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Biogeochemical Characteristics of the Lower Mississippi River, USA, During June 2003

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ABSTRACT: During June 2003, a period of mid level discharge (17,400 m^{-3} s^{-1}), a parcel of water in the lower Mississippi River was sampled every 2 h during its 4-d transit from river km 362 near Baton Rouge to km 0 at Head of Passes, Louisiana, United States. Properties measured at the surface during each of the 48 stations were temperature, salinity, dissolved organic carbon (DOC), total dissolved nitrogen, dissolved macronutrients (NO_3 + NO_2, PO_4, $Si(OH)_4$), chlorophyll *a* (chl *a*; three size fractions: < 5 μm, 5–20 μm, and > 20 μm), pigment composition by HPLC, total suspended matter (TSM), particulate organic carbon (POC), and particulate nitrogen (PN). Air-water CO_2 flux was calculated from surface water dissolved inorganic carbon and pH. During the 4 d transit, large particles appeared to be settling out of the surface water. Concentrations of chl *a* containing particles > 20 μm declined 37%, TSM declined 43%, POC declined 42% and PN declined 57%. Concentrations of the smaller chl *a* containing particles did not change suggesting only large particulate materials were settling. There was no measurable loss of dissolved NO_3, PO_4, or $Si(OH)_4$, consistent with the observation that chl *a* did not increase during the 4-d transit. DOC declined slightly (3%). These data indicate there was little autotrophic or heterotrophic activity in the lower Mississippi River at this time, but the system was slightly net heterotrophic.

Introduction

The Mississippi River annually discharges an average of 380 km^3 freshwater and 150 × 10^9 kg suspended sediment into the northern Gulf of Mexico (Meade et al. 1990; Meade 1995). River water contains high concentrations of dissolved inorganic nutrients, natural and anthropogenic, that greatly stimulate biological production after river water is discharged via the Mississippi River delta (Riley 1937; Lohrenz et al. 1999; Dagg and Breed 2003). River water also contains high concentrations of dissolved organic matter (DOM) that, by microbial activity and photodegradation after discharge, stimulate bacterial production in the buoyant plume (Benner and Opsahl 2001; Hernes and Benner 2003). Numerous studies have been conducted to better understand cycling of these dissolved constituents and planktonic ecosystem responses in areas of the northern gulf influenced by Mississippi River discharge (reviewed by Dagg and Breed 2003).

Processes in the lower river, immediately prior to discharge, are less well understood. Phytoplankton production in large, turbid rivers is generally thought to be severely light limited because of high turbidity and turbulence (Cole et al. 1992; Reynolds and Descy 1996; Skidmore et al. 1998). Bacterial production in such rivers is generally thought to be limited because riverine DOM is highly refractory (Hedges et al. 1997). Many large rivers, including the Mississippi River, are anthropogenically influenced and there have been significant changes in both the nutrient concentrations and the sources and characteristics of riverine DOM in these systems (Repeta et al. 2002; Bianchi et al. 2004). These changes may affect in-river processes and it is not clear whether such systems are net autotrophic or net heterotrophic.

We examined these assumptions regarding in situ utilization of macronutrients and DOM in the lower Mississippi River in order to determine how these biogeochemical properties of the water changed during the final 4 d of transit prior to discharge into the northern Gulf of Mexico, and we determined the metabolic state of the lower river during this time.

Methods and Materials

We used a simple physical model (Walden 1992), originally developed to predict the transport of chemical spills in the lower Mississippi River, to calculate water transit during the final 4 d before discharge at Head of Passes, Louisiana, United States (Fig. 1). The model incorporates channel characteristics in each reach of the river and uses

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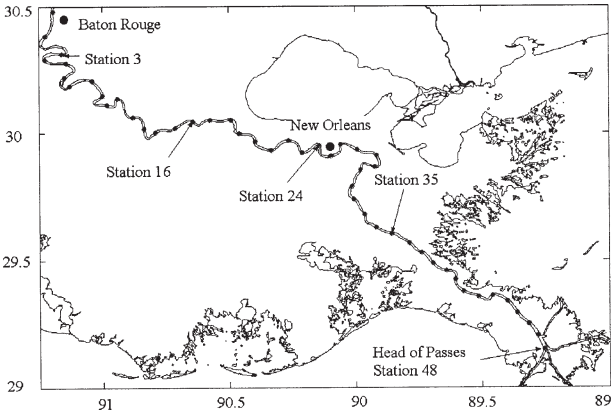

Fig. 1. Sampling locations on the lower Mississippi River, June 20–24, 2003. Stations, indicated by dots on the river, were occupied at 2-h intervals.

advection-diffusion equations to predict when the peak concentration of a contaminant from a chemical spill will reach a given point downriver. The model also calculates the degree a spill will spread and reports the leading and trailing edges. The program is general enough that a spill can be replaced with a water parcel, and we used it to prepare our cruise plan. Walden's (1992) model uses the traditional Mississippi River convention of river mile as the unit of distance. This unit is a statute mile (1,609.3 m) along the center of the river. In this paper we have converted all distances to kilometers. Head of Passes in the Mississippi River delta (Fig. 1) is river km 0 and distances increase in the upriver direction.

Our goal was to monitor geochemical and biological properties in the central portion of the lower Mississippi River during its final 4 d of transit to the Gulf of Mexico. The starting point for our cruise was determined by incorporating the river discharge on June 19, 2003 (17,400 $m^3 s^{-1}$) into the model, which estimated water at river km 0 would have originated 96 h earlier at river km 362, near Baton Rouge, Louisiana (Fig. 1). Because water in the river's center moves faster than water near the boundaries, the parcel we began following at km 362 became diluted and elongated as it moved downriver. Assuming the parcel at river km 362 was a volume equal to 6 h of river flow, the Walden (1992) model indicated 54% of this original water mass would remain in the same volume at river km 0. The calculated upstream and downstream spreading of the initial parcel indicated the leading edge would be approximately 34 river km (10.5 h) ahead of the mean and the trailing edge would be 61 river km (18 h) behind the mean after 4 d. These calculations indicate that, depending on how much the characteristics of each property vary along the river, properties of our initial water could be modified by mixing during our 4-d study.

