 in the PR.

MR. Pheophytin *a*, chlorophyllide *a*, and pheophorbide *a* represented 46%, 23%, and 22% of total chl *a* in the PR, respectively. Pheopigments represented a lower percentage of total chl *a* (9–74%) than in the MR and were dominated by pheophytin *a* (58%)

with chlorophyllide being the least abundant (11%). Chl *a*, and in some cases certain pheopigments, showed large seasonal variation in both rivers, and the ratios of chl *a* : POC showed the same seasonal pattern as chl *a* in both rivers. In

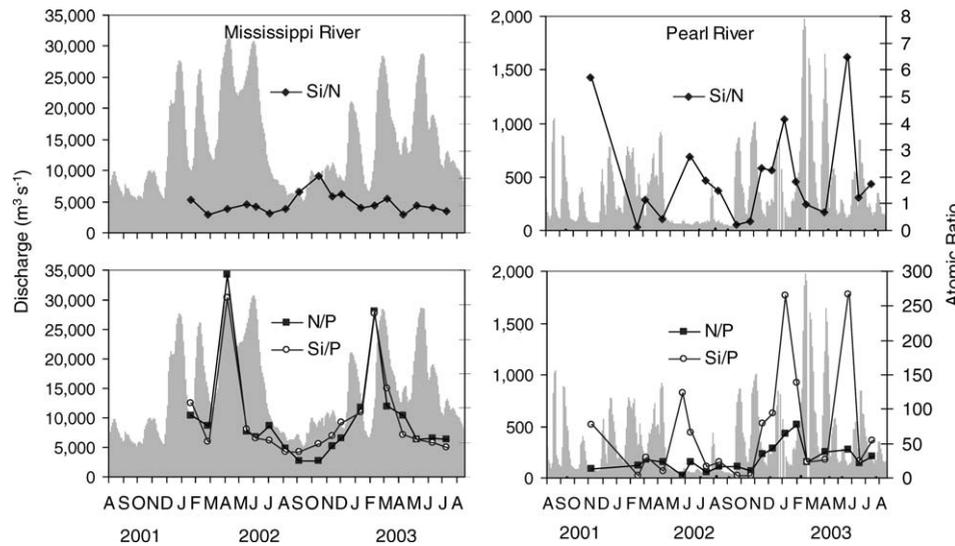


Fig. 5. Atomic ratios of Si : N, N : P, and Si : P in the lower Mississippi and Pearl Rivers.

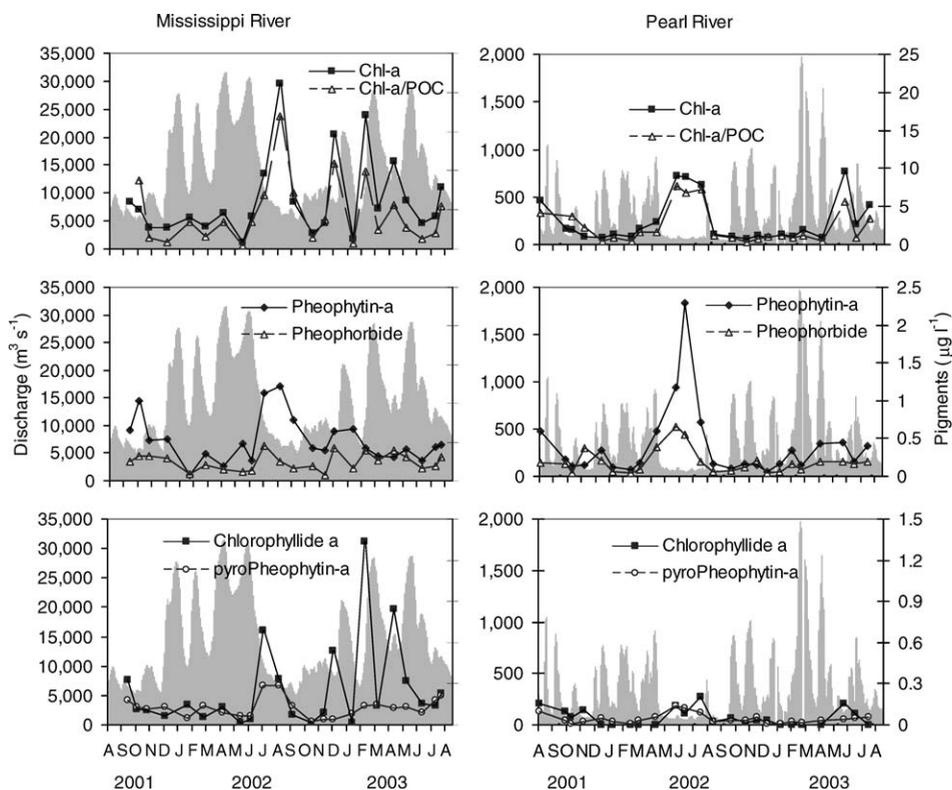


Fig. 6. Chl *a*, the ratio of carbon in chl *a* to total POC (chl *a* : POC), pheophytin *a*, and pheophorbide *a*, chlorophyllide *a*, and pyropheophytin *a* in the lower Mississippi and Pearl Rivers from August 2001 to August 2003. Pheophytin *a*, pheophorbide *a*, chlorophyllide *a*, and pyropheophytin *a* are all degradation products of chl *a*.

particular, in both rivers chlorophyllide *a* generally followed the same seasonal variation as chl *a*. Other pheopigments only showed detectable peaks in summer 2002 for the PR.

Spatial variability in phytoplankton biomass and bulk C was significant in both rivers. A gradual decrease in chl *a* concentrations occurred in the lower MR, from 7.35 below Baton Rouge to 1.86  $\mu\text{g l}^{-1}$  at Head of Passes (Fig. 7). Chl *a* concentrations in the PR in June were higher than the lower MR and increased from 5.53 above Jackson to 32.6  $\mu\text{g l}^{-1}$  at Columbia, Mississippi, followed by decrease to 10.8  $\mu\text{g l}^{-1}$  at the Stennis Space Center site. Chl *a* concentrations in both rivers generally followed the spatial changes in POC with some areas of decoupling.

