



## Microbial Metabolism and Nutrient Cycling in the Mississippi and Atchafalaya River Plumes

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Spatial distributions of chlorophyll, bacterial abundances and production, community respiration, and dissolved C, N, P and Si were measured in the Mississippi River (MRP) and Archafalaya River (ARP) plumes during July 1993. Dark bottle incubations were used to estimate net flux rates of inorganic nutrients, community respiration, and changes in chlorophyll concentrations in unfiltered water samples. Concentrations of total dissolved N (TDN) and soluble reactive P (SRP) in the Mississippi River were 55  $\mu\text{M}$  and 3  $\mu\text{M}$  higher, respectively, compared with those in the Archafalaya River. Concentrations of dissolved organic carbon (DOC) and nitrogen (DON) in the Archafalaya River, however, were 35 and 11  $\mu\text{M}$  higher, respectively than in the Mississippi River. Elevated chlorophyll concentrations, bacterial abundances and production, and community respiration rates were observed at intermediate (5–25) salinities of both plumes. Property-salinity plots indicated net sinks of dissolved N, P and Si at intermediate salinities consistent with photosynthetic utilization of these substances within the plumes. The distribution of dissolved P, N and chlorophyll suggested phytoplankton-mediated transformation of riverine- $\text{NO}_3^-$  to DON at intermediate salinities of the MRP, and a similar transformation of riverine SRP to dissolved organic P (DOP) at intermediate salinities of the ARP. Net regeneration of dissolved Si and  $\text{NH}_4^+$  was observed in regions of elevated chlorophyll concentrations and net removal rates in both plumes. Nitrification rates in the MRP were c. 10-fold higher than in the ARP. Estimates of C fixation by nitrifying bacteria equalled or exceeded heterotrophic bacterial C production in the low salinity region of the MRP, but were negligible compared to heterotrophic bacterial production in the ARP. Dissolved inorganic N:P, Si:P and DOC:DON:DOP ratios suggested the potential for P limitation in both plume systems during the period investigated.

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### Introduction

The Mississippi River ranks seventh in the world in volume of annual discharge (Milliman & Meade, 1983) and has a significant impact on the biogeochemistry of the northern Gulf of Mexico (Fox *et al.*, 1987; Lohrenz *et al.*, 1990; Chin-Leo & Benner, 1992; Lopez-Veneroni & Cifuentes, 1994; Pakulski *et al.*, 1995; Rabalais *et al.*, 1996; Lohrenz *et al.*, 1997). Historical data indicate that fertilizer use in the

Mississippi watershed has dramatically increased nutrient loading from the Mississippi River to the Louisiana Shelf (Turner & Rabalais, 1991) and has contributed to the seasonal development of extensive (6–16 500  $\text{km}^2$ ) areas of hypoxic bottom water extending westward from the Mississippi Delta (Justic *et al.*, 1996; Rabalais *et al.*, 1996).

Nutrients delivered to the Gulf of Mexico via the Mississippi River system are transported over a large

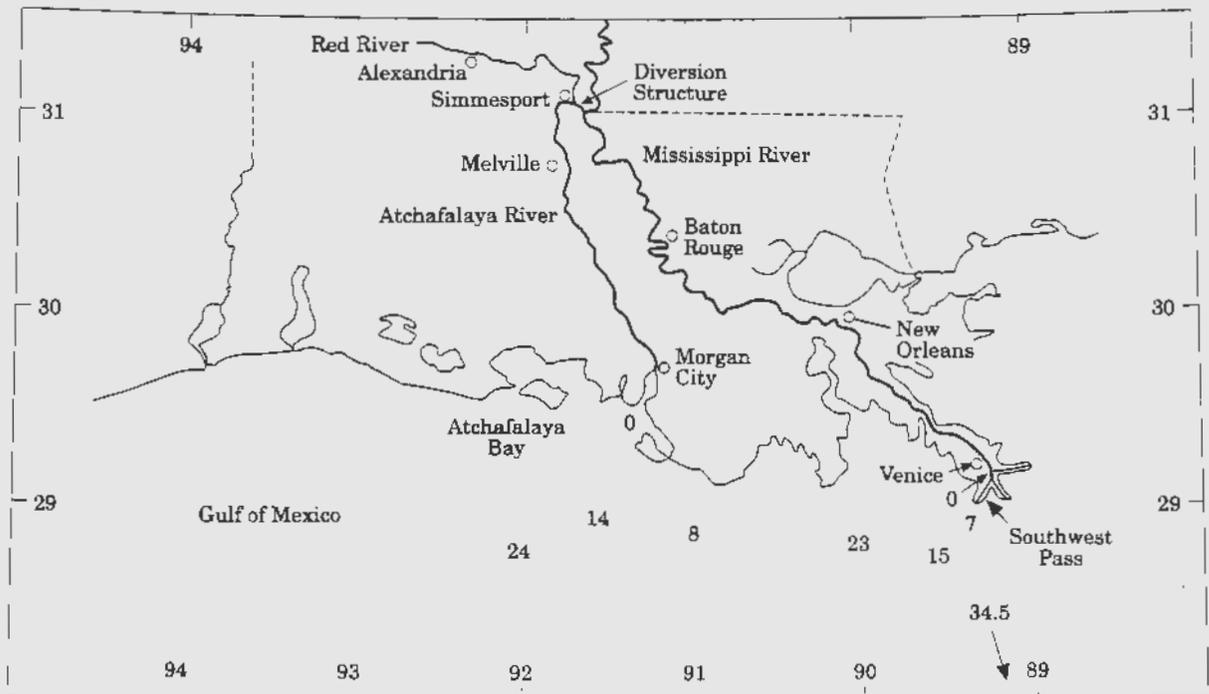


FIGURE 1. Location of the Red, Mississippi and Atchafalaya Rivers. Numerals indicate the location and salinities of stations in the Gulf of Mexico. The high salinity (34.5) station was located at  $27^{\circ}16.5'N$ ,  $89^{\circ}47.1'W$ .

spatial continuum originating in the upper Mississippi River basins and terminating on the outer Louisiana Shelf. Inputs, removal or transformations of nutrients may occur at any point along this continuum which may subsequently influence nutrient cycling downstream in the river (Anrweiler *et al.*, 1995) and along surface plume salinity gradients on the Louisiana Shelf (Pakulski *et al.*, 1994). Biogeochemical processes in the lower Mississippi basins may thus influence the nutrient chemistry of the river prior to discharge into the Gulf of Mexico.