The sampling interval was 2 h ± 10 min. Adjacent stations were 8–10 km apart in the upper reaches of our study area, and 6–8 km apart in the lower reaches (Fig. 1). Upon reaching river km 0, the survey was turned over to a larger vessel, the RV *Pelican*, and continued into the open Gulf of Mexico. Results from this plume portion of the study will be reported elsewhere.

At each station, the sampling vessel RV *Eugenie* was allowed to drift with the current during sampling. Surface temperature and salinity were measured using a handheld YSI conductivity meter. 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. Dissolved inorganic carbon (DIC) samples were immediately taken from the Niskin bottle through silicon tubing, and fixed with mercuric chloride. The remainder of the water sample was drained into a carboy and taken into the vessel laboratory where the water was gently mixed to ensure uniform distribution of particulate materials and subsampled for specific analyses.

Total suspended matter (TSM) concentrations were measured gravimetrically, using preweighed Millipore filters (0.2 μm, 47 mm diameter) and a filter funnel and bell jar apparatus. After the last aliquot of sample water passed through the filter, 5 ml of deionized water were added to rinse down the sides of the funnel. The filter was removed, folded in half, and stored in a refrigerator until sampling was completed. Filters were transported back to a shore lab, dried at 40°C, and weighed. TSM concentration was calculated as the weight of the dried filter with sediments minus the original filter weight divided by the volume filtered.

Water samples for nutrient analyses were filtered (0.2 μm) on shipboard and frozen for later analysis. In the laboratory, samples were thawed and analyzed with a Lachat QuickChem FIA+ Automated Ion Analyzer. Nitrate (NO_3) was first reduced to nitrite (NO_2) with copper coated cadmium and then $NO_3 + NO_2$ was determined by diazotization with sulfanilamide under acidic conditions to form a diazonium ion, coupled with N-(1-naphthyl) ethylenediamine dihydrochloride and measured at 520 nm (Anderson 1979). Colorimetric phosphate (PO_4) determinations were based on the formation of 12-molybdophosphoric acid from PO_4 and molybdate in acid solution and subsequent reduction by ascorbic acid and the end product was determined at 880 nm (Murphy and Riley 1962). Silicate ($Si(OH)_4$) concentrations were determined by forming a silicomolybdate complex followed by

reduction with a metol oxalic acid solution (Mullin and Riley 1955).

Chlorophyll *a* (chl *a*) concentration was determined in three size classes (< 5 μm, 5–20 μm, and > 20 μm) using a cascade filtration system fitted with a 20 μm polycarbonate filter, a 5 μm polycarbonate filter, and a GF/F glass fiber filter. An additional water sample was filtered through a separate GF/F filter to determine total chl *a* concentration. Filters were extracted in 90% acetone for 24 h at −20°C in the dark, and the extract was measured with a Turner Designs fluorometer before and after acidification to determine chl *a* and phaeopigment concentrations (Strickland and Parsons 1972).

An additional sample was taken for pigment analysis by High Performance Liquid Chromatography (HPLC) according to the methods of Chen et al. (2001) and Bianchi et al. (1995). Each filter was extracted overnight with 100% acetone and blown to dryness under a stream of N_2. 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 DHI Water and Environment Co., Denmark) were run individually to determine retention times and spectra. Pigment identification was performed by comparing retention times and ultraviolet spectra of the peaks in each sample chromatogram to those of the standards. Detection limits were 1 nmol l^{-1}.

Samples for dissolved organic carbon (DOC) and total dissolved nitrogen (TDN) were filtered (ca. 100–150 ml) on shipboard through precombusted (450°C) GF/F glass fiber filters (25 mm, nominal pore size 0.7 μm) into 40 ml precombusted amber vials. Each vial then received 100 μl of 2N HCl to remove inorganic C. The samples were kept frozen onboard and analyzed within a few days of collection. Both DOC and TDN measurements were performed on a Shimadzu TOC-$V_{CSH/CSN}$ analyzer using high-temperature catalytic oxidation and chemiluminescence, respectively. The precision for DOC (± 2%) and TDN (± 2%) analyses was estimated using a coefficient of variation (n = 3).

Samples (100 ml) for analysis of particulate organic carbon (POC) and particulate nitrogen (PN) were filtered on shipboard onto precombusted 25 mm glass fiber filters, frozen and returned to the laboratory, then thawed and placed into individual glass containers. Several of these dishes were placed in a sealed container and exposed to hydrochloric acid fumes for 24 h. The filters were then removed and placed in a 60°C drying oven for 2 h before being folded and packed in tin analytical capsules. Samples were analyzed using a CE Elantech elemental analyzer.

In the laboratory, $HgCl_2$-preserved DIC samples were equilibrated to room temperature before analysis. Water pH (National Institute of Standards Scale) was measured by submerging an Orion Ross combination electrode into each bottle immediately before DIC analysis. DIC was measured with an automated DIC analyzer (Cai and Wang 1998; Wang and Cai 2004). The system integrates the (pCO_2) signal in a Li-Cor Li-6262 H_2O/CO_2 analyzer after a 0.5 ml water sample is acidified in a stripping reactor. The resulting CO_2 gas is purged out into the Li-Cor analyzer. The system was calibrated using certified reference material (CRM) from A. G. Dickson of Scripps Institution of Oceanography, La Jolla, California, and has a precision of 0.1%. A 25-ml water sample was used to determine total alkalinity by Gran titration (Gran 1952) to an end point pH of 3.2 using a HCl solution. The titrations were carried out by an automatic device consisting of two Kloehn digital syringe and drive modules (Kloehn, Las Vegas, Nevada). The Dickson CRM was also used to calibrate the HCl standard solution. The precision of the titration was better than 0.1%.