Seasonal composition of phytoplankton contrasted significantly between the MR and PR (Fig. 8). Based on pigment concentrations, diatoms were found to be the most abundant group (21–86% of total biomass,  $\bar{x} = 49$ , CV = 35%), followed by chlorophytes ( $\bar{x} = 26$ , CV = 31%). The most abundant group of phytoplankton in the PR were the chlorophytes (16–82%,  $\bar{x} = 48$ , CV = 33%), followed by the diatoms ( $\bar{x} = 21$ , CV = 71%). Cryptophytes and cyanophytes accounted for almost

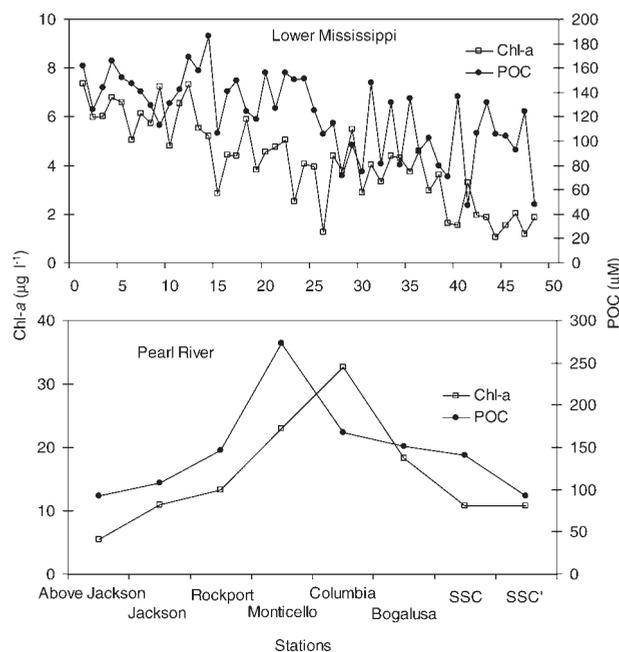


Fig. 7. Spatial variations in phytoplankton abundance (chl *a*) and POC in the lower Mississippi and Pearl Rivers in June 2003. Chl *a* and POC are in  $\mu\text{g l}^{-1}$  and  $\mu\text{M}$ , respectively.

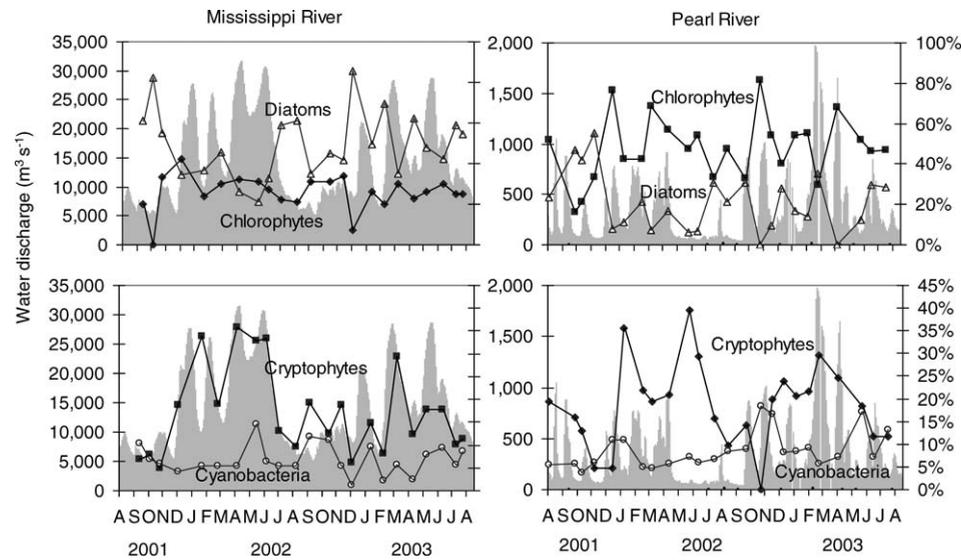


Fig. 8. Composition of phytoplankton (%) in the lower Mississippi and Pearl Rivers based on the results of CHEMTAX. The percentages of dinoflagellates and euglenophytes were generally below 4% and are not listed.

the same fraction of total phytoplankton biomass (17–19% and 7–9%, respectively) in both rivers. Diatoms accounted for more than 60% of total phytoplankton biomass in the MR when chl *a* concentrations were high (Figs. 8 and 6), and the contribution of diatoms was correlated with chl *a* concentration ( $r^2 = 0.48$ ,  $n = 22$ ; Table 2). Chlorophytes and cryptophytes generally showed opposite seasonal trends to diatoms and were more important during the high flow periods of 2001–2002 and fall of 2002 (Fig. 2) in the MR. Diatom and chlorophytes showed opposite seasonal trends in the PR (Fig. 8). Overall trends of phytoplankton abundance and composition in the PR were not significantly correlated with the measured physical variables. Dinoflagellates and euglenophytes represented less than 4% of the phytoplankton community in the PR (data not shown).

**Discussion**

**HYDROLOGIC CONTROLS ON PHYTOPLANKTON ABUNDANCE**

Seasonal variation of phytoplankton biomass in the lower MR was more variable than in the PR due to differential effects of water pulsing events in the drainage basins on source inputs of phytoplankton biomass. Periods of high phytoplankton biomass in the PR only occurred in summer during low flow periods when light availability was high, likely indicating the importance of in situ phytoplankton production. Chl *a* concentrations in the PR were correlated with temperature ( $r^2 = 0.43$ ,  $n = 24$ ,  $p = 0.001$ ), optical property (UV absorbance) and generally decreased with water discharge (Fig. 9). PCA showed that chl *a*, temperature, and UV absorbance were also correlated with the first axis,

TABLE 2. Rotated component matrix of physical parameters, nutrients, and phytoplankton biomass and composition in the Mississippi River (MR) and Pearl River (PR), calculated by principal component analysis. Components 1, 2, and 3 accounted for 37%, 19%, and 16% of total variance in the PR and for 32%, 23%, and 14% of total variance in the lower MR, respectively.

	PR Component			MR Component		
	1	2	3	1	2	3
Discharge		-0.536		0.642		
TSS		-0.688			0.727	
Temp	0.905				0.626	-0.503
UV <sub>254</sub>	-0.867			0.619		
PO <sub>4</sub>					0.842	
NO <sub>x</sub>		0.772				0.817
DSi		0.725				0.639
Chl <i>a</i>	0.820			-0.846		
% chlorophytes			-0.906	0.873		
% diatoms*			0.953	-0.962		

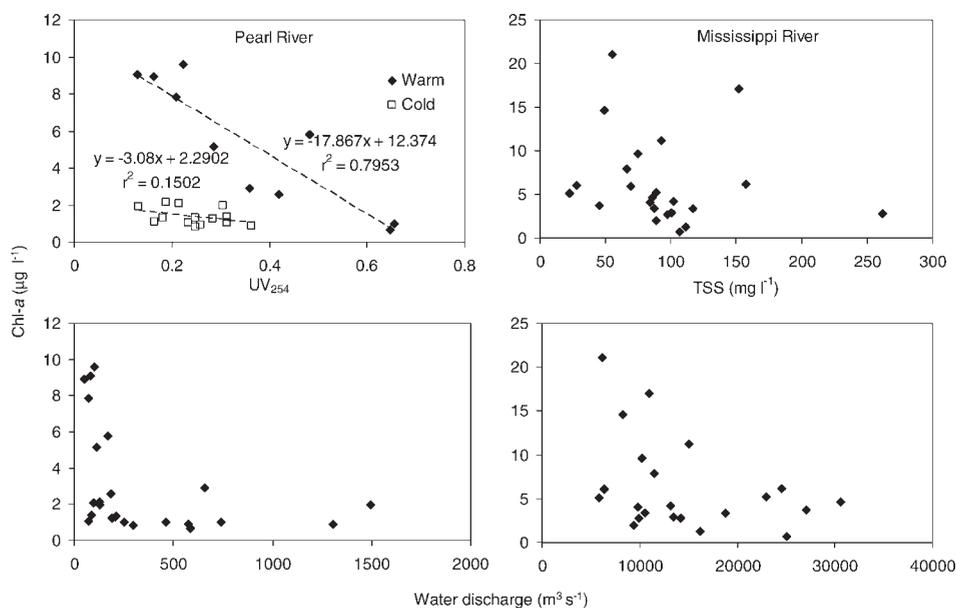


Fig. 9. Correlations between phytoplankton abundance (chl *a*) and total suspended solids (TSS, in the MR), ultraviolet (UV) absorbance at 254 nm ( $UV_{254}$ , in the Pearl River), and water discharge. In the graph of chl *a* versus  $UV_{254}$  in the PR, linear regressions are drawn for the data with temperature [ $t$ ] > 20°C (warm) and  $t$  < 20°C (cold), respectively.