The Mississippi River discharges into the Gulf of Mexico at two locations: the Mississippi Delta and via the Atchafalaya River (Figure 1). The Atchafalaya River originates at the confluence of the Red and Mississippi Rivers through a diversion channel near Simmesport, Louisiana (Figure 1). The U.S. Army Corps of Engineers diverts 30% of the Mississippi River to the Atchafalaya basin at this junction. The Atchafalaya River passes through wetlands and the shallow (*c.* 2 m) waters of Atchafalaya Bay prior to discharge into the open Gulf of Mexico. In contrast, the Mississippi River below the Simmesport diversion has been extensively channelized, reducing the interaction of the river with historical floodplains.

Biological transformations and hydrological processes (e.g. tributary inflow, exchange with ground waters) may alter the organic and inorganic chemistry

of Mississippi River water diverted to the Atchafalaya basin. Differences in the chemistries of the Mississippi and Atchafalaya Rivers may subsequently influence the development of biological communities in their respective plumes and other processes on the inner Louisiana Shelf. As part of the NECOP (Nutrient Enhanced Coastal Ocean Productivity Program) investigating processes associated with the development of hypoxic bottom water on the Louisiana Shelf, the influence of the Mississippi and Atchafalaya Rivers on biological activity and nutrient cycling in the surface waters of Mississippi outflow region during July 1993 was investigated.

### Methods

Sample collections and experiments were conducted from 4–13 July 1993, aboard the RV *Loughorn*. Stations in the Mississippi River plume (MRP) were located along a transect originating in the Head of Passes in the Mississippi River and extending westward from the Southwest Pass of the Mississippi Delta (Figure 1). Samples from the Atchafalaya River plume (ARP) were collected along a transect originating in Atchafalaya Bay. Stations along each transect were by CTD survey and identified by salinity (e.g. station M7 for salinity 7 in the MRP, A23 for salinity 23 in the ARP). Salinities were measured with a Reichert

refractometer. Stations along both transects were located within the general area of hypoxic bottom water formation during 1993. Because of the unusual extent of fresh water on the Louisiana Shelf during the study period, the high salinity endmember for both transects (M34.5) was located c. 170 km to the south of the Mississippi Delta (Figure 1).

Samples were collected from bucket casts into a clean (1 M HCl and sample rinsed) polyethylene carboy and subsequently dispensed into clean 300 ml glass BOD and 250 ml polycarbonate bottles. The carboy was agitated to ensure dispersion of particles while dispensing water to sample bottles. Bottles were incubated in the dark at *in situ* temperatures. Incubation temperatures did not vary from initial values over the course of the incubations. At 3–6 h intervals during each 12–24 h incubation period, two triplicate sets of bottles were removed for dissolved O<sub>2</sub> and dissolved inorganic C determinations. An additional triplicate set of bottles was also removed at each time point to determine changes in nutrients, dissolved organic C, N and P, chlorophyll concentrations, and bacterial abundances and production.

Dissolved O<sub>2</sub> concentrations were measured by the precision Winkler method (Oudot *et al.*, 1988; Graneli & Graneli, 1991) using a Mettler DL-21 autotitrator equipped with a platinum combination electrode. The mean coefficient of variation for all O<sub>2</sub> determinations was 1.3%. Dissolved inorganic carbon (DIC) was measured with a UTC Model 5120 coulometer, using sampling procedures described by Dickson and Goyer (1991). Samples for DIC analyses were poisoned with 50 µl of saturated HgCl<sub>2</sub> at each time-point and stored (<4 h) in the dark until analysed. The mean coefficient of variation for all DIC determinations was 0.21%.

Analyses for NH<sub>4</sub><sup>+</sup>, NO<sub>2</sub><sup>-</sup>, NO<sub>3</sub><sup>-</sup>, soluble reactive P (SRP) and dissolved reactive Si were performed aboard ship using automated techniques (Hitchcock & Whitley, 1992) with an Alpkem rapid flow analyser. Dissolved inorganic N (DIN) was estimated as the sum of mean NH<sub>4</sub><sup>+</sup>, NO<sub>2</sub><sup>-</sup>, and NO<sub>3</sub><sup>-</sup> concentrations within each triplicate set of bottles. Over the extremely wide range of concentrations encountered along the plume transects, mean coefficients of variation (% CV) for all analyses were: SRP=6%, reactive Si=2%, NO<sub>2</sub><sup>-</sup>=7%, NH<sub>4</sub><sup>+</sup>=18%, NO<sub>3</sub><sup>-</sup>=3%.

Samples for dissolved organic C (DOC) and N (DON) analyses were filtered through precombusted (475 °C, 4 h) GF/F filters directly onto precombusted glass scintillation vials using low (<5 mm Hg) vacuum and frozen immediately. Dissolved organic C was measured by high temperature combustion (HTC) with a Shimadzu TOC 500 carbon analyser (Benner

& Strom, 1993). The mean coefficient of variation for DOC analyses was 4%. Total dissolved N (TDN) was measured using a modified Shimadzu TOC 5000 analyser coupled to an ANTEK-720 chemiluminescent detector (Lopez-Veneroni & Cifuentes, 1994). The mean coefficient of variation for all TDN analyses was 9%. Concentrations of DON were determined by subtracting mean DIN concentrations from mean TDN values.

Samples for total dissolved phosphorus (TDP) were obtained from the Atchafalaya River transect and at M34.5. Total dissolved P was determined by dry oxidation of filtered (GF/F) samples using the method of Solorzano and Sharp (1980), with the exception that 0.6 M HCl was used to hydrolyze oxidized samples. Dissolved organic P (DOP) was determined as the difference between sample SRP and TDP concentrations. The mean coefficient of variation for all TDP analyses was 19%.