Water properties measured at each station were regressed against distance (river km) using a model 1 least squares regression. The residuals were tested for autocorrelation for lags of 1–15, and an analysis of variance was employed to test if the regressed linear slopes were significantly different from 0. With the exception of DIC, all water properties were free of autocorrelation in the residuals, suggesting linear fits were appropriate.

Results

The long-term average daily discharge from the Mississippi River ranges between a maximum of approximately 22,500 $m^3 s^{-1}$ in the spring and a minimum of approximately 6,400 $m^3 s^{-1}$ in the fall. A salt wedge does not pass river km 0 (Fig. 1) unless discharge falls below about 9,000 $m^3 s^{-1}$ (Soileau et al. 1989). During our cruise, discharge was approximately 17,400 $m^3 s^{-1}$ and there was no salinity-induced stratification in the lower river at this time. Surface salinity was 0 at all stations. Surface water temperature increased from 24.7°C to 26.1°C between river km 362 and 0 (Fig. 2).

Concentration of TSM in the surface water ranged between a maximum of 105 mg l^{-1} at km 299 to a minimum of 23 mg l^{-1} at km 0 (Fig. 3). Surface TSM concentration calculated from a linear regression through all data (Table 1) indicated a 43% decline during the 4-d transit period.

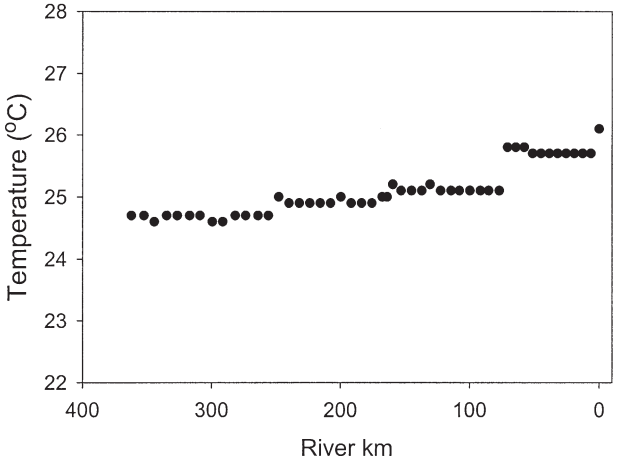

Fig. 2. Temperature of surface water.

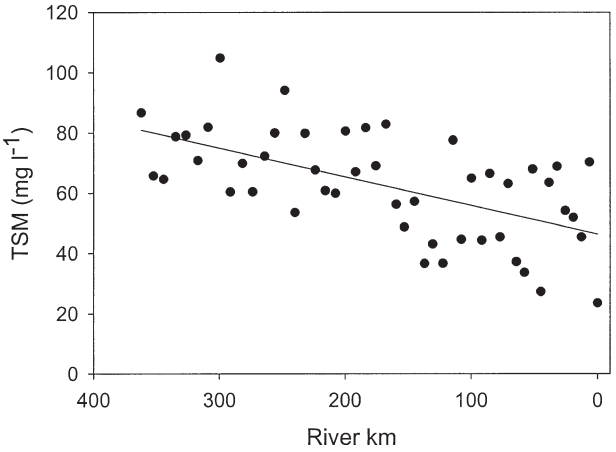

Fig. 3. The concentration (mg l^{-1}) of total suspended matter (TSM) in surface water of the lower Mississippi River, June 20–24, 2003.

Concentrations of $NO_3 + NO_2$ and $Si(OH)_4$ were high during the lower river transit (Fig. 4). Although small, the slope of the $NO_3 + NO_2$ line was statistically significant suggesting an increase from 113.7 to 116.1 μM between km 362 and 0 (Table 1). There was no significant trend to the $Si(OH)_4$ concentration, which averaged 97.8 μM (SD = 1.2 μM). PO_4 concentration (Fig. 4) was high in all samples and increased significantly from km 362 to 0 (Table 1). $NO_3 + NO_2$ increased at a rate equivalent to approximately 0.006% km^{-1} whereas the rate of PO_4 increase was about 10 times greater, equivalent to 0.07% km^{-1}. The ratio of $NO_3 + NO_2 : PO_4$ decreased from 62 at river km 362 to 51 at river km 0 (Fig. 4 and Table 1).

Chl *a* concentrations at the upstream station were high, approximately 8.3 μg l^{-1} measured by fluorometry and 7.6 μg l^{-1} measured by HPLC. Concentrations declined at a statistically significant rate to about 5.6 μg l^{-1} (fluorometry) and 2.8 μg l^{-1} (HPLC) at Head of Passes (Fig. 5 and Table 1). Size fractionated samples analyzed by fluorometry indicated the largest portion of total chl *a* was in the > 20 μm size category (Fig. 5) and the downriver pattern in total chl *a* was primarily determined by this size category. The concentrations of smaller cells remained approximately constant. The < 5 μm size category comprised only a small fraction of the total chlorophyll, typically < 0.5 μg l^{-1}, and the 5–20 μm fraction averaged about 2 μg l^{-1}. HPLC analyses indicated the concentrations of fucoxanthin, alloxanthin, zeaxanthin, and chlorophyll *b* (indicative of diatoms, cryptophytes, cyanobacteria, and chlorophytes, respectively) all declined in the downriver direction (Fig. 6). Pheopigment concentrations measured by fluorescence (not shown) were also high, approximately 4 μg l^{-1} at km 362, with the highest concentrations in the > 20 μm size category. Pheopigment particles > 20 μm declined in the downriver direction, similar to chlorophyll particles in this size fraction, and pheopigment particles in the two smaller categories remained essentially constant. Pheophytin *a* concentration measured by HPLC also declined significantly (36%) in the downriver direction (Table 1).