which explained 37% of the total variance (Table 2). Temperature and water discharge have been found to be important factors of phytoplankton production in rivers (Baker and Baker 1979; Descy et al. 1987; Admiraal et al. 1994). High chl *a* concentrations in summer low flow periods are likely due to enhanced in situ production of phytoplankton, something commonly found in other river systems (Skidmore et al. 1998; Knowlton and Jones 2000; Sullivan et al. 2001). The spatial survey during the summer low discharge period (June 2003) also showed an increase in chl *a* concentration in the first few sites from upstream Jackson to Columbia (Fig. 7). Flooding events in the PR may have caused a loss of phytoplankton production through hydraulic flushing and by decreasing light availability (Pinder et al. 1997; Reynolds 1988). Peak concentrations of chl *a* in the PR in summer 2003 can generally be divided into two brief periods that were clearly in response to local flooding events in the region (Fig. 6). In large rivers, such as the MR, peak phytoplankton biomass generally occurred during interim periods of flooding events: in winter or early spring as well as a summer low flow period. High chl *a* concentrations in summer low flow periods in the lower MR are likely due to enhanced in situ production of phytoplankton as found in the PR. Flooding events (in winter and spring) in the lower MR not only resulted in a decrease of chl *a* (likely from lower in situ production due to higher TSS), but also increased at times due to an introduction of

phytoplankton biomass from the upper tributaries. Chl *a* concentrations decreased with increasing water discharge (Fig. 9); PCA showed that the first principal axis was correlated with percent diatoms, percent chlorophytes, chl *a*, and discharge (Table 2), highlighting the importance of hydraulic flushing on phytoplankton biomass and composition. Other variables (e.g., temperature, TSS, or nutrients) were not coupled with chl *a* (see Figs. 2, 4, and 6, Table 2), suggesting that phytoplankton in the lower MR were not solely from in situ sources.

Phytoplankton inputs from reservoirs (and navigation locks), and in some cases from oxbow lakes and adjacent wetlands primarily within the Missouri River and upper MR (Junk et al. 1989; Knowlton and Jones 1997; Wehr and Sheath 2003), may be important in seeding phytoplankton populations in the main stem MR. High chlorophyll concentrations were observed in both the upper MR (up to 190  $\mu\text{g l}^{-1}$ ; Baker and Baker 1979) and the Missouri River (4.5–107  $\mu\text{g l}^{-1}$ ; Knowlton and Jones 2000), compared with relatively lower chl *a* concentrations observed in the Ohio River (1.1–17.7  $\mu\text{g l}^{-1}$ , Sellers and Bukaveckas 2003). Recent chl *a* data from U.S. Environmental Protection Agency (unpublished data) Great River Ecosystem in Environmental Monitoring and Assessment Program also showed significantly higher chl *a* concentrations and larger spatial variations in the upper MR and Missouri River, likely reflecting the effect of reservoirs or navigation locks on the phytoplankton biomass in these tributaries. High phytoplankton biomass

in some oxbow lakes in the upper river (e.g., in the Missouri Basin; Knowlton and Jones 1997) are likely important sources of phytoplankton to the lower river. If we accept the potential role of these sources of inputs, we must also assume that the seeded phytoplankton are tolerant of low light conditions if they are to survive their transit to the lower MR and ultimately the Gulf of Mexico. Further studies are needed to examine spatial variability of phytoplankton biomass upstream of our sampling site to better evaluate whether these potential sources of inputs may be significant.

#### POTENTIAL EFFECTS OF TSS AND CDOM ON PHYTOPLANKTON

Although in situ light measurements were not made in this study, phytoplankton biomass in the MR and PR were likely light limited due to shading effects from TSS and CDOM, respectively. Negative effects on phytoplankton abundance from TSS loading are well documented in many river systems (e.g., Ittekkot 1988; Sullivan et al. 2001). The combination of in situ production and allochthonous inputs of phytoplankton biomass, as discussed in the last paragraph, explains for the poor correlation between TSS and chl *a* concentration in the lower MR (Fig. 9, Table 2). Concentrations of TSS in the MR were three times higher than the PR (Table 1) and were comparable to those found in other studies of the lower MR (95.4–240 mg l<sup>-1</sup>, Rostad 1997; 170 mg l<sup>-1</sup>, Kendall 2001; near St. Francisville, Louisiana. Despite high TSS loading, concentrations of chl *a* in the lower MR (0.70–21.1 µg l<sup>-1</sup>,  $\bar{x}$  = 6.34) were comparable to those found in many human-affected rivers, such as the Columbia River, U.S. (0.7–19.8 µg l<sup>-1</sup>; Sullivan et al. 2001), Ohio River, U.S. (1–15 µg l<sup>-1</sup>; Sellers and Bukaveckas 2003), and Danube River, near Vienna, Austria (0.1–40 µg l<sup>-1</sup>; Schagerl and Donabaum 1998). These concentrations are significantly higher than some of the larger less human-affected tropical rivers (e.g., the Amazon River; Saliot et al. 2001). Chl *a* concentrations in the MR were remarkably similar and in some cases higher than those found downstream in eutrophic estuarine and coastal waters (e.g., the MR plume; Lohrenz et al. 1999; 0.4–27.7 µg l<sup>-1</sup>, Wysocki et al. 2003), Lake Pontchartrain (0.3–6.9 µg l<sup>-1</sup>,  $\bar{x}$  = 2.3; Bianchi and Argyrou 1997), and large brackish water systems such as the Baltic Sea ( $\bar{x}$  = 2.2–11.7 µg l<sup>-1</sup>; Wasmund et al. 1999). These high concentrations of phytoplankton biomass in the MR, despite where it may be occurring, indicate that certain large river systems are not only conduits for the transport of terrigenous materials from the continents to the oceans, but also represent potential sources of labile phytodetritus to the coastal margin, something that

has been largely ignored in many global ocean budgets.