Bacterial abundances were measured by epifluorescence microscopy of DAPI stained samples (Porter & Feig, 1980). Bacterial production was measured using [<sup>3</sup>H]-leucine incorporation (Kirchman *et al.*, 1985; Amon & Benner, 1998). Leucine incorporation rates were converted to bacterial C assuming a conversion factor of 3.1 kg bacterial C produced per mole incorporated leucine (Simon & Azam, 1989). Previous research in the Mississippi River plume (Benner *et al.*, 1992) indicated that this conversion factor compares well with empirically derived thymidine incorporation C conversion factors. Chlorophyll samples were collected on glass-fibre filters (GF/F), extracted in 90% (v/v) acetone and quantified fluorometrically.

The NH<sub>4</sub><sup>+</sup>, NO<sub>2</sub><sup>-</sup>, NO<sub>3</sub><sup>-</sup>, SRP, DOC and reactive Si data were analysed (paired Student's *t*) to determine significant differences in concentrations between the two rivers. Mississippi River TDN samples were analysed in duplicate (concentration values=206.3 and 208.9 µM) which precluded statistical comparisons with the Atchafalaya River TDN concentrations (triplicate mean ± 95% confidence interval=152.6 ± 19.2 µM). Because estimates of DIN, DON and DOP were calculated as single values, we could not statistically compare differences in concentrations of these constituents between the two rivers or during bottle incubations.

Net flux rates of NH<sub>4</sub><sup>+</sup>, NO<sub>2</sub><sup>-</sup>, NO<sub>3</sub><sup>-</sup>, SRP, O<sub>2</sub> consumption, DIC production and net changes in chlorophyll concentrations were determined from the slope of the time course least squares regression line obtained from bottle experiments (except where noted, Table 2 and 3). Slopes of regression lines used to estimate flux rates were significant at *P*<0.05 (except where noted, Table 3). Where flux rates were

TABLE 1. Chlorophyll concentrations, net changes in chlorophyll concentrations ( $\Delta$  Chl), initial bacterial abundances and heterotrophic bacterial production measured during dark incubations of unfiltered water from the Mississippi and Atchafalaya River plumes, July 1993. Positive and negative values for  $\Delta$  Chl indicate significant ( $P < 0.05$ ) net increases or decreases, respectively, in chl concentrations during experimental incubations

| Station (salinity)      | Chl <i>a</i> ( $\mu\text{g l}^{-1}$ ) | $\Delta$ Chl ( $\text{ng l}^{-1} \text{h}^{-1}$ ) | Bacterial abundance ( $10^6$ cells $\text{ml}^{-1}$ ) | Bacterial production ( $\mu\text{g C l}^{-1} \text{h}^{-1}$ ) |
|-------------------------|---------------------------------------|---|---|---|
| Mississippi River plume |                                       |   |   |   |
| M0                      | 0.50                                  | ND  | 3.2   | 0.43  |
| M7                      | 0.77                                  | - 22  | 2.0   | 0.25  |
| M15                     | 9.33                                  | - 273   | 9.9   | 1.01  |
| M23                     | 0.25                                  | NS  | 3.8   | 6.50  |
| M34.5                   | 0.015                                 | ND  | 0.1   | 0.20  |
| Atchafalaya River plume |                                       |   |   |   |
| A0                      | 0.32                                  | ND  | 2.0   | 1.50  |
| A8                      | 3.08                                  | - 50  | 6.1   | 0.61  |
| A14                     | 1.23                                  | - 29  | 9.7   | 0.62  |
| A24                     | 0.68                                  | - 56  | 1.9   | 2.02  |

NS=not significant.  
ND=not determined.

determined from initial and final concentrations, the data were analysed (paired Student's *t*) to determine significant changes in concentrations between the two time points. Data from BOD and polycarbonate bottles were pooled for  $\text{NH}_4^+$ ,  $\text{NO}_2^-$ ,  $\text{NO}_3^-$ , and soluble reactive P (SRP) flux measurements. It should be emphasized that flux rates reported herein are net rates, and not all forms (dissolved, particulate, and gaseous) and phases (organic, inorganic) of C, N, P and Si were accounted for during bottle incubations. As a result, the nutrient flux data reported herein are not necessarily amenable to mass balance analyses.

## Results

Chlorophyll concentrations in both rivers were similar (Table 1). Highest chlorophyll concentrations were observed at M15 in the MRP and at A8 in the ARP (Table 1). Chlorophyll removal rates were greatest at M15 in the MRP but varied little across the ARP salinity gradient (Table 1). Bacterial cell abundances were similar in both rivers and enhanced at intermediate salinities in both plumes (Table 1). Bacterial production in the Atchafalaya River was *c.* 3-fold greater compared to the Mississippi River. In both plumes, the highest rates of heterotrophic bacterial production were observed at salinities  $>20$  (Table 1).

Oxygen consumption in bottle experiments was linear with time (data not shown). At M7 and A24, however,  $\text{O}_2$  concentrations declined asymptotically over the course of the incubations. At these two stations,  $\text{O}_2$  consumption rates were determined

from the initial concentrations and the first time point. The shape of these two  $\text{O}_2$  curves suggested that  $\text{O}_2$  consumption rates at these stations were underestimated.

Community  $\text{O}_2$  consumption rates were similar in both rivers and enhanced at intermediate salinities in both plumes (Table 2). Community DIC production rates were similar to  $\text{O}_2$  consumption rates (Table 2). In the MRP, highest  $\text{O}_2$  consumption rates were spatially coincident with elevated chlorophyll and bacterial concentrations at M15, but not with

TABLE 2. Dark incubation dissolved  $\text{O}_2$  consumption and inorganic carbon (DIC) production rates from the Mississippi and Atchafalaya River plumes, July 1993

| Station (salinity)      | $\text{O}_2$ consumption ( $\mu\text{M h}^{-1}$ ) | DIC production ( $\mu\text{M h}^{-1}$ ) |
|-------------------------|---|---|
| Mississippi River plume |   |   |
| M0                      | 0.50 <sup>a</sup>                                 | ND                                      |
| M7                      | 1.90 <sup>a</sup>                                 | 1.75                                    |
| M15                     | 3.15  | 3.25                                    |
| M23                     | 0.95  | 0.97                                    |
| M34.5                   | 0.37 <sup>a</sup>                                 | ND                                      |
| Atchafalaya River plume |   |   |
| A0                      | 0.26  | ND                                      |
| A8                      | 1.60  | 1.24                                    |
| A14                     | 0.92  | 0.53                                    |
| A24                     | 1.69 <sup>a</sup>                                 | ND                                      |

<sup>a</sup>Oxygen consumption rates determined from initial and final dissolved oxygen concentrations.  
ND=not determined.