POC and PN concentrations declined in the downriver direction but PN declined at a slightly greater rate, as indicated by an increase in the ratio of particulate C : N (Fig. 7). The slopes of all three regressions are statistically significant (Table 1). There was also a statistically significant decline in DOC in the downriver direction (Fig. 8) but this decline, from 276 to 267 μM, was small (3%) compared to the 42% decline in POC (Table 1). In contrast to DOC, dissolved organic nitrogen (DON), computed by subtracting dissolved inorganic nitrogen (DIN) from TDN, did not change significantly in the downriver direction (Fig. 8).

DIC was the only property that showed an autocorrelation of residuals, suggesting that the decrease in DIC (Fig. 9) was not linear, and that there was some kind of sink for DIC located near river km 80. There was a statistically significant increase in pCO_2, and an associated decrease in pH; both of these appeared linear.

Discussion

Changes that occur in our study region of the lower Mississippi River cannot be due to inputs from tributaries or a floodplain because the river is confined within its banks by a system of levees. Inputs from patchy fringes of willow tree stands that occur between the river shoreline and the levee are possible, but would have minimal effects on the parameters measured in this study.

TABLE 1. Summary of the linear relationships between surface water property and distance (km). Change (%) is from river km 362 to river km 0. A slope of 0 indicates a statistically nonsignificant regression.

Property	Slope	Intercept	r^2	Change (%)
TSM (mg l^{-1})	0.0956	46.2	0.35	− 43
$NO_3 + NO_2$ (μM)	−0.0067	116.1	0.33	+ 3
$Si(OH)_4$ (μM)	0	97.8		0
PO_4 (μM)	−0.0012	2.28	0.29	+ 23
$NO_3 + NO_2 : PO_4$	0.0311	50.7	0.23	− 18
Chl total (mg l^{-1})	0.0074	5.58	0.57	− 33
Chl > 20 μm (μg l^{-1})	0.0059	3.32	0.51	− 39
Chl 5–20 μm (μg l^{-1})	0	1.93		0
Chl < 5 μm (μg l^{-1})	0.0008	0.27	0.25	− 54
Chl HPLC (μg l^{-1})	0.0132	2.81	0.77	− 63
Fucoxanthin (μg l^{-1})	0.0013	0.957	0.40	− 33
Alloxanthin (μg l^{-1})	0.0003	0.057	0.61	− 63
Zeaxanthin (μg l^{-1})	0.0003	0.029	0.62	− 76
Chlorophyll *b* (μg l^{-1})	0.0007	0.226	0.61	− 52
Phaeophytin a (μg l^{-1})	0.0004	0.245	0.11	− 36
POC (μM)	0.1855	90.5	0.39	− 42
PN (μM)	0.0218	6.3	0.54	− 57
POC : PN	−0.0084	13.9	0.53	+ 22
DOC (μM)	0.0249	267.1	0.25	− 3
TDN (μM)	0	128.0		0
DON (μM)	0	13.1		0
PH	0.0002	7.71	0.65	− 1
pCO_2 (μatm)	−0.2739	1023.7	0.54	+ 9

Declines in POC (42%), PN (57%), TSM (43%), and chl *a* containing particles > 20 μm (39%) suggest large particles were settling from the surface during our 4-d study of the lower river. Other studies (Demas and Curwick 1988; Mossa 1996) have shown that particulate materials accumulate on the bottom in the lower Mississippi River during periods of low or declining discharge, to be resuspended and flushed out to the Gulf of Mexico during subsequent periods of high discharge. At low discharge there are large differences in cross sectional area between upriver and downriver locations and the deepening of the channel and thalweg results in decreased velocities downstream, promoting sediment deposition. During higher discharge stages, the differences in upriver-downriver cross sectional area are smaller and increased current velocities are accompanied by steeper downstream surface-water gradients resulting in resuspension of bottom sediments (Mossa 1996). Although river discharge was moderate during our study, it had recently declined from a level approximately 2 times higher (Fig. 10) and conditions for maintaining large particles in suspension had weakened over the 2–3 wk prior to our study.

It is unlikely that zooplankton grazing led to the observed reduction of phytoplankton and other large particles because pheopigments, indicative of grazing, also declined in the downriver direction.

Although both POC and PN declined during the lower river transit, the POC : PN ratio increased because the decline in PN was greater than the decline in POC. N rich particles could be sinking faster than other particles or N regeneration could be preferentially occurring. Under the latter circumstances, conversion of the missing PN (1.8 μM) into ammonium (NH_4) would probably not be detectable in the TDN signal, which averaged 128 μM. Under these conditions, there also would be a DIC increase of about 18 μM (assuming a C : N of 10) but this too would not be detectable in the large and variable DIC signal.

Most dissolved constituents remained constant or nearly so. DIN ($NO_3 + NO_2$) increased slightly (3%), DON did not change, dissolved $Si(OH)_4$ did not change, and DOC decreased slightly (3%). The exception to this pattern was dissolved PO_4, which increased by 23%. The source of this PO_4 is not clear. At the observed river discharge (17,400 $m^3 s^{-1}$), an input of 5.6×10^4 kg d^{-1} (56 T d^{-1}) of PO_4 would be required to increase the riverine PO_4 concentration by the observed amount (0.4 μM). The increase appeared to be linear and this would not be expected if it came from a point source. The small amount of biological decomposition of organic matter indicated by the decline in DOC would cause an increase in PO_4 of about 0.1 μM, considerably less than the observed increase of 0.4 μM. The major source is probably an inorganic process such as desorption. Large amounts of particle bound P are exported to the shelf via the Mississippi River (Sutula et al. 2004) and a portion of this may be desorbed during transit through the lower river.