Unlike the turbid waters of the MR, chl *a* concentrations in the PR (0.68–9.59 µg l<sup>-1</sup>,  $\bar{x}$  = 3.03) were significantly lower than the MR, likely due to intense shading of CDOM. Low chl *a* concentrations in the PR are consistent with many other small black rivers (e.g., <1 µg l<sup>-1</sup> in the Suwannee River, U.S.; Bledsoe and Philips 2000). Although the PR was relatively low in TSS (e.g., only 33% of the TSS found in the MR), UV absorbance was approximately 2 to 3 times higher than in the MR (Table 1). UV absorbance was negatively correlated with phytoplankton biomass when temperatures were above 20°C (or warm), suggesting that phytoplankton production in the PR was limited by both temperature and light availability. These results are consistent with other studies that show significant absorption of light by CDOM limits primary production in small blackwater rivers (e.g., the Suwannee River; Bledsoe and Philips 2000) and their receiving waters (e.g., Charlotte Harbor, Florida; McPherson and Miller 1987).

The unexpectedly high phytoplankton biomass in the lower MR is likely the result of decreasing TSS that has been documented over the past few decades. The construction of high and low dams in the drainage basin is in part responsible for the decreasing TSS concentrations. The Missouri River has been the principal supplier of sediment since the end of the last ice age because its western tributaries drain young orogenic belts (Turner and Rabalais 2004). Since the completion of a series of large dams during 1950s in the Missouri River, in addition to the lock-and-dam systems in the upper MR and Ohio River, there has been a significant drop in TSS. Increases in light availability might have stimulated phytoplankton production in these regions (as discussed earlier) where nutrients remain high, as well as particle settlement from the water column (Thorp and Delong 1994; Wehr and Thorp 1997; Knowlton and Jones 2000). Downstream effects of dam construction have also been observed in the lower MR, e.g., TSS concentrations at Tarbert Landing dropped from 800 mg l<sup>-1</sup> in the 1950s to 200 mg l<sup>-1</sup> through the 1990s (U.S. Geological Survey unpublished data) and most of the decrease occurred from 1950 to 1966 (Keown et al. 1986; Meade et al. 1990). Although no long-term data of phytoplankton biomass are available for the MR, phytoplankton abundance in other rivers (e.g., River Danube, Hungary) have showed a 10-fold increase during the 1970s, as a result of changes in TSS due to construction of reservoirs (Szemes 1967; Kiss 1994).

Although degradation products of chl *a* accounted for less than 40% of chl *a* at most times

in both rivers, higher percentages of senescent may indicate that phytoplankton are removed from the water column primarily by cell senescence during their downriver transport. Chlorophyllide was highly coupled with chl *a* in both rivers ( $r^2 = 0.56$  in the MR and 0.50 in the PR,  $p < 0.05$ ), but was significantly higher in the MR than in the PR ( $p < 0.01$ , one-way ANOVA). The abundance of chlorophyllide has been shown to be correlated with cell senescence in turbid estuarine waters (Bianchi and Argyrou 1997). As suggested earlier, if phytoplankton are introduced farther upstream in the MR, it is likely that under such turbid conditions cell lysis will occur during transport. While there was no microscopic taxonomy work performed in this study, other studies have shown that phytoplankton in the upper MR and Ohio River consist primarily of centric diatoms (e.g., *Melosira granulata*, *Melosira italica*, and *Cyclotella meneghiniana*) most of the year, with occasional blooms of cyanobacteria (e.g., *Aphanizomenon flos aquae*, *Aphanothece saxicola*, *Merismopedia punctata*, and *Synechococcus* spp.) and Chlorococcales (e.g., *Scenedesmus* spp.) in summer (Baker and Baker 1981; Huff 1986; Wehr and Thorp 1997). Cole et al. (1992) showed that gross and net primary production in the Hudson River, U.S., were severely light limited and that phytoplankton cells may spend as much as 18–22 h  $d^{-1}$  below the 1% light level. Although light levels were not measured in our study, TSS loading in the MR is significantly higher than the Hudson River, clearly suggestive of the importance of light limitation in contributing to phytoplankton cell senescence in the MR. The observed decreases in both chl *a* and POC (and TSS) during the spatial sampling, were likely due to loss of sinking senescent phytoplankton (produced upstream) during the falling stage of river discharge (Fig. 7; also see Dagg et al. 2005). Pheopigments such as pheophorbide was only moderately correlated with chl *a* in both rivers, suggesting that top-down or grazing effects were less important than cell senescence in controlling the removal of phytoplankton in both rivers. These results support other research in the MR that showed that more novel pigment grazing indicators (e.g., pheophorbide sterol esters and carotenol chlorin esters) were virtually absent in the lower MR although they were highly abundant in the MR plume waters (Chen et al. 2003a,b). Other studies also indicate that zooplankton biomass in lotic environments is lower than in standing waters (Pace et al. 1992; Thorp et al. 1994) and that phytoplankton-zooplankton interactions are weak in many river systems (Köhler 1995; Basu and Pic 1996). Unlike the MR, chlorophytes were the dominant phytoplankton in the PR, consistent with what has been found in the blackwater systems, such as tributaries of the

Amazon River (Saliot et al. 2001). The reduction of light by CDOM in the blackwaters of the PR also most likely contributed to the high abundance of chlorophyllide and phytoplankton senescence. This also supports other studies that have shown blackwater rivers and estuaries to commonly be light limited (Bledsoe and Philips 2000; Wainright et al. 1992).

#### NUTRIENT CONTROLS ON PHYTOPLANKTON COMPOSITION

High nutrient concentrations are also important in maintaining the diatom-dominated phytoplankton biomass in the lower MR. Diatoms have been shown highly competitive in nutrient-rich environments (Wetzel 2001; Wehr and Sheath 2003). High concentrations of nitrate and SRP in the MR, particularly during high water discharge periods have been shown to be linked with anthropogenic inputs, particularly chemical fertilizers in agricultural belts of the Midwest U.S. as well as urban sewage effluents in major cities along the MR (Meybeck 1982; Goolsby et al. 2000). Although there are inputs of nutrients from agricultural sources in the upper PR, anthropogenic loading of nutrients was significantly lower than in the MR, making the influence of local runoff inputs from recycled nutrients in soils more important at certain times of the year. The dominance of chlorophytes over diatoms in the PR was a reflection of the differences in nutrient regimes between these two rivers. Chlorophytes tend to be more competitive in lower nutrient environments due to their small size (McCormick et al. 2001) and may be better adapted to gathering light in humic-rich waters due to difference in the accessory pigments (e.g., chlorophyll *b*) compared to diatoms, although this remains purely speculative at this time. Other blackwater river work in the Suwannee River, found that small cell size species, such as *Chlorella*-like green algae, *Cryptomonad* spp., and small-sized diatoms (Bledsoe et al. 2000), dominated the phytoplankton.

Nutrient uptake by phytoplankton at certain times of the year may have resulted in detectable reductions of nutrient levels in both the MR and PR in spite of expected light limitation most of the year. Because specific uptake rates were not measured in this study we can only speculate based on inferences from regression analyses. DS<sub>i</sub> was not found to be significantly correlated with chl *a* concentrations (Table 2) in the MR, but decreases in DS<sub>i</sub> were observed in August 2002 and February–April 2003 when phytoplankton biomass was at its highest (Fig. 3), likely reflecting DS<sub>i</sub> uptake by diatom-dominated phytoplankton. DS<sub>i</sub> concentrations in the lower MR have decreased by half from the

beginning of this century to 1990s (Turner and Rabalais 1991; Rabalais et al. 1996) and to 58–120  $\mu\text{M}$  at present (Table 1). DSi consumption by phytoplankton could occur in the standing waters (e.g., reservoirs and navigation locks) of these tributaries (Rabalais et al. 1996). Lower values of DSi in the lower MR, compared to the Missouri (130–280  $\mu\text{M}$ , Knowlton and Jones 2000) and Ohio Rivers (118–171  $\mu\text{M}$ , Wehr and Thorp 1997), suggest further removal of DSi by phytoplankton in the lower MR. These relationships remain speculative without specific uptake rates and better constraints on the seasonal variability of natural and anthropogenic loading for each element; more work is clearly needed on this topic.