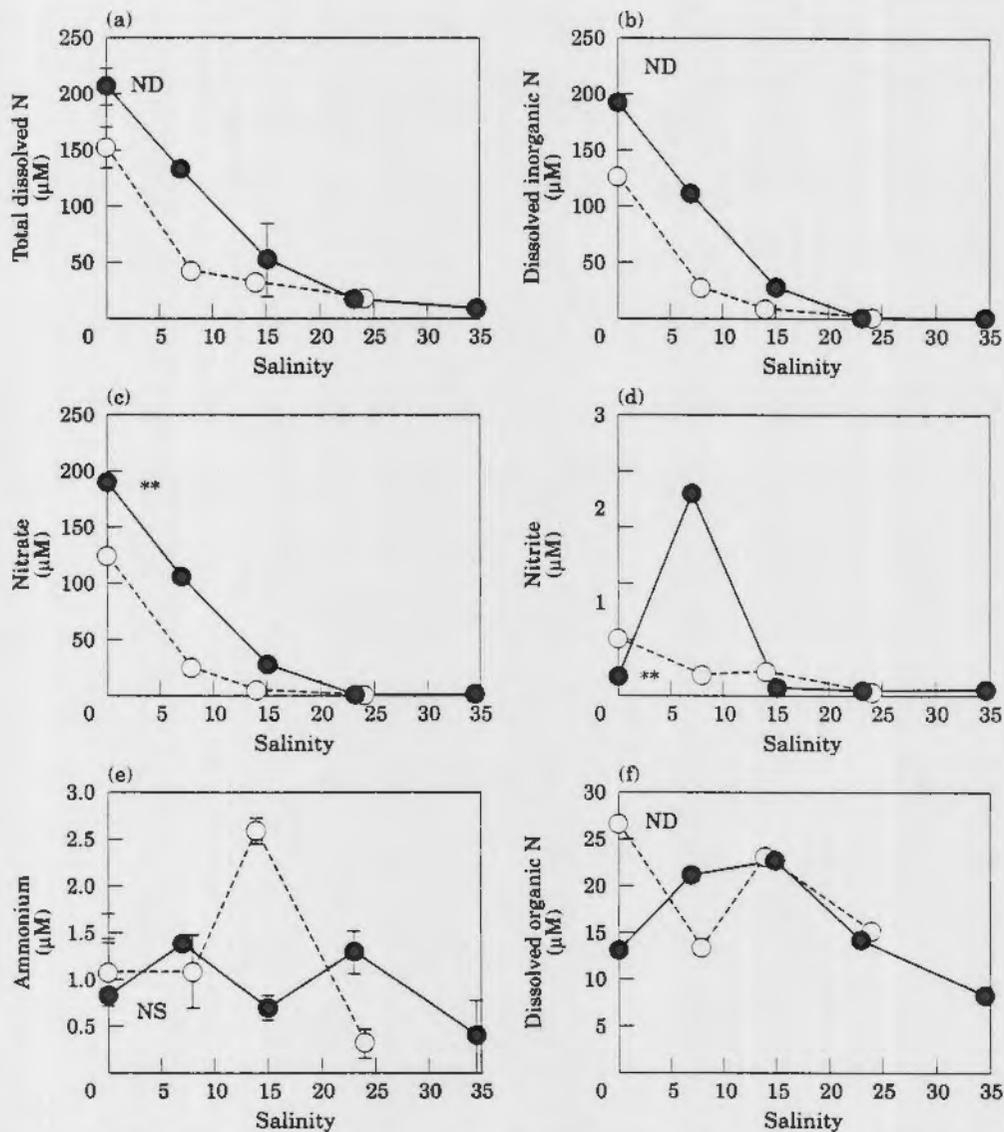


FIGURE 2. Property-salinity plots of dissolved organic and inorganic nutrients in the Mississippi River plume (closed circles) and Atchafalaya River plume (open circles). (a) Total dissolved N (b) dissolved inorganic N (c) nitrate (d) nitrite (e) ammonium (f) dissolved organic N. Error bars=95% confidence intervals. Where confidence intervals appear to be absent, the symbol is larger than the bars. No confidence intervals were determined for DON or DIN concentrations. \*\*=Concentrations in the Mississippi River significantly different from the Atchafalaya River ( $P < 0.05$ , paired Student's  $t$ ). ND=Statistical differences not determined, NS=not significant.

heterotrophic bacterial production (Table 1). In contrast, community  $\text{O}_2$  consumption in the ARP (Table 2) exhibited no apparent spatial trends with either chlorophyll or bacterial concentrations (Table 1).

Differences were observed in the nutrient chemistry of the rivers (Figures 2 and 3). Concentrations of TDN,  $\text{NO}_3^-$  and SRP in the Mississippi River were 55, 67 and 3  $\mu\text{M}$  higher, respectively, than in the Atchafalaya River (Figures 2 and 3). Concentrations of DOC and DON in the Atchafalaya River were 35  $\mu\text{M}$  and 11  $\mu\text{M}$  higher, respectively, than in the

Mississippi River (Figures 2 and 3). Concentrations of  $\text{NH}_4^+$ ,  $\text{NO}_2^-$  and Si in both rivers, however, were similar. Property-salinity plots (Figures 2 and 3) indicated depletion of TDN, DIN,  $\text{NO}_3^-$ , Si and SRP relative to conservative mixing at intermediate salinities consistent with photosynthetic utilization of these substances within both plumes. In the MRP, DON and  $\text{NO}_2^-$  concentrations were enhanced relative to conservative mixing at intermediate salinities, indicating net sources of these substances within the plume (Figure 2). In the ARP,  $\text{NH}_4^+$ , DOP concentrations

were enhanced at intermediate salinities, whereas DON concentrations exhibited no consistent trend across the plume salinity gradient (Figures 2 and 3).