Because PO_4 increased more than $NO_3 + NO_2$ in our study, the N : P ratio calculated from these

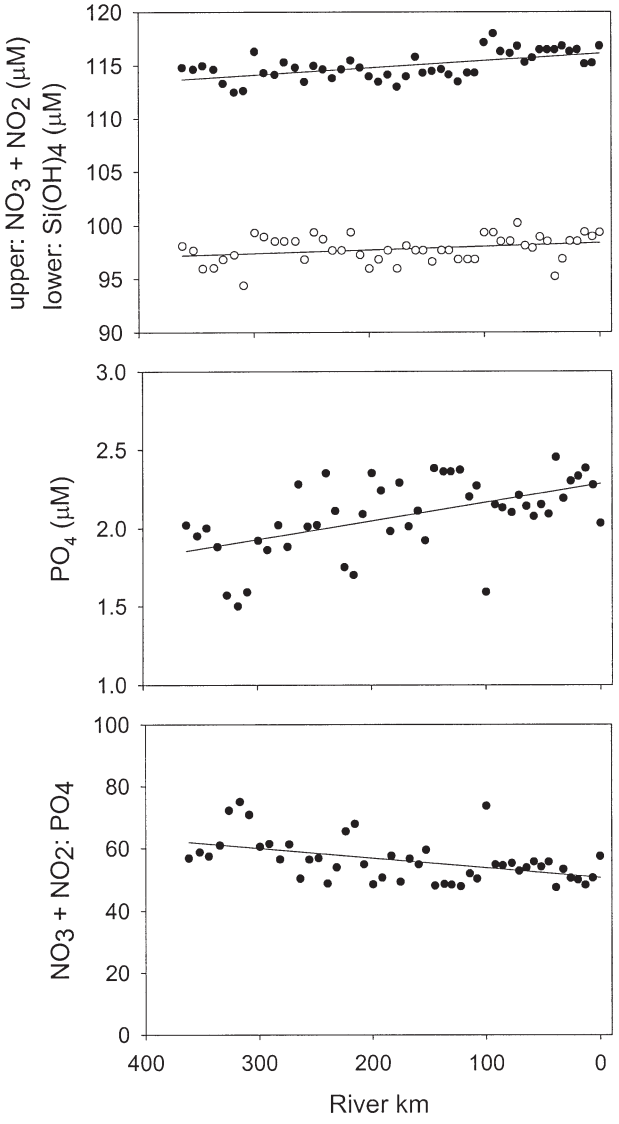

Fig. 4. The concentration (μM) of dissolved nutrients in the lower Mississippi River, June 20–24, 2003: NO_3 + NO_2 and $Si(OH)_4$, PO_4, and DIN : DIP ratio.

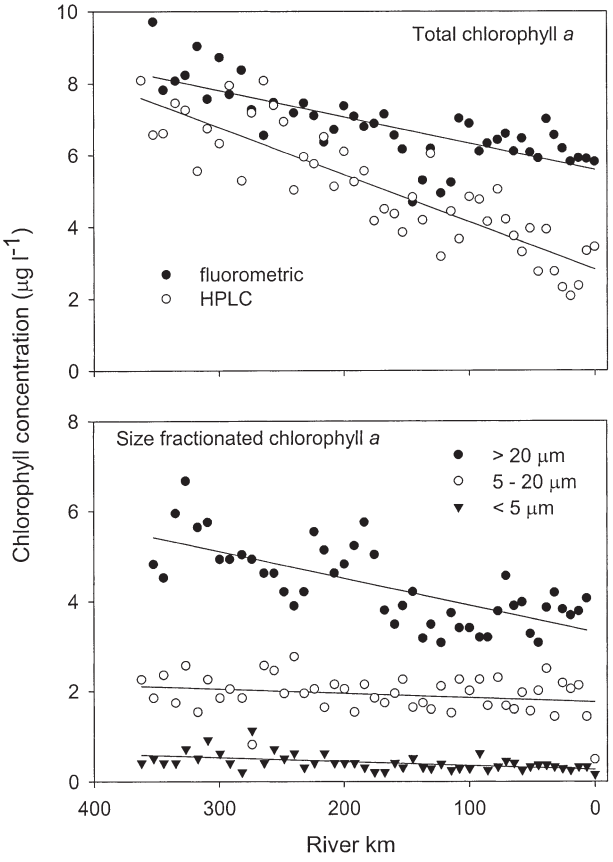

Fig. 5. The concentration (μg l^{-1}) of chlorophyll *a* in the lower Mississippi River, June 20–24, 2003 from fluorometric analysis: total and three size fractions: > 20, 5–20, and < 5 μm, and HPLC (total).

concentrations declined, from 62 at km 362 to 51 at km 0. For comparison, the DIN : SRP ratio from a separate study at a station located at km 378 ranged, over a 2-yr period, between 23 and 294, with a mean of 90 (Duan unpublished data). Earlier work (Justic et al. 1993, 1995; Rabalais et al. 1996) reported much lower ratios, between 9 and 15, but these were derived using total P and are not directly comparable to our calculated ratios.

Phytoplankton represents a significant fraction of the total POC in the lower river. Assuming a C : chl ratio of 50 for phytoplankton, the total chlorophyll (6–8 μg l^{-1}) represents 300–400 μg l^{-1} of phytoplankton C, equivalent to approximately 20–25% of POC during our study. During the 2-yr study by Duan (unpublished data), phytoplankton biomass represented an average of 8.1% of total POC, with highest values approaching 20% when phytoplankton biomass was high.

There was no net growth or production of phytoplankton in the lower river during our study. Based on chlorophyll and other phytoplankton pigments, there was no increase in phytoplankton in the lower river, even though the settling of TSM would lead to an improved light environment. All three size-categories of chl *a* measured fluorometrically, total chlorophyll measured by HPLC, and other pigments representing the dominant phytoplankton groups in the river, either declined or remained constant during the 4-d transit. Net autotrophy was not indicated by pCO_2, which did not decrease but increased slightly (11%). The lack of any measurable reduction of macronutrients (NO_3 + NO_2, $Si(OH)_4$, PO_4) also suggests that gross phytoplankton production was negligible at this time, but there was a significant amount of