#### IMPLICATIONS FOR GLOBAL CHANGES IN RIVERINE ORGANIC MATTER COMPOSITION

If phytoplankton biomass is becoming a more significant component of total organic matter in large turbid rivers it could have serious long-term effects on the lability and age of riverine organic matter entering the oceans. Using an assumed chlorophyll (chl *a* and chlorophyll *b*) content of 2% for phytoplankton (ash-free dry weight; Reynolds 1984), a 6% N content (Hecky and Kilham 1988), and a 42% content of C (weight ratio of C : N = 7), we estimated the annual flux of phytoplankton C and N to be  $64.4 \times 10^6$  kg and  $9.2 \times 10^6$  kg, respectively. Phytoplankton biomass represented an average of 8.1% and 11.8% of total POC and PN, respectively; the highest values approaching 20% for both C and N occurred when phytoplankton biomass was high in the MR. Knowlton and Jones (2000) also found that phytoplankton biomass contributed approximately 23% of PN in the lower Missouri River. Because our samples were collected in surface waters, these C, N, and TSS flux estimates may be underestimated since TSS is generally higher in bottom waters. Thorp and Delong (1994) demonstrated that phytoplankton were an important source of organic C in the trophic dynamics of the Ohio River food web. Contributions of phytoplankton to the total C and N pools in the less disturbed smaller blackwater rivers like the PR were considerably less (3.5% of POC and 5.7% of PN). In larger tropical river systems with numerous blackwater tributaries, such as the Amazon River, phytoplankton have been estimated to only represent <2% of the total organic C (Salot et al. 2001). Blackwater systems typically have a significant fraction of their POC represented by terrestrial C sources (Moran et al. 1990, 1999). POC and PN annual fluxes in this study were estimated at  $0.796 \times 10^9$  kg and  $0.078 \times 10^9$  kg, respectively, approximately three times lower

than previous estimates ( $2.53 \times 10^9$  kg C, Trefry 1994;  $0.206 \times 10^9$  kg N  $\text{yr}^{-1}$ , Goodsby 2000). The relative contribution of PN to the total N pool was shown to have decreased from 58% to 40% in the MR from 1950 to 1982, due to settlement of particulates from increased damming (Mayer et al. 1998). Phytoplankton represent a relatively labile source of organic matter in rivers, and as the number of dams increases in our global river systems we can expect the age of riverine POM to decrease and lability to increase (Ittekkot et al. 1988; Raymond and Bauer 2001; Repeta et al. 2002; Bianchi et al. 2004).

Increasing phytoplankton biomass in large heavily human-affected rivers like the MR may also alter the stoichiometric balance of nutrients delivered to coastal margins, affecting important coastal issues impacted by rivers, such as eutrophication and hypoxia. As described earlier, nutrient (N and P) inputs are from agricultural belts and cities, whereas DSi is primarily from chemical weathering in the watersheds (Ittekkot et al. 2000; Treguer et al. 1995). The Si : N : P ratio (DSi : nitrate : total phosphate) in the lower MR has changed from 40 : 9 : 1 in the 1950s to 14 : 15 : 1 in the 1980s, approaching Redfield ratios as nitrate and phosphate increased, DSi decreased (Turner and Rabalais 1991; Rabalais et al. 1996; Justic et al. 1995), and the same ratios of Si : N are still kept at present (Fig. 5). Significant decreases in DSi have been found in rivers like the Danube and Nile (decreases up to 80 and 200  $\mu\text{mol l}^{-1}$ , respectively; Humborg et al. 1997, 2000; Whaby and Bishara 1980), along with many other river systems in the world (see review by Turner et al. 2003). These changes have occurred in the presence and absence of damming in mainstream (Ittekkot et al. 2000), although much of the change in nutrient stoichiometry has been related to damming activities (Humborg et al. 1997, 2000). It should be noted that greater losses of DSi in the river, due to phytoplankton uptake, translates into a higher abundance of particulate biogenic Si (e.g., diatoms), which now represents a greater fraction of what gets delivered to the coastal margin (Conley 1997). Changes in the Si : N : P in the MR have resulted in nutrient changes in the northern Gulf of Mexico, causing the coastal waters of Louisiana have become close to the Redfield ratio (Justic et al. 1995). This has led to the enhancement of phytoplankton productivity (Lohrenz et al. 1997; Rabalais et al. 2004), shifts of phytoplankton species from diatom to harmful or noxious algae blooms (Dortch and Whitledge 1992; Justic et al. 1995; Turner et al. 2003), and widespread hypoxia (Rabalais et al. 1996). If changes in the relative importance of phytoplankton in large rivers becomes more widespread, then more active cycling of nutrients in the river-proper will certainly alter river

chemistry (e.g., DOM, nutrients, metals), affecting the sources and fate of C in coastal regions.

#### ACKNOWLEDGMENTS

We would like to thank Steven Eichinger, Alan M. Shiller, and Lyndsie Gross for assistance with field sampling. Alan M. Shiller provided the data for water temperature. We thank Bob Gillett and the Louisiana Department of Environmental Quality for assistance with sample collection on the Mississippi River aboard the Water Witch. We would also like to thank Alan M. Shiller and Rebecca Green for reviewing earlier drafts of the manuscript. This project was supported by grants from the National Science Foundation, EAR-0001286 and EAR-0001049.