Net production of DIN, indicating the remineralization of organic N, was observed at low and inter-

mediate salinities of both plumes (Table 3). Rates of net DIN production in the MRP were 2 to 5-fold higher than at comparable salinities in the ARP. High rates of net  $\text{NH}_4^+$  regeneration were observed in regions of elevated chlorophyll concentrations and removal rates in both plumes (Table 3).

No significant changes in  $\text{NO}_3^-$  concentrations were observed during bottle experiments in either river (Table 3). Net regeneration of  $\text{NO}_3^-$  indicative of nitrification was observed in the low salinity region of both plumes (Table 3). Nitrate regeneration rates in the MRP were *c.* 10-fold greater than those measured at comparable salinities in the ARP. Enhanced concentrations and net production of  $\text{NO}_2^-$ , also consistent with nitrification, were observed at M7 (Figure 3, Table 3). Net regeneration of SRP was observed in all stations in the MRP whereas only net uptake of SRP was observed in the ARP (Table 3). Net production of dissolved Si was observed in the Atchafalaya River and in the regions of elevated chlorophyll concentrations and chlorophyll removal rates in both plumes (Tables 1 and 3).

Molar ratios of dissolved N:P and Si:P were  $>16:1$  and  $>300$ , respectively, at intermediate salinities of both plumes (Table 4). Molar ratios of dissolved Si:N were  $<1$  in both rivers and generally increased with salinity (Table 4). Ratios of DIN:DON and  $\text{NO}_3^-:\text{NH}_4^+$  declined with increasing salinities, indicating a transition from oxidized and inorganic forms of N in the rivers to reduced and organic forms of N offshore. The ratio of DOC:DON was higher in the Mississippi River compared to the Atchafalaya River but were generally similar in both plumes (Table 4). Molar ratios of DOC:DON:DOP indicated that dissolved organic matter in the Atchafalaya River and plume was depleted in P relative to C and N (Table 5).

## Discussion

### *Nutrient chemistry of the Mississippi and Atchafalaya Rivers, July 1993*

During the summer of 1993, extensive flooding in the upper Mississippi River Basin mobilized and

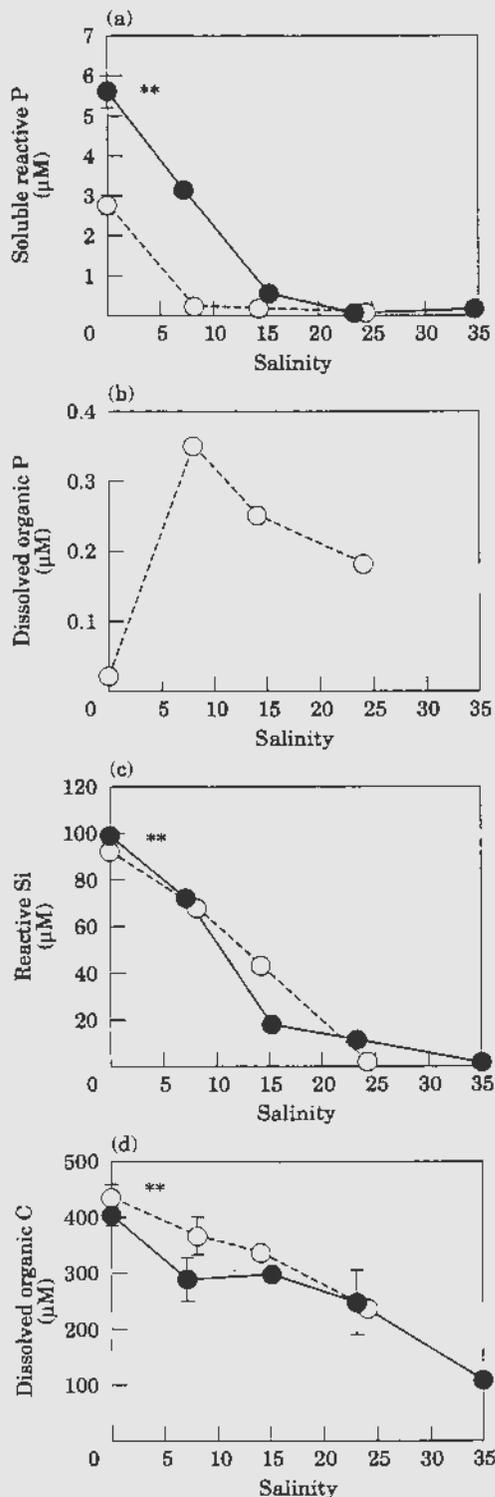


FIGURE 3. Property-salinity plots of dissolved organic and inorganic nutrients in the Mississippi River plume (closed circles) and Atchafalaya River plume (open circles). (a) soluble reactive P (b) dissolved organic P (c) dissolved reactive Si (d) dissolved organic carbon. Error bars=95% confidence intervals. Where confidence intervals appear to be absent, the symbol is larger than the bars. No confidence intervals were determined for dissolved organic P values. \*\*=Concentrations in the Mississippi River significantly different from the Atchafalaya River ( $P<0.05$ , paired Student's *t*).

TABLE 3. Net flux rates dissolved inorganic N (DIN),  $\text{NO}_3^-$ ,  $\text{NO}_2^-$ ,  $\text{NH}_4^+$ , soluble reactive P (SRP) and dissolved reactive Si during dark bottle incubations of unfiltered water from the Mississippi and Atchafalaya River plumes, July 1993. Positive values = net production; negative values = net uptake; NS = no significant flux