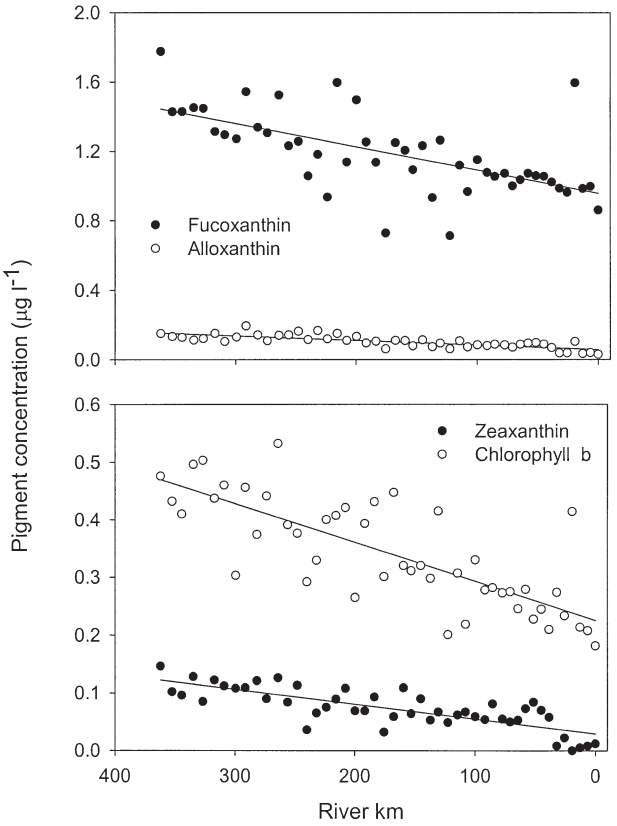

Fig. 6. The concentration (μg l^{-1}) of phytoplankton pigments fucoxanthin, alloxanthin, zeaxanthin, and chlorophyll *b*, indicators of diatoms, cryptophytes, cyanobacteria, and chlorophytes, respectively.

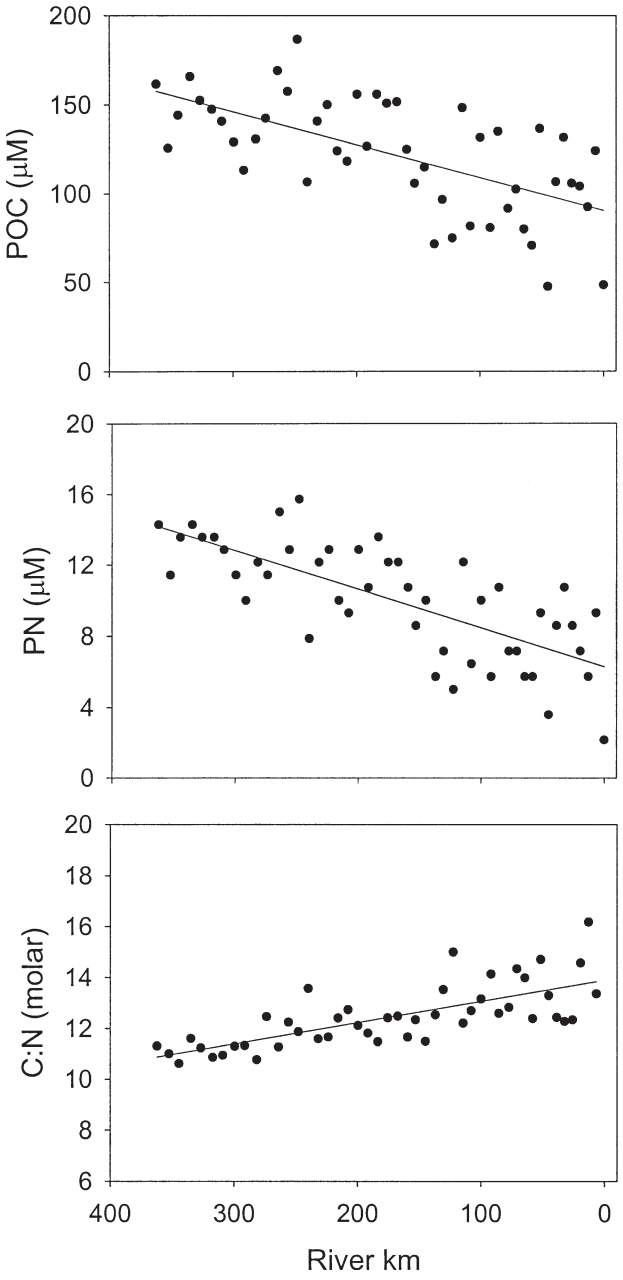

Fig. 7. Particulate organic carbon (POC) and total particulate nitrogen (PN) in the lower Mississippi River, June 20–24, 2003: POC, PN, and POC : PN ratio.

phytoplankton in the water. Initial stocks at km 362 were approximately 8 μg chl l^{-1}. This must have come from farther upriver but the source is unclear. In a separate study, Duan (unpublished data) reported chl *a* concentrations from a station located at km 378 ranged between 0.75 and 23.18 μg l^{-1} over a 2-yr period. They showed that chlorophyll concentrations were highest during periods of low river flow, suggesting in situ production during periods of lowest suspended matter load and highest light penetration. They did not definitively identify the location of this production. Some phytoplankton production may occur at the river edges where flow is slow, sediment can settle, and light can penetrate a larger fraction of the water column. It does not seem likely that this could provide sufficient production to support observed stocks in the river, and the main source must lie farther upriver. In situ production could occur in the relatively quiet waters behind dams located far up the river or in other upriver locations (e.g., Sellers and Bukaveckas 2003) and then be carried downriver. This is broadly consistent with the view that dynamics of downstream reaches are intimately linked with processes occurring farther upstream (Vannote et al. 1980; Thorpe and Delong 1994). Our data indicate in situ production did not occur between river km 362 and 0 during our study period, and the sources of the high concentrations of chlorophyll in our study remain undetermined.