#### LITERATURE CITED

- ADMIRAAL, W., L. BREEBAART, G. M. J. TUBBING, B. ZENTEN, E. D. SW RUYTER VAN STEVENINCK, AND R. BIJKERK. 1994. Seasonal variation in composition and production of planktonic communities in the lower River Rhine. *Freshwater Biology* 32:519–531.
- ANDERSON, L. 1979. Simultaneous spectrophotometric determination of nitrite and nitrate by flow injection analysis. *Analytica Chimica Acta* 110:123–128.
- BAKER, A. L. AND K. K. BAKER. 1979. Effects of temperature and current discharge on the concentration and photosynthetic activity of the phytoplankton in the upper Mississippi River. *Freshwater Biology* 9:191–198.
- BAKER, K. K. AND A. L. BARKER. 1981. Seasonal succession of the phytoplankton in the upper Mississippi River. *Hydrobiologica* 83:295–301.
- BASU, B. K. AND F. R. PICK. 1996. Factors regulating phytoplankton and zooplankton biomass in temperate rivers. *Limnology and Oceanography* 41:1572–1577.
- BIANCHI, T. S. AND M. E. ARGYROU. 1997. Temporal and spatial dynamics of particulate organic carbon in the Lake Pontchartrain estuary, southeast Louisiana, USA. *Estuarine Coastal and Shelf Science* 45:557–569.
- BIANCHI, T. S., R. DAWSON, AND P. SAWANGWONG. 1988. The effects of macrobenthic deposit-feeding on the degradation of chloropigments in sandy sediments. *Journal of Experimental Marine Biology and Ecology* 122:243–255.
- BIANCHI, T. S., C. LAMBERT, P. H. SANTISCHI, M. BASKARAN, AND L. GUO. 1995. Plant pigments as biomarkers of high-molecular-weight dissolved organic-carbon. *Limnology and Oceanography* 40:422–428.
- BIANCHI, T. S., T. FILLEY, K. DRIA, AND P. G. HATCHER. 2004. Temporal variability in sources of dissolved organic carbon in the lower Mississippi River. *Geochemica et Cosmochimica Acta* 68:959–967.
- BIANCHI, T. S., S. FINDLAY, AND D. FONTVIELLE. 1991. Experimental degradation of plant materials in Hudson River sediments. I. Heterotrophic transformations of plant pigments. *Biogeochemistry* 12:171–187.
- BLEDSE, E. L. AND E. J. PHILIPS. 2000. Relationships between phytoplankton standing crop and physical, chemical, and biological gradients in the Suwannee River and Plume region, USA. *Estuaries* 23:458–473.
- CANFIELD, D. E. 1997. The geochemistry of river particulates from the continental USA: Major elements. *Geochemica et Cosmochimica Acta* 61:3349–3365.
- CARTAXANA, P., B. JESUS, AND V. BROTAS. 2003. Pheophorbide and pheophytin a-like pigments as useful markers for intertidal microphytobenthos grazing by *Hydrobia ulvae*. *Estuarine Coastal and Shelf Science* 58:293–297.
- CHEN, N. H., T. S. BIANCHI, AND J. M. BLAND. 2003a. Novel decomposition products of chlorophyll-alpha in continental shelf (Louisiana shelf) sediments: Formation and transformation of carotenol chlorin esters. *Geochemica et Cosmochimica Acta* 67:2027–2042.
- CHEN, N. H., T. S. BIANCHI, AND J. M. BLAND. 2003b. Implications for the role of pre- versus post-depositional transformation of chlorophyll-a in the Lower Mississippi River and Louisiana shelf. *Marine Chemistry* 81:37–55.
- CHEN, N. H., T. S. BIANCHI, B. A. MCKEE, AND J. M. BLAND. 2001. Historical trends of hypoxia on the Louisiana shelf: Application of pigments as biomarkers. *Organic Geochemistry* 32:543–561.
- CHIN, Y. P., G. AIKEN, AND E. O. LOUGHLIN. 1994. Molecular weight, polydispersivity, and spectroscopic properties of aquatic humic substances. *Environmental Science and Technology* 28:1853–1858.
- COLE, J. J., N. F. CARACO, AND B. PEIERLS. 1992. Can phytoplankton achieve a positive carbon balance in a turbid river, the Hudson River, New York? *Limnology and Oceanography* 37:1608–1617.
- CONLEY, D. J. 1997. Riverine contribution of biogenic silica to the oceanic silica budget. *Limnology and Oceanography* 42:774–777.
- DAGG, M. J., T. S. BIANCHI, G. A. BREED, W.-J. CAI, S. DUAN, H. LIU, B. M. MCKEE, R. T. POWELL, AND M. C. STEWART. 2005. Biogeochemical characteristics of the lower Mississippi River, USA, during June 2003. *Estuaries* 28:664–674.
- DEMASTER, D. J., G. B. KNAPP, AND C. A. NITTROUER. 1983. Biological uptake and accumulation of silica on the Amazon continental shelf. *Geochemica et Cosmochimica Acta* 47:1713–1723.
- DESCY, J. P., H. W. HIGGINS, D. J. MACKAY, J. P. HURLEY, AND T. M. FROST. 2000. Pigment ratios and phytoplankton assessment in northern Wisconsin lakes. *Journal of Phycology* 36:274–286.
- DESCY, J. P., P. SERVAIS, J. S. SMITZ, G. BILLEN, AND E. EVERBECK. 1987. Phytoplankton biomass and production in the River Meuse (Belgium). *Water Research* 21:1557–1566.
- DORTCH, Q. AND T. E. WHITLEDGE. 1992. Does nitrogen or silicon limit phytoplankton production in Mississippi River Plume and nearby regions. *Continental Shelf Research* 12:1293–1309.
- GAILLARDET, J., B. DUPRE, AND C. J. ALLEGRE. 1999. Geochemistry of large river suspended sediments: Silicate weathering or recycling tracer? *Geochemica et Cosmochimica Acta* 63:4037–4051.
- GOOLSBY, D. A., W. A. BATTAGLIN, B. T. AULENBACH, AND R. P. HOOPER. 2000. Nitrogen flux and sources in the Mississippi River Basin. *The Science of the Total Environment* 248:75–86.
- HECKY, R. E. AND P. KILHAM. 1988. Nutrient limitation of phytoplankton in freshwater and marine environment. *Limnology and Oceanography* 33:796–822.
- HEDGES, J. I. AND R. G. KEIL. 1995. Sedimentary organic-matter preservation—An assessment and speculative synthesis. *Marine Chemistry* 49:81–115.
- HEDGES, J. I. AND J. H. STERN. 1984. Carbon and nitrogen determinations of carbonate-containing solids. *Limnology and Oceanography* 29:657–663.
- HUFF, D. R. 1986. Phytoplankton communities in navigation pool No 7 of the upper Mississippi River. *Hydrobiologia* 136:47–56.
- HUMBORG, C., D. J. CONLEY, L. RAHM, F. WULFF, A. COCIASU, AND V. ITTEKKOT. 2000. Silicon retention in river basins: Far-reaching effects on biogeochemistry and aquatic food webs in coastal marine environments. *AMBIO* 29:45–50.
- HUMBORG, C., V. ITTEKKOT, A. COCIASU, AND B. V. BODUNGEN. 1997. Effect of Danube River dam on Black Sea biogeochemistry and ecosystem structure. *Nature* 386:385–388.
- ITTEKKOT, V. 1988. Global trends in the nature of organic-matter in river suspensions. *Nature* 332:436–438.
- ITTEKKOT, V., C. HUMBORG, AND P. SCHAFER. 2000. Hydrological alterations and marine biogeochemistry: A silicate issue? *Bioscience* 50:776–782.
- JEFFREY, S. W. 1980. Algal pigment systems, p. 33–57. In P. G. Falkowski (ed.), *Primary Productivity in the Sea*, Volume 19. Plenum Publishing Corp., New York.
- JUNK, W. J., P. B. BAYLEY, AND R. E. SPARKS. 1989. The flood-pulse concept in river-floodplain system. *Canadian Journal of Fishery and Aquatic Science* 106:110–127.