| Station<br>(salinity)   | DIN<br>( $\text{nM h}^{-1}$ ) | $\text{NO}_3^-$<br>( $\text{nM h}^{-1}$ ) | $\text{NO}_2^-$<br>( $\text{nM h}^{-1}$ ) | $\text{NH}_4^+$<br>( $\text{nM h}^{-1}$ ) | SRP<br>( $\text{nM h}^{-1}$ ) | Si<br>( $\text{nM h}^{-1}$ ) |
|-------------------------|-------------------------------|---|---|---|-------------------------------|------------------------------|
| Mississippi River plume |                               |   |   |   |                               |                              |
| M0                      | +20                           | NS <sup>b</sup>                           | NS <sup>b</sup>                           | NS <sup>b</sup>                           | NS <sup>b</sup>               | NS <sup>b</sup>              |
| M7                      | +550                          | +530                                      | +40                                       | -24                                       | +19                           | NS                           |
| M15 <sup>a</sup>        | +530                          | +61                                       | +2  | +439                                      | +2                            | +110                         |
| M23                     | -90                           | +3  | -3  | -38                                       | +5                            | NS                           |
| M34.5                   | -<10                          | NS <sup>b</sup>                           | -2 <sup>b</sup>                           | -10 <sup>b</sup>                          | NS <sup>b</sup>               | NS <sup>b</sup>              |
| Atchafalaya River plume |                               |   |   |   |                               |                              |
| A0                      | -50                           | NS  | NS  | -28                                       | NS                            | +230                         |
| A8 <sup>a</sup>         | +210                          | +51                                       | -20                                       | +243                                      | -7                            | +270                         |
| A14                     | +50                           | +12                                       | +7 <sup>c</sup>                           | +54                                       | -2                            | NS                           |
| A24                     | +70                           | NS  | +1  | +35                                       | -1                            | NS                           |

<sup>a</sup>Plume chlorophyll maximum.

<sup>b</sup>Net flux rate determined from initial and final concentrations.

<sup>c</sup> $P < 0.10$ .

TABLE 4. Molar ratios of total dissolved N (TDN), total dissolved P (TDP), dissolved inorganic N (DIN), dissolved organic N (DON), dissolved organic C (DOC) and inorganic N, P and Si from the Mississippi and Atchafalaya River plumes, July 1993

| Station<br>(salinity)   | TDN:TDP | TDN:SRP | DIN:SRP | DIN:DON | Si:DIN | Si:SRP | $\text{NO}_3^-:\text{NH}_4^+$ | DOC:DON |
|-------------------------|---------|---------|---------|---------|--------|--------|-------------------------------|---------|
| Mississippi River plume |         |         |         |         |        |        |                               |         |
| M0                      | ND      | 38      | 35      | 8.2     | 0.5    | 18     | 233                           | 30      |
| M7                      | ND      | 43      | 36      | 5.2     | 0.7    | 24     | 78                            | 14      |
| M15                     | ND      | 1024    | 576     | 1.3     | 0.7    | 374    | 40                            | 13      |
| M23                     | ND      | 780     | 74      | 0.1     | 7.8    | 571    | 0.1                           | 16      |
| M34.5                   | 66      | 100     | 7       | 0.07    | 2.8    | 19     | 0.4                           | 12      |
| Atchafalaya River plume |         |         |         |         |        |        |                               |         |
| A0                      | 56      | 56      | 46      | 4.7     | 0.7    | 34     | 116                           | 16      |
| A8                      | 75      | 739     | 145     | 2.1     | 2.4    | 353    | 24                            | 28      |
| A14                     | 72      | 163     | 45      | 0.4     | 5.4    | 245    | 2                             | 15      |
| A24                     | 77      | 102     | 21      | 0.03    | 5.3    | 112    | 3                             | 15      |

ND = not determined.

transported substantial quantities of fertilizer and other agricultural chemicals to the Gulf of Mexico (Goolsby *et al.*, 1993; Whittedge, 1993; Boyles & Humphrie, 1994; Goolsby, 1994). Nitrate concentrations in the Mississippi River during the present study were *c.* 3-fold higher than typical July values (35 year mean *c.* 70  $\mu\text{M}$ ; Bratkovich & Dinnel, 1992) and reflected the enhanced input of dissolved N from the upper Mississippi Basin. The difference in  $\text{NO}_3^-$  concentrations between the Mississippi and Atchafalaya Rivers (67  $\mu\text{M}$ ) was *c.* 2-fold greater than the average annual variation in Mississippi River  $\text{NO}_3^-$  concentrations (*c.* 35  $\mu\text{M}$ ; Bratkovich & Dinnel, 1992). It is

thus unlikely that differences between the two rivers could be attributed to short term (hourly, daily) variation in  $\text{NO}_3^-$  concentrations.

Water quality data published in the United States Geological Survey (USGS; Dantin *et al.*, 1994) indicated that  $\text{NO}_3^- + \text{NO}_2^-$  and DON concentrations in the Mississippi River did not change appreciably below the Mississippi-Atchafalaya junction during June and July 1993, whereas there was a downstream decline in  $\text{NO}_3^- + \text{NO}_2^-$  and an increase in DON concentrations in the Atchafalaya River during this period. Concentrations of DON were *c.* 2-fold higher and total P *c.* 2-fold lower in the Atchafalaya River

TABLE 5. Molar ratios of dissolved organic C, N and P in the Atchafalaya River plume, July 1993

| Station salinity | DOC:DON:DOP  |
|------------------|--------------|
| A0               | 21750:1345:1 |
| A8               | 1051:37:1    |
| A14              | 1340:92:1    |
| A24              | 1244:82:1    |
| M34.5            | 2080:168:1   |

compared with the Mississippi River. Concentrations of dissolved Si in both rivers were similar. These supporting nutrient data suggested that the Atchafalaya basin was a net sink for  $\text{NO}_3^-$  and total P and a net source of DON. As Mississippi River flow and nutrient concentrations were abnormally high, however, it was uncertain whether the differences in the chemistries of the rivers was typical or a consequence of the unusual conditions prevailing during the study period.

#### Biological activity

Although higher concentrations of dissolved N and P were present in the Mississippi River, chlorophyll concentrations, bacterial abundances and community respiration rates in both plume systems were similar. Amon and Benner (1998) however, reported bacterial abundances and *in situ* fluorescence distributions from the MRP and ARP from a much larger set of data collected during the present study. The spatial distributions of pigment fluorescence, bacterial abundances and production reported by Amon and Benner (1998) were identical to the distributions of chlorophyll and bacteria reported herein. These data indicate that concentrations of bacteria and chlorophyll were maximal in the low (<10) salinity region of the ARP and in the mid-salinity (10–20) region of the MRP. As turbidity and light penetration are important factors influencing the distribution of photosynthesis on the Louisiana Shelf (Lohrenz *et al.*, 1990), and results in enhanced photosynthesis at intermediate (c. 5–30) salinities, differences in turbidity between the two rivers may have facilitated the development of a low salinity chlorophyll maximum in the ARP and a mid-salinity chlorophyll maximum in the MRP.