The concentration of DOC decreased from 276 to 267 μM, about 3%, during our 4-d study. In

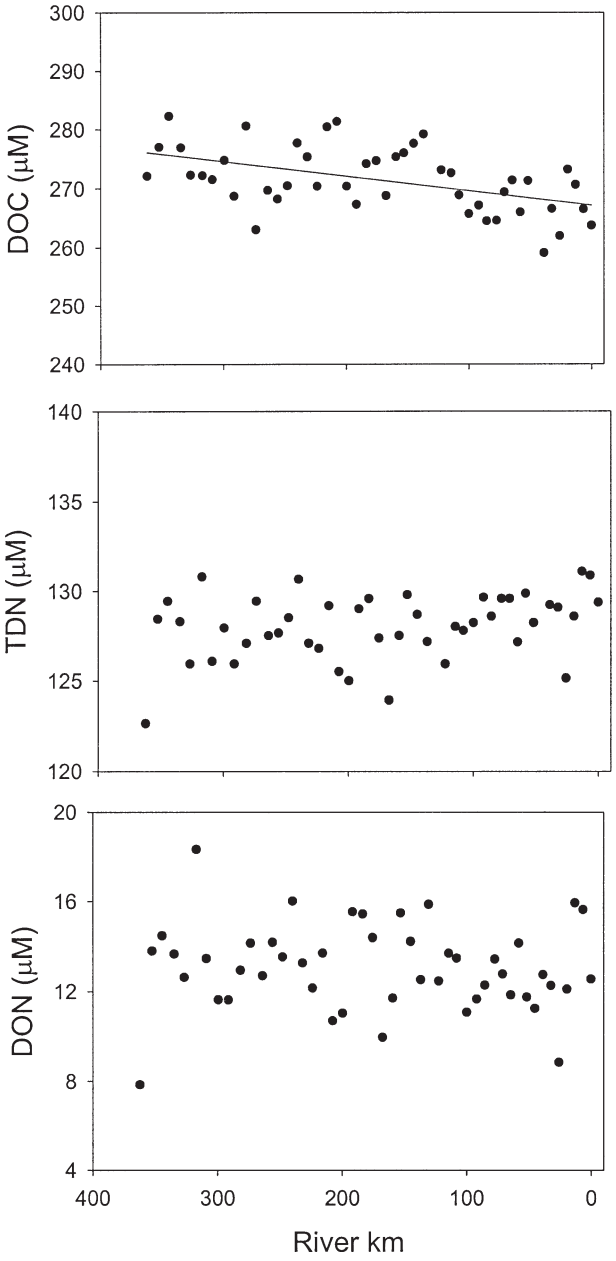

Fig. 8. Dissolved organic carbon and nitrogen (DOC and DON) in the lower Mississippi River, June 20–24, 2003: DOC, TDN, and DON (mean = 13.1).

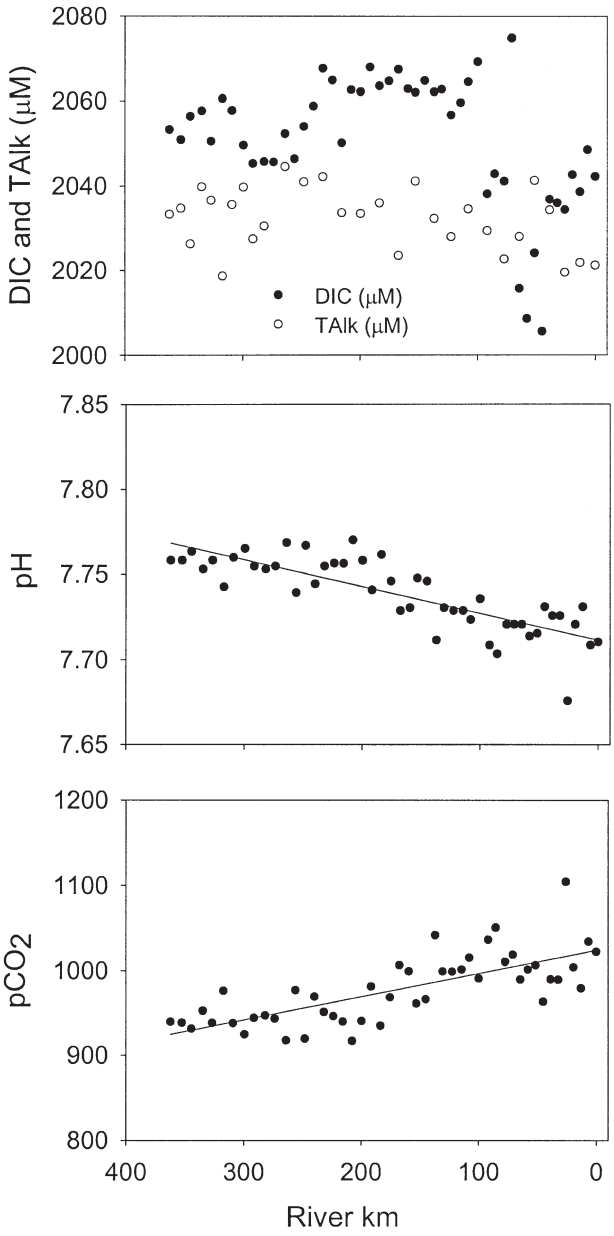

Fig. 9. Dissolved inorganic carbon, total alkalinity (TAlk), pH, and pCO_2 in the lower Mississippi River, June 20–24, 2003: DIC and TAlk, pH, and pCO_2.

a separate study conducted at a different time, there was a 21% decline in DOC in river water incubated for 10 d in the dark on shipboard (Hernes and Benner 2003). These data indicate a component of the river DOC is labile. Our bulk analyses may mask a more dynamic system with inputs of highly labile materials occurring simultaneously with decomposition. Other studies (Repeta et al. 2002; Bianchi et al. 2004) suggest labile DOC may originate from phytoplankton in the river. Since the amount of phytoplankton varies widely, the amount of labile DOC in river water should also vary widely. pCO_2 in river water increased from 925 to 1024 μatm, supporting our observation of net heterotrophy. The DIC signal did not support these observations. Assuming the change in our DOC signal was due to microbial decomposition, the amount of CO_2 released would be 9 μM, and DIC should increase by 9 μM. This would be difficult to detect in our DIC data, which were variable and ranged between