- JUSTIC, D., N. N. RABALAIS, AND R. E. TURNER. 1995. Stoichiometric nutrient balance and origin of coastal eutrophication. *Marine Pollution Bulletin* 30:41–46.
- KENDALL, C., S. R. SILVA, AND V. J. KELLY. 2001. Carbon and nitrogen isotopic compositions of particulate organic matter in four large river systems across the United States. *Hydrological Process* 15:1301–1346.
- KEOWN, M. P., E. A. DARDEAU, AND E. M. CAUSEY. 1986. Historic trends in the sediment flow regime of the Mississippi River. *Water Resource Research* 22:1555–1564.
- KISS, K. T. 1994. Trophic level and eutrophication of the River Danube in Hungary. *Internationale Vereinigung fuer Theoretische und Angewandte Limnologie Verhandlungen*. 25:1688–1691.
- KNOWLTON, M. F. AND J. R. JONES. 1997. Trophic status of Missouri River floodplain lakes in relation to basin type and connectivity. *Wetlands* 17:468–475.
- KNOWLTON, M. F. AND J. R. JONES. 2000. Seston, light, nutrients and chlorophyll in the lower Missouri River, 1984–1998. *Journal of Freshwater Ecology* 15:283–297.
- KÖHLER, J. 1995. Growth, production and losses of phytoplankton in the lowland River Spree: Carbon balance. *Freshwater Biology* 34:501–512.
- LEWITUS, A. J., D. L. WHITE, R. G. TYMOWSKI, M. E. GEESEY, S. N. HYMEL, AND P. A. NOBLE. 2005. Adapting the CHEMTAX method for assessing phytoplankton taxonomic composition in southeastern US estuaries. *Estuaries* 28:160–172.
- LOHRENZ, S. E., G. L. FAHNENSTIEL, D. G. REDALJE, G. A. LANG, X. G. CHEN, AND M. J. DAGG. 1997. Variations in primary production of northern Gulf of Mexico continental shelf waters linked to nutrient inputs from the Mississippi River. *Marine Ecology Progress Series* 155:45–54.
- LOHRENZ, S. E., G. L. FAHNENSTIEL, D. G. REDALJE, G. A. LANG, M. J. DAGG, T. E. WHITLEGE, AND Q. DORTCH. 1999. Nutrients, irradiance, and mixing as factors regulating primary production in coastal waters impacted by the Mississippi River plume. *Continental Shelf Research* 19:1113–1141.
- MACKEY, M. D., D. J. MACKEY, H. W. HIGGINSAND, AND S. WRIGHT. 1996. CHEMTAX-A program for estimating class abundances from chemical markers: Application to HPLC measurements of phytoplankton. *Marine Ecology Progress Series* 144:265–283.
- MAYER, L. M., R. G. KEIL, S. A. MACKO, S. B. JOYE, K. C. RUTTENBERG, AND R. C. ALLER. 1998. Importance of suspended particulates in riverine delivery of bioavailable nitrogen to coastal zones. *Global Biogeochemical Cycles* 12:573–579.
- MCCORMICK, P. V., M. B. O'DELL, R. B. E. SHUFORD, J. G. BACKUS, AND W. C. KENNEDY. 2001. Periphyton responses to experimental phosphorus enrichment in a subtropical wetland. *Aquatic Botany* 71:119–139.
- MCPHERSON, B. F. AND R. L. MILLER. 1987. Cause of light attenuation in Tampa Bay and Charlotte Harbor, southwestern Florida. *Water Resource Bulletin* 30:43–53.
- MEADE, R. H., T. R. YUZYK, AND T. J. DAY. 1990. Movement and storage of sediment in rivers of the United States and Canada, p. 255–280. *In* M. G. Wolman and H. C. Riggs (eds.), *Surface Water Hydrology*. Geological Society of America, Boulder, Colorado.
- MEYBECK, M. 1982. Carbon, nitrogen, and phosphorus transport by world rivers. *American Journal of Science* 282:401–450.
- MILLIMAN, J. 1991. Flux and fate of fluvial sediment and water in coastal seas, p. 69–90. *In* R. F. C. Mantoura, J. Martin, and R. Wollast (eds.), *Ocean Margin Processes in Global Change*. Wiley, New York.
- MORAN, M. A. AND R. E. HODSON. 1990. Bacterial production on humic and nonhumic components of dissolved organic carbon. *Limnology and Oceanography* 35:1744–1756.
- MORAN, M. A., W. M. SHELDON, AND J. E. SHELDON. 1999. Biodegradation of riverine dissolved organic carbon in five estuaries of the southeastern United States. *Estuaries* 22:55–64.
- MULLIN, J. B. AND J. P. RILEY. 1955. The colorimetric determination of silicate with special reference to sea and natural waters. *Analytica Chimica Acta* 12:162–176.
- MURPHY, J. AND J. P. RILEY. 1962. A modified single solution method for determination of phosphate in natural waters. *Analytica Chimica Acta* 26:31–36.
- ONSTAD, G. D., D. E. CANFIELD, P. D. QUAY, AND J. I. HEDGES. 2000. Sources of particulate organic matter in rivers from the continental USA: Lignin phenol and stable carbon isotope compositions. *Geochimica et Cosmochimica Acta* 64:3539–3546.
- PACE, M. L., S. E. G. FINDLAY, AND D. LINTS. 1992. Zooplankton in advective environments—the Hudson River community and a comparative analysis. *Canadian Journal of Fisheries and Aquatic Sciences* 49:1060–1069.
- PATTON, C. J. AND S. R. CROUCH. 1977. Spectrophotometric and kinetics investigation of the Berthelot reaction for the determination of ammonia. *Analytical Chemistry* 49:464–469.
- PINDER, L. C. V., A. F. H. MARKER, A. C. PINDER, J. K. G. INGRAM, D. V. LEACH, AND G. D. COLLETT. 1997. Concentrations of suspended chlorophyll alpha in the Humber rivers. *The Science of the Total Environment* 194:373–378.
- PRESLEY, B. J., J. H. TREFRY, AND R. F. SHOKES. 1980. Heavy-metal inputs to Mississippi delta sediments—A historical view. *Water, Air and Soil Pollution* 13:481–494.
- RABALAIS, N. N., N. ATILLA, C. NORMANDEAU, AND R. E. TURNER. 2004. Ecosystem history of Mississippi River-influenced continental shelf revealed through preserved phytoplankton pigments. *Marine Pollution Bulletin* 49:537–547.
- RABALAIS, N. N., R. E. TURNER, D. JUSTIC, Q. DORTCH, W. J. WISEMAN JR., AND B. SEN GUPTA. 1996. Nutrient changes in the Mississippi River and system responses on the adjacent continental shelf. *Estuaries* 19:386–407.
- RAYMOND, P. A. AND J. E. BAUER. 2001. Riverine export of aged terrestrial organic matter to the North Atlantic Ocean. *Nature* 409:497–500.
- REPETA, D. J., T. M. QUAN, L. I. ALUWIHARE, AND A. ACCARDI. 2002. Chemical characterization of high molecular weight dissolved organic matter in fresh and marine waters. *Geochimica et Cosmochimica Acta* 66:955–962.
- REYNOLDS, C. S. AND J. W. G. LUND. 1988. The phytoplankton of an enriched, soft-water lake subject to intermittent hydraulic flushing (Grasmere, English Lake District). *Freshwater Biology* 19:379–404.
- REYNOLDS, C. S. 1984. *The Ecology of Freshwater Phytoplankton*. Cambridge University Press, Cambridge, Massachusetts.
- RIDOUT, P. S. AND R. J. MORRIS. 1985. Short-term variations in the pigment composition of a spring phytoplankton bloom from an enclosed experiment ecosystem. *Marine Chemistry* 87:7–11.
- SALOT, A., L. MEJANELLE, P. SCRIBE, J. FILLAUX, C. PEPE, A. JABAUD, AND J. DAGAUT. 2001. Particulate organic carbon, sterols, fatty acids and pigments in the Amazon River system. *Biogeochemistry* 53:79–103.
- SCHAGERL, M. AND K. DONABAUM. 1998. Epilithic algal communities on natural and artificial substrata in the River Danube near Vienna (Austria). *Archiv Fur Hydrobiologie* 2:153–165.
- SELLERS, T. AND P. A. BUKAVECKAS. 2003. Phytoplankton production in a large, regulated river: A modeling and mass balance assessment. *Limnology and Oceanography* 48:1476–1487.
- SKIDMORE, R. E., S. C. MABERLY, AND B. A. WHITTON. 1998. Patterns of spatial and temporal variation in phytoplankton chlorophyll *a* in the River Trent and its tributaries. *The Science of the Total Environment* 210/211:357–365.
- SMITH, V. H., G. D. TILMAN, AND J. C. NEKOLA. 1999. Eutrophication: Impacts of excess nutrient inputs on freshwater, marine, and terrestrial ecosystems. *Environmental Pollution* 100:179–196.
- SPOONER, N., H. R. HARVEY, G. E. S. PEARCE, C. B. ECKARDE, AND J. B. MAXWELL. 1994. Biological defunctionalisation of chlorophyll in the aquatic environment. 2. Action of endogenous algal enzymes and aerobic bacteria. *Organic Geochemistry* 22:773–780.