In both plumes, enhanced heterotrophic bacterial production was observed at higher salinities relative to the chlorophyll maxima. The potentially greater availability of labile substrates released during grazing (Lampert, 1970) or from nutrient limitation of primary production (Ittekkot *et al.*, 1981) at intermediate

salinities may have contributed to enhanced heterotrophic bacterial production at higher salinities in both systems (Amon & Benner, 1998).

The distribution of chlorophyll,  $\text{O}_2$  consumption and DIC regeneration was similar to those reported previously in the MRP (Benner *et al.*, 1992; Pakulski *et al.*, 1995). Enhanced respiratory activity at mid-salinity indicated that respiration in both plumes was supported primarily by primary production within the plumes rather than inputs of terrigenous organic matter. Oxygen consumption rates in the MRP were similar to values measured during July 1990 ( $0.7\text{--}1.3 \mu\text{M h}^{-1}$ , Benner *et al.*, 1992); May 1992 ( $0.6\text{--}3.65 \mu\text{M h}^{-1}$ , Pakulski *et al.*, 1995), and June 1993 ( $1.41 \mu\text{M h}^{-1}$ , Pomeroy *et al.*, 1995) but were substantially higher than  $\text{O}_2$  consumption rates ( $<0.03\text{--}0.53 \mu\text{M h}^{-1}$ , Pomeroy *et al.*, 1995) in the pelagic waters of the north-east Gulf of Mexico during June 1993.

#### Nitrogen cycling

Substantial differences were observed in the cycling and fate of N between the two plumes. In the low salinity region of the MRP,  $\text{NO}_3^-$  and  $\text{NO}_2^-$  accounted for all of the DIN regenerated in bottle experiments. The low rate of net  $\text{NH}_4^+$  uptake relative to net  $\text{NO}_3^-$  production at M7 further indicated that nitrification was tightly coupled to the mineralization of organic N. As the nitrification maximum preceded the chlorophyll maximum along the MRP salinity gradient, nitrification in the low salinity region of the MRP may have been supported, in part, by the transformation and mineralization of terrigenous N. In contrast,  $\text{NH}_4^+$  was the principal end product of community N metabolism A8, indicating that N oxidation was a relatively less important process in the low salinity region of the ARP.

Based on the distributions of DIN, DON and chlorophyll, Lopez-Veneroni and Cifuentes (1994) concluded that Mississippi-derived  $\text{NO}_3^-$  was transformed into phytoplankton-derived DON at intermediate salinities in the MRP. In the present investigation, concentrations of chlorophyll and DON in the MRP were enhanced, whereas concentrations of DIN were depressed, relative to those expected from the conservative mixing. These distributions were similar to those reported by Lopez-Veneroni and Cifuentes (1994) and also suggested that DON production in the MRP was mediated by photosynthetic uptake and transformation of Mississippi River  $\text{NO}_3^-$  at intermediate salinities. Similar distributions of DIN, DON and chlorophyll, however, were not observed in the ARP.

The DOC:DON ratio in the Atchafalaya River was lower than the Mississippi River and reflected the higher concentrations of DON present in the Atchafalaya. Molar DOC:DON ratios in the MRP were similar to those reported by Gardner and Stephens (1978) for a south-eastern U.S. estuary and to C:N ratios of high-molecular-weight DOM collected in the MRP during the present study (Eadie *et al.*, 1995). The distribution of DOC:DON ratios observed in the MRP presumably reflected the higher C:N ratios of terrigenous organic matter in the Mississippi River and its subsequent dilution and mixing with marine DOM with increasing salinity.

Elevated chlorophyll removal rates were associated with  $\text{NH}_4^+$  regeneration in both plumes. Micro- and meso-zooplankton are often abundant at intermediate salinities of the MRP (Dagg & Whitley, 1990; Fahnenstiel *et al.*, 1992) and can consume a substantial portion of plume primary production in the summer months (Dagg & Ortner, 1992; Fahnenstiel *et al.*, 1992). Gardner *et al.* (1994) reported that organisms in the  $>1 \mu\text{m}$  size-fraction were responsible for  $>70\%$  of community  $\text{NH}_4^+$  regeneration in the MRP. The distributions of net  $\text{NH}_4^+$  regeneration and chlorophyll removal rates suggested that zooplankton grazing mediated regeneration of  $\text{NH}_4^+$  in both plumes.

Highest rates of nitrification in the MRP were observed in low salinity waters characterized by relatively low bacterial and chlorophyll concentrations, whereas highest rates of nitrification in the low salinity waters of the ARP occurred where chlorophyll and bacteria concentrations were relatively low. Turbidity inhibits photosynthesis at low salinities in the MRP (Lohrenz *et al.*, 1990). As nitrification is sensitive to photoinhibition (Hooper & Terry, 1974; Ward, 1985; Horrigan & Springer, 1990), turbidity may have facilitated the development of nitrification in the low salinity region of the MRP (Owens, 1986; Lipshultz *et al.*, 1985). Phytoplankton and heterotrophic bacteria, however, can out-compete  $\text{NH}_4^+$  oxidizing bacteria for available  $\text{NH}_4^+$  (Ward, 1985; Verhagen & Laanbroek, 1991) and may influence nitrification where light availability is sufficient to support photosynthesis and where high concentration heterotrophic bacteria are present. Differences in the intensity and distribution of nitrification between the two plumes may thus have resulted from a variety of factors, including reduced photoinhibition of nitrification in the turbid low salinity region of the MRP, and competition for available  $\text{NH}_4^+$  among nitrifying bacteria and other organisms in the low salinity region of the ARP.