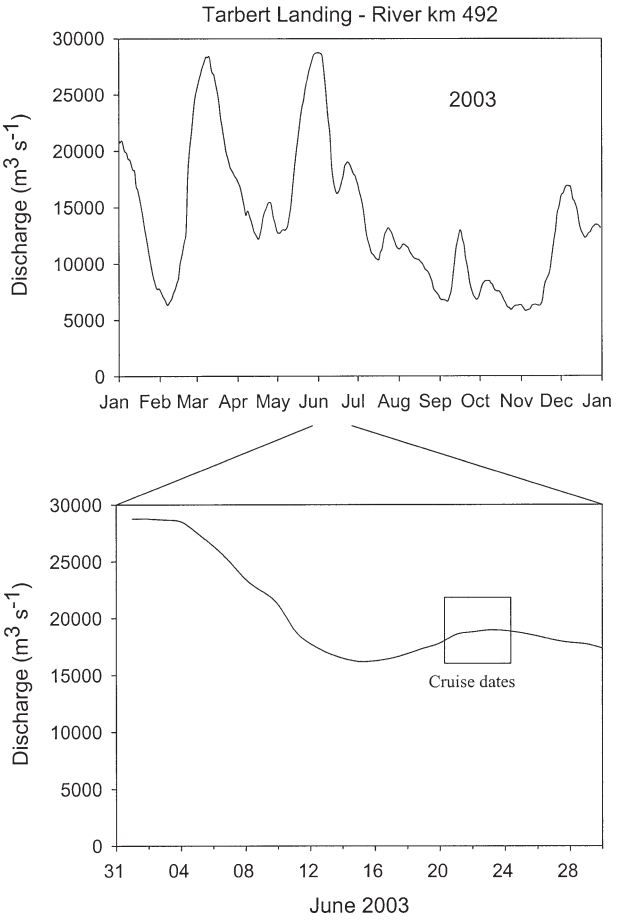

Fig. 10. Freshwater discharge in June 2003. The box indicates the dates of our 4 d study.

about 2,005 and 2,075 μM. Between the beginning and end of our study, the riverine DIC did not increase but decreased, indicating a loss of CO_2 to the atmosphere, which further masked any signal of heterotrophic CO_2 production. We are unable to explain this shift in DIC fully or to account for the uniqueness of this change compared to all our other properties. While CO_2 evasion to the atmosphere can account for the DIC decrease, we are not sure why the decrease occurred only in the lower stretch of the river. During the 4 d, there was no significant change in wind speed or the width of the river, factors that can cause a change in the rate of CO_2 evasion. At average wind speed of 4 m s^{-1} and water temperature of 28°C, gas transfer velocity was calculated as 5.88 cm h^{-1} (or 1.4 m d^{-1}) during this cruise We calculated, after Wanninkhof (1992), that the average rate of CO_2 loss to air would be 4.5 mmol m^{-3} d^{-1} (or μM d^{-1}). During the 4-d transit, the CO_2 loss to air appears to be higher than the microbial respiration rate (approximately 1.5 μM d^{-1} from DOC decrease). The CO_2 evasion rate would imply a DIC decrease of only a few μM in 4 d of transit. The inconsistencies in these data make interpretation difficult but it seems reasonable to conclude that some heterotrophic activity in river water was occurring during our study. Studies in the Mississippi River discharge plume show low rates of bacterial activity in the low salinity (most river-like) portions (Amon and Benner 1998). Community O_2 consumption rates have been found to be either insignificant (Pakulski et al. 1995) or small (Pakulski et al. 2000) near the zero salinity zone in the river plume. The implication is that riverine DOC in our study was highly refractory but there probably was a small pool of reactive substrate.

DON was only a small portion (9%) of TDN. Recent data from the U.S. Geological Survey (USGS; http://water.usgs.gov/nasqan/) for 1999–2003 indicate a range of 8–35% with an average of 17%. In the USGS data, DON ranged between 14 and 35 μM while DIN ranged from 36 to 212 μM, indicating that most of the variability in the percentages is due to changes in the amount of DIN not DON.

For most of the properties we measured during our brief study, the ranges observed are within those observed over longer time scales in this system. In a separate study at river km 376, a site slightly upriver from the starting point of our study, monthly sampling over a 2-yr period indicated wider ranges in many properties (Duan unpublished data). In that study, TSM ranged between 22 and 262 mg l^{-1}, POC between 48 and 250 μM, PN between 6 and 30 μM, NO_3 between 51 and 121 μM, $Si(OH)_4$ between 58 and 121 μM, PO_4 between 0.28 and 2.80 μM, and chl *a* between 0.75–23.18 μg l^{-1} (Duan unpublished data). It is possible that autotrophic and heterotrophic processing of river constituents may be important under some of these conditions, although they were not under the conditions of our study. In the Amazon River, strong seasonal cycling of biogeochemical properties has been observed and attributed to both variations in inputs and in situ processing (Devol and Hedges 2001).

Vannote et al. (1980) proposed a river continuum concept that incorporated the view that headwaters would be net heterotrophic because of shading and inputs from riparian vegetation, intermediate reaches would be net autotrophic because of reduced inputs of terrestrial organic matter and increased in situ phytoplankton production, and lower reaches would again be net heterotrophic because of organic matter from upstream and phytoplankton light limitation associated with depth and turbidity. Subsequent studies have refined this initial conceptual model (Junk et al. 1989; Sedell et al. 1989). Although the Mississippi River is highly constrained, our study indicates that the river

must have displayed significant autotrophic activity somewhere upstream of our starting point and appeared to be slightly net heterotrophic within the lower river. We do not yet have a complete understanding of all the processes occurring in this large river system but, in comparison to the very high biological rates that occur in plume waters shortly after river water is discharged into the Gulf of Mexico (Dagg and Breed 2003), there is much less biological activity in the lower Mississippi River.

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