- STALLARD, R. F. AND J. M. EDMOND. 1983. Geochemistry of the Amazon. 2. The influence of geology and weathering environment on the dissolved load. *Geophysical Research Letter (Atmosphere)* 88:9671–9688.
- STROM, S. L. 1993. Production of pheopigments by marine protozoa—Results of laboratory experiments analyzed by HPLC. *Deep-Sea Research I* 40:57–80.
- SULLIVAN, B. E., F. G. PRAHL, L. F. SMALL, AND P. A. COVERT. 2001. Seasonality of phytoplankton production in the Columbia River: A natural or anthropogenic pattern? *Geochemica et Cosmochimica Acta* 65:1125–1139.
- SZEMES, G. 1967. Das phytoplankton der Donau. *Limnologie Donau* 5:158–159.
- THORP, J. H. AND M. D. DELONG. 1994. The river production model: An heuristic view of carbon sources and organic processing in large river ecosystems. *Oikos* 70:305–308.
- TREFRY, J. H., S. METZ, T. A. NELSEN, R. P. TROCINE, AND B. J. EADIE. 1994. Transport of particulate organic carbon by Mississippi River and its fate in the Gulf of Mexico. *Estuaries* 17:839–849.
- TREGUER, P., D. M. NELSON, A. J. VAN BENNEKOM, D. J. DEMASTER, A. LEYNAERT, AND B. QUEGUINER. 1995. The silica balance in the world ocean: A reestimate. *Science* 268:375–379.
- TURNER, R. E. AND N. N. RABALAIS. 1991. Changes in Mississippi River water quality this century. *Bioscience* 41:140–147.
- TURNER, R. E. AND N. N. RABALAIS. 2004. Suspended sediment, C, N, P, and Si yields from the Mississippi River Basin. *Hydrobiologia* 511:79–89.
- TURNER, R. E., N. N. RABALAIS, AND D. JUSTIC, et al. 2003. Global patterns of dissolved N, P and Si in large rivers. *Biogeochemistry* 64:297–317.
- VANNOTE, R. L., G. W. MINSHALL, K. W. CUMMINS, J. R. SEDELL, AND C. E. CUSHING. 1980. The river continuum concept. *Canadian Journal of Fishery and Aquatic Science* 37:130–137.
- WAINRIGHT, S. C., C. A. COUCH, AND J. L. MEYER. 1992. Fluxes of bacteria and organic matter into a blackwater river from river sediments and floodplain soils. *Freshwater Biology* 28:37–48.
- WALDEN, M. G. 1992. Mississippi River time-of-travel: User's manual. CLIWS-WQR 91.06/M. Waldon. Louisiana Department of Environmental Quality IAG# 24400-91-19. Baton Rouge, Louisiana.
- WASMUND, N., M. ZALEWSKI, AND S. BUSCH. 1999. Phytoplankton in large river plumes in the Baltic Sea. *ICES Journal of Marine Science* 56:23–32.
- WEHR, J. D. AND J. P. DESCY. 1998. Use of phytoplankton in large river management. *Journal of Phycology* 3:741–749.
- WEHR, J. D. AND R. G. SHEATH. 2003. *Freshwater Algae of North America—Ecology and Classification*. Academic Press, San Diego, California.
- WEHR, J. D. AND J. M. THORP. 1997. Effects of navigation dams, tributaries, and littoral zones on phytoplankton communities in the Ohio River. *Canadian Journal of Fishery and Aquatic Science* 54:378–395.
- WETZEL, R. G. 2001. *Limnology: Lake and River Ecosystems*, 3rd edition. Academic Press, San Diego, California.
- WHABY, S. D. AND N. F. BISHARA. 1980. The effect of the River Nile on Mediterranean water, before and after the construction of the High Dam at Aswan, p. 311–318. In J. M. Martin, J. D. Burton, and D. Eisma (eds.), *River Inputs to Ocean Systems*. UNEP-UNESCO, Gland, Switzerland.
- WRIGHT, S. W., S. W. JEFFREY, R. F. C. MANTOURA, C. A. LLEWELLYN, T. BJORNLAND, D. REPETA, AND N. WELSCHMEYER. 1991. Improved HPLC method for the analysis of carotenoids from marine phytoplankton. *Marine Ecology Progress Series* 77:183–196.
- WYSOCKI, L. A., T. S. BIANCHI, AND T. FILLEY. 2003. Sources of organic carbon on the Louisiana Shelf: The use of chemical biomarkers to trace organic matter in Mississippi River Plume sediments. *Abstracts of Papers of the American Chemical Society* 225:U922-U922 071-GEOC Part 1.

#### SOURCES OF UNPUBLISHED MATERIALS

- PEARL RIVER BASIN TEAM. unpublished data. 2000. Pearl River Basin 2000 Status Report. <http://www.deq.state.ms.us>
- U.S. GEOLOGICAL SURVEY. unpublished data. <http://gulfsoci.usgs.gov/missriv/reports/ofrshelf>
- U.S. ENVIRONMENTAL PROTECTION AGENCY. unpublished data. 2004. <http://www.epa.gov/emap/greatriver>

Received, October 25, 2005

Revised, February 2, 2006

Accepted, February 28, 2006