There were substantial differences between the two plumes in the contribution of nitrifying bacteria to

community bacterial production. Ratios of C fixation to N oxidization by estuarine  $\text{NH}_4^+$  and  $\text{NO}_2^-$  oxidizing bacteria range from 0.07–0.18 and 0.002–0.04, respectively (Owens, 1986; Feliatra & Bianchi, 1993). Assuming that  $\text{NO}_3^-$  production was equal to  $\text{NH}_4^+$  and  $\text{NO}_2^-$  oxidation rates, C fixation by  $\text{NH}_4^+$  and  $\text{NO}_2^-$  oxidizing bacteria at M7 and A8 was estimated to be 0.46–1.1 and 0.001–0.03  $\mu\text{g C l}^{-1} \text{h}^{-1}$ , respectively. Heterotrophic bacteria production at these two stations was 0.25 and 0.61  $\mu\text{g C l}^{-1} \text{h}^{-1}$ , respectively. Carbon fixation by nitrifying bacteria at M7 was thus potentially 2- to 4-fold greater than heterotrophic bacterial production. In contrast, C fixation by nitrifying bacteria at A8 was equivalent to  $<3\%$  of heterotrophic bacterial production. This comparison suggested that autotrophic C fixation by nitrifying bacteria equalled or exceeded heterotrophic bacterial production in the low salinity region of the MRP, but was negligible relative to heterotrophic bacterial production in the low salinity region of the ARP.

Due to low rates of *in situ*  $\text{NH}_4^+$  and  $\text{NO}_2^-$  oxidation (Ward *et al.*, 1982; Lipshultz *et al.*, 1985; Berounsky & Nixon, 1990; Feliatra & Bianchi, 1993; and others), low growth efficiencies (Owens, 1986; Feliatra & Bianchi, 1993), and low cell abundances (Ward, 1984), nitrifying bacteria are not generally considered to contribute significantly to community bacterial production in marine systems. The present study and previous work (Pakulski *et al.*, 1995), however, suggested that carbon fixation by nitrifying bacteria may at times comprise a substantial portion of bacterial production on the inner Louisiana Shelf.

#### Phosphorus cycling

The spatial distribution of net SRP regeneration suggested that terrigenous P was an important component of the MRP phosphorus cycle. As only net uptake of SRP was observed in the ARP, however, it was not possible to evaluate the role of terrigenous P in the Atchafalaya system. Depletion of SRP in the regions of elevated chlorophyll concentrations indicated that phytoplankton assimilation influenced the distribution of SRP at intermediate salinities in both plumes. In the ARP, SRP concentrations declined whereas DOP concentrations were enhanced at intermediate salinities. The distributions of SRP, DOP and chlorophyll suggested a transformation of riverine SRP to plume-derived DOP in the ARP.

#### Silicon cycling

Little is known regarding water column Si regeneration in marine systems (d'Elia *et al.*, 1983). Whereas

reactive Si concentrations in both rivers were similar, net Si regeneration rates suggested active cycling of terrigenous Si in Atchafalaya River but not in the Mississippi River. Silicate regeneration rates measured in the present investigation ( $112\text{--}270\text{ nM h}^{-1}$ ) were nearly an order-of-magnitude greater than values ( $4\text{--}17\text{ nM h}^{-1}$ ) reported from the Wadden Sea (Van Bennekon *et al.*, 1974). Although regeneration of dissolved Si occurred within both plumes, property-salinity plots suggested that diatom production was the dominant process influencing the distribution of Si within the plumes.

In both plumes, Si regeneration was associated with elevated chlorophyll concentrations and removal rates. This suggested that Si regeneration was mediated by diatom grazers. Recent work, however, has indicated that bacterial hydrolysis rather than digestive dissolution may be the principal mechanism responsible for Si regeneration in marine systems (Cowie & Hedges, 1996; Bidle & Azam, 1999). Bacterial hydrolysis of biogenic silica in zooplankton fecal material may thus have contributed to net regeneration of Si in the plumes.

*Potential nutrient limitation in the Mississippi-Atchafalaya outflow region, July 1993*

Diatom production often depletes Si over large areas on the inner Louisiana Shelf in the spring and summer (Dortch *et al.*, 1992; Nelson & Dortch, 1996) and has been implicated in the development of hypoxia in the region (Turner & Rabalais, 1994). Reduced Si:N ratios ( $<1$ ) at low concentrations ( $<1\text{ }\mu\text{M}$ ) of Si and N may result in Si limitation of diatom production in Louisiana coastal waters (Dortch & Whitedge, 1992). In the present investigation, Si:N ratios  $<1$  were observed only in the MRP where both Si and DIN concentrations exceeded  $15\text{ }\mu\text{M}$ . At higher salinities in both plumes, Si:N ratios were  $>1$  and concentrations of Si generally exceeded  $1\text{ }\mu\text{M}$ . Elevated concentrations of dissolved Si and favourable Si:N ratios suggested that Si availability was sufficient to support diatom production over much of the inner Louisiana Shelf during the study period.

Ratios of DOC:DON:DOP, N:P and Si:P generally exceeded Redfield values (Redfield *et al.*, 1963) in both plumes. Property-salinity plots further indicated that dissolved P was depleted at lower salinities relative to dissolved N and Si in both systems. Previous research (Ammerman, 1992; Chin-Leo & Benner, 1992; Smith & Hitchcock, 1994; Pakulski *et al.*, 1995; Pomeroy *et al.*, 1995) has suggested that P limitation may be prevalent in the Mississippi outflow region in the spring and summer months. The distribution of

dissolved Si, N and P and the high dissolved N:P and Si:P ratios observed within the study area strongly suggested the potential for P limitation of biological activity on the inner Louisiana Shelf during the summer of 1993.

## Conclusions

The nutrient chemistry of the Mississippi and Atchafalaya Rivers differed dramatically during the study period and suggested that hydrological and biogeochemical processes may modify the N and P content of Mississippi River water diverted to the Atchafalaya Basin. The cycling and fate of dissolved N and P in the Mississippi and Atchafalaya plumes also appeared to be influenced by differences in nutrient loading from the two rivers. Although the present study focused on the dissolved components of the two rivers, the distributions of dissolved N, P and Si flux rates suggested that terrigenous particulate material played an important role in the nutrient cycles of both plumes. Finally, the high rates of N oxidation observed in the present study and reported from previous work in the Mississippi River plume suggested that enhanced nitrification may be a unique feature of the microbial ecology of the inner Louisiana Shelf.